Journal of Food Research; Vol. 6, No. 5; 2017
ISSN 1927-0887 E-ISSN 1927-0895
Published by Canadian Center of Science and Education

Deterioration of Extra Virgin Olive Oil Caused by Different Processes

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Received: June 26, 2017 Accepted: August 4, 2017 Online Published: August 21, 2017

doi:10.5539/jfr.v6n5p59 URL: https://doi.org/10.5539/jfr.v6n5p59

Abstract

Extra virgin olive oil is recognized as a very stable oil because of its composition in fatty acids and its content in natural antioxidants (tocopherols and polyphenols). In the bibliography are works that address different aspects of this stability, from the duration of its useful life to its performance in the frying of foods. Some works also link their stability with the content of natural antioxidants. For example, Franco et al. (2014) studied the content of phenols and their antioxidant capacity in olive oils of seven different varieties. Baccouri et al. (2008) found a good correlation between the oxidative stability (measured in Rancimat) of the oils studied and the concentration of total phenols and tocopherols.

Keywords: Extra virgin olive oil, autoxidation, oxidative stability, thermoxidation

1. Introduction

Extra virgin olive oil is recognized as a very stable oil because of its composition in fatty acids and its content in natural antioxidants (tocopherols and polyphenols). In the bibliography are works that address different aspects of this stability, from the duration of its useful life to its performance in the frying of foods. Some works also link their stability with the content of natural antioxidants. For example, Franco *et al.* (2014) studied the content of phenols and their antioxidant capacity in olive oils of seven different varieties. Baccouri *et al.* (2008) found a good correlation between the oxidative stability (measured in Rancimat) of the oils studied and the concentration of total phenols and tocopherols.

The useful life of the extra virgin olive oil has been studied by several authors. The most commonly used control parameters are peroxide index (primary oxidation) and ultraviolet absorbance (K232 and K270). Psomiadou and Tsimidou (2002) studied the autoxidation of extra virgin olive oil stored for 24 months as well as the content of tocopherols and polar phenols. Morello *et al.* (2004) studied the changes that take place in Arbequina virgin olive oils during storage for 12 months. They found that alpha-tocopherol completely disappeared during storage and that total phenols dropped significantly. Gómez-Alonso *et al.* (2007) studied the evolution of the minor components and the oxidation rates of virgin olive oils of Cornicabra with different tocopherols and polyphenols contents during 21 months of storage at room temperature in the dark. The reduction of the total phenols was between 43 % and 73 % and its reduction was greater in the samples whose initial content of phenols was higher. Mancebo-Campos *et al.* (2014) studied the activity of some antioxidants in a purified olive oil, stored at 25 ℃ and 40 ℃ noting that tocopherol behaved as a pro-oxidant at the temperatures studied.

Other authors studied the oxidative stability of olive oils stored at temperatures above ambient. Hrncirik and Fritsche (2005) studied the antioxidants and quality of extra virgin oils of the Koroneiki, Coratina and Picual varieties stored at 60 ℃ in the dark. Stability was determined by the peroxide index; correlated these values with the OSI index determined at 100 ℃ and the content and composition of phenols and tocopherols. On the one hand they found that the higher the antioxidant content of oils, the longer their OSI times. On the other hand, the stability ratios of the oils were maintained with respect to the increase of their peroxide index and the ultraviolet absorbance (K232 and K270) with the heating time. Lerma-García *et al.* (2009) studied the chemical changes of a sample of extra virgin olive oil in the presence and absence of its phenolic fraction during accelerated storage at 60 ℃ for 7 weeks, they observed an increased of the oxidized products with decreased of the antioxidants.

Thermoxidation changes in oils during the frying of foods or in the absence of food could be very different from those of autoxidation. In the autoxidation there is an increase in the peroxide index and the ultraviolet

absorbance (K232 and K270). In the thermoxidation there is no increase in the peroxide index because these are very unstable at high temperatures, so that the formation of polar compounds predominates. Many countries have regulations regarding the maximum permissible content of polar compounds in oils used in repeated frying of foods. Velasco and Dobarganes (2002) studied virgin olive oil during storage and at high temperature (frying and baking). They discussed the differences between low and high temperature mechanisms.

The thermoxidation of the oil in the absence of food and without bubbling of air in them was studied by several authors. Valdés and García (2006) studied the evolution of physico-chemical parameters at 150 ℃ and 225 ℃ for 1-15 days. Carrasco-Pancorbo *et al.* (2007) evaluated the influence of the composition of the antioxidants on oxidative stability and its deterioration by the thermoxidation of the oil at 180 ℃. Mancebo-Campos *et al.* (2007) studied the oxidation under accelerated conditions in a Rancimat apparatus compared with storage at room temperature (25 ℃) for a long period. They found a lack of correlation between the results of induction times and storage at room temperature. They also found that polyphenols and tocopherols were rapidly degraded under such thermoxidation conditions. Maggio *et al.* (2011) studied three samples of extra virgin olive oil subjected to heating at 180 °C in the oven for 30, 60, 90, 120, 150 and 180 minutes.

Studies on the thermoxidation of oils in the absence of food but with bubbling of air are also found in the literature. Bester *et al.* (2008) studied the behavior of 7 samples of extra virgin olive oil in a Rancimat equipment at 100 ℃ and with air bubbles of 10 L / h for 142 hours. After that treatment the tocopherols disappeared completely and the total content of biophenols dropped to about half. Campanella *et al.* (2008) studied the atmospheric oxidation at different temperatures (98, 120, 140, 160 and 180 ℃) with air bubbling. The almost total disappearance of phenols occurred at increasingly shorter times as the temperature increased.

Discontinuous frying of potatoes is often used as a model to study the behavior of oils since they do not contribute lipids to the medium. Silva *et al.* (2010) studied the frying of potatoes in olive oil for 60 minutes at 180 ℃, in the absence and presence of food. All the components of the polyphenols decreased their concentration with the heat treatment and that decrease was much greater in the presence of food. Casal *et al.* (2010) studied the frying of potatoes in a domestic fryer at 170 ℃, until reaching a polar compound content of 25 %. They used an extra virgin olive oil, two virgin monovarietals and a mixture of refined oil with virgin. All these oils reached 25% of compounds in a range of 3 days but in all the oils the phenols disappeared in less than a day. They showed that in these conditions the phenols are very labile so there was no significant difference between the behavior of the different types of oils used. Santos *et al.* (2013) made a literature review on the effect of cooking on the different qualities of olive oil (virgin extra, virgin, refined). They found that the performance of virgin olive oil under conditions of prolonged thermal processes (frying in depth and surface, microwave, boiled, toasted) is equal to or higher than other refined vegetable oils due to its composition. As most of these bioactive compounds (including phenolic compounds) are gradually lost there are no differences in behavior between the different grades of olive oil. In addition, the polyphenols content is affected by the thermal process, but their loss depends on their molecular structure (Gómez-Alonso *et al.*, 2003; Carrasco-Pancorbo *et al.*, 2007; Cheikhousman *et al.*, 2005; Daskalaki *et al.*, 2009; Romero *et al.*, 2003).

In conclusion, most of the works consulted refer to the stability of the extra virgin olive oil in different processes: storage at relatively low temperatures, thermoxidation at high temperatures and frying of foods. Many of them also determine the deterioration of their antioxidants. No studies were found that, with the same extra virgin olive oils, their stability is compared in all those processes that lead to such different mechanisms of deterioration.

On the other hand, the OSI induction period is generally used as an index of stability of the oils. However, this is determined under certain operating conditions (with air bubbling and generally at 110 ℃) which are very different from those of storage at room temperature or food frying at 180 ℃. It is therefore important to determine the applicability of these results in different deterioration situations.

The aim of this work was to evaluate the behavior of two extra virgin monovarietal oils (Coratina and Arbequina, with a very different content of polyphenols) compared to storage at room temperature, storage at 60 ℃, thermoxidation at 180 ℃ and fry at 180 ℃. These results are also compared with oxidative stability at 110 ℃ as determined by induction time (OSI).

2. Materials and Methods

2.1 Raw Materials

Monovarietal extra virgin olive oils from Arbequina and Coratina, from Uruguayan industrial processing (Finca Babieca, Maldonado, Uruguay).

2.2 Thermal Study

Storage at room temperature and 60 ℃:

The oils were packed in amber bottles (volume, 100 mL and surface/volume ratio, 0.05 cm^{-1}). One bottle group was stored at 25 °C for 40 weeks and another group was stored at 60 °C for 7 weeks. During that period, a weekly sample (one bottle) of each of the oils was analyzed. Once this sample was taken, the rest of the oil contained in the bottle was discarded. Samples were stored at -20 ℃ until analysis.

Thermoxidation of oils:

The oils (quantity: 600 grams) were placed in Bohemia glasses of 1 L. Surface/volume ratio of the oil: 0.087 cm^{-1}. To heat them were used heating plates with magnetic stirrer. The oil was heated at 180 ℃ for 1 hour, cooled to 120 ℃ and reheated to 180 ℃. These cycles were repeated for a total of 20 hours. Small samples of 1 g of oil were removed every 5 hours (the small size of the sample does not significantly alter the initial surface / volume ratios of the oil). Samples were stored at -20 ℃ until analysis.

2.3 Discontinuous Frying of Potatoes

The potatoes were peeled, washed and cut into parallelepipeds of similar size (canes). They were fried in batches of 100 g in 300 g of oil (ratio 1:3). The frying tests with the two types of oil were carried out simultaneously using two identical frying pan, with a surface to volume ratio of approx. 1.5 cm^{-1}.

The initial frying temperature, in all cases, was 180 ℃. Twenty frying operations were carried out for 4 minutes each (80 minutes in total). Each frying operation was performed with the same amount of oil because the oil lost in the previous frying was recovered (determined by weighing before and after the frying).

At the end of each frying, the oil was cooled at room temperature and a sample of 1 g of oil was withdrawn. The samples were stored at -20 °C until analyzed.

2.4 Analytical Determinations

The Polyphenols were determined by High Resolution Liquid Chromatography (HPLC). Column type C18 (length 250 mm, diameter 4.6 mm, particle size 5 μm). Solvent system: acetonitrile, methanol, phosphoric acid 0.2 % - water. Analysis time: 82 minutes. Method IOC / T.20 / DOC 29, November 2009.

The content of tocopherols was determined by HPLC according to the method described in Andrikopolus *et al.* (1991).

The Total polar compound content was determined analyzed by Standard method IUPAC 2.507. They were determined in duplicate.

The Acidity was determined by Standard method IUPAC 2.201. They were determined in duplicate.

The Peroxide index was determined by Standard method IUPAC 2.501. They were determined in duplicate.

The p-anisidine index was determined by Standard method IUPAC 2.504. They were determined in duplicate.

The Absorbance in ultraviolet (K232 and K270) were determined by Method COI / T.20 / Doc. No 19 / Rev. 3, "Spectrophotometric investigation in the ultraviolet". They were determined in duplicate.

The Oxidation stability index at 110 ℃ (OSI induction times) was determined by Standard method AOCS Cd-12b-92. They were determined in triplicate.

The determination of fatty acids composition was made by derivatization of the triglycerides to methyl esters by the standard method AOCS Ch 1-91 and its subsequent analysis by gas chromatography, standard method AOCS Ce 1e-91.

3. Results and Discussion

3.1 Characterization of the Raw Materials: Extra Virgin Oils of Arbequina and Coratina

The characteristics of the oils studied are shown in Table 1.

The peroxide index, the acidity and the absorbance to the ultaviolet (K232 and K270) of the two oils were similar so that the two oils can be considered of the same quality. The p-anisid index indicated that both oils were at a similar level of secondary oxidation.

Regarding to fatty acid composition, Coratina oil has more oleic acid and less linoleic acid than Arbequina oil (Table 1) and, hence it is expected that the oil of Coratina is more stable to the oxidation. The Arbequina oil has an inherent stability of 2.1 and this Coratina oil, 1.7. By means of the inherent stability, it is possible to estimate the effect of the composition on fatty acids on their resistance to oxidation. The inherent stability number of a

fatty material is defined in terms of the relative oxidation rates of the unsaturated fatty acids at 37 ℃ and their percentage content. Smaller is the number, greater is the stability of the fatty material. Reference is made to the value 1 for the oxidation rate of oleic acid; as a function of it linoleic acid has a relative velocity of 10 and linolenic of 25 (Gunstone and Hilditch, 1946; Erickson and List, 1985).

The OSI times at 110 ℃ were very different since the Coratina oil was 2.4 times higher than that of the Arbequina oil, which could indicate a greater resistance to the oxidation of the Coratina oil. This is linked to their different contents of antioxidants since they do not differ significantly in their composition in fatty acids. Coratina oil has 18% more tocopherols than Arbequina oil as well as triple polyphenols. As in this work, Baccouri *et al.* (2008) found a good correlation between the oxidative stability (measured in Rancimat) of the oils studied and the concentration of total phenols and tocopherols.

Table 1. Characterization of virgin olive oils of the Arbequina and Coratina varieties

	Arbequina	Coratina
Acidity (%)	0.16 ±0.01	0.14 ±0.01
Peroxide index	4.4 ±0.1	4.2 ±0.2
K232	1.54 ±0.15	1.33 ±0.13
K270	0.102 ±0.015	0.082 ±0.012
p-anisidine index	4.3 ±0.1	5.9 ±0.1
Tocopherols (ppm)	174 ±9	205 ±10
Polyphenols (ppm)	129 ±6	389 ±19
OSI time (h) at 110 ℃	11.7 ±0.8	28.2 ±0.3
Polar compound (%)	3 ±1	2 ±1
Fatty acid composition (%)		
16:0	14.0	10.1
16:1	1.3	0.4
18:0	1.6	1.8
18:1	70.2	80.0
18:2	11.7	6.3
18:3	0.9	1.1

3.2 Storage at Room Temperature

The results obtained for the peroxide index and the ultraviolet absorbance (K232 and K270) are given in **Table 2** as a function of the storage time of the oils at room temperature (25 ℃) and protected from light. As in general, extra virgin olive oils are given one-year expiration, from week 13 it was passed to week 40 as a way to study that period.

The IOC 2015 standard establishes limits for the extra virgin olive oils: K232 ≤ 2.50, K 270 ≤ 0.22, peroxide index ≤ 20. Therefore, Arbequina oil at week 13 had lost its quality of Extra virgin according to the value of K232 and at week 40 according to its peroxide index. Coratina oil had lost its extra virgin status in week 40, both for its K232 and for its peroxide index. However, at week 40 Arbequina oil had a higher peroxide index (41.23) than Coratina oil (36.98). On the other hand, the K232, K270 and the peroxide index of the Coratina oil were always smaller than the corresponding ones of the Arbequina oil. These findings indicate a lower rate of oxidative deterioration at room temperature of the Coratina oil compared to the Arbequina oil, that is to say, a slightly longer shelf-life. From the OSI times determined it was expected that the Coratina oil would be more stable than Arbequina, but since the ratio of the induction periods was 2.4 times it was also expected that the differences in stability at room temperature would be more pronounced (which would also be justified by the differences in the initial contents of antioxidants of the two oils). Baccouri *et al.* (2008) found a good correlation between the stability determined in Rancimat and the concentration of polyphenols and tocopherols.

The tocopherols content of both oils decreased considerably during storage to 22 % in the Coratina oil and to 24 % in the Arbequina oil (Table 2). Although the initial tocopherols content of Coratina oil was 1.2 times higher than that of Arbequina oil, after 40 weeks their ratio only decreased to 1.1. Therefore, as the first 11 weeks of storage passed, the oils lost tocopherols at a similar ratio.

The polyphenol content of both oils also decreased considerably during storage to 27 % in Coratina oil and 36 % in Arbequina oil (Table 2). That as to say, the polyphenol content decreased more rapidly in the oil with the higher initial concentration of polyphenols, similar conclusion to that obtained by Gómez-Alonso *et al.* (2007).

In spite of this, the polyphenol content of Coratina oil was always higher than that of Arbequina oil. This could explain the greater stability of Coratina oil.

These results agree with those found by Morello *et al.* (2004), where the alpha-tocopherol disappeared completely and the total phenols decreased significantly during 12 months of storage. Conversely, Psomiadou and Tsimidou (2002) observed that the losses of tocopherols and polyphenols were similar after 24 months of storage. This is probably because the oils were different and that such oxidation studies were not done exactly under the same conditions.

Table 2. Evolution of peroxide index, K232 and K270 of the virgin olive oils of the Arbequina and Coratina varieties as a function of the storage time at 25 ℃

	initial	week 5	week 9	week 13	week 40
Arbequina					
Peroxide index	4.4 ±0.2	7.5 ±0.3	14.2 ±0.5	17.5 ±0.5	41.2 ±0.7
K232	1.54 ±0.15	1.81 ±0.18	2.40 ±0.24	2.42 ±0.24	5.06 ±0.51
K270	0.102 ±0.015	0.094 ±0.014	0.095 ±0.014	0.116 ±0.017	0.161 ±0.024
Tocopherols (ppm)	174 ±9	86 ±4	61 ±3	52 ±2	42 ±2
Polyphenols (ppm)	129 ±6	123 ±6	89 ±4	94 ±5	47 ±2
Coratina					
Peroxide index	4.2 ±0.2	3.5 ±0.2	8.1 ±0.3	15.0 ±0.2	37.0 ±0.7
K232	1.33 ±0.13	1.65 ±0.17	1.61 ±0.16	1.64 ±0.16	2.90 ±0.29
K270	0.082 ±0.012	0.090 ±0.014	0.132 ±0.020	0.138 ±0.021	0.134 ±0.020
Tocopherols (ppm)	205 ±10	180 ±9	119 ±6	84 ±4	46 ±2
Polyphenols (ppm)	389 ±19	215 ±11	213 ±11	228 ±11	106 ±5

3.3 Storage at 60 ℃.

The results obtained for the peroxide index and the ultraviolet absorbance (K232 and K270) are given in **Table 3**, as a function of the storage time at a temperature of 60 ℃ in the absence of light.

The data show that the rate of the increase of the peroxide index was higher for the Arbequina oil than for the Coratina oil. Because of this, at 6 weeks Arbequina oil had a peroxide index of almost 40 while at 10 weeks the peroxide index of Coratina oil was only about 25. Therefore, under accelerated conditions at 60 ℃, Coratina oil was much more stable than Arbequina oil. Similar conclusions are drawn regarding K232 and K270. This is consistent with the stability determined by the OSI times for the initial oils.

The decrease in the concentration of tocopherols and polyphenols in both oils produced in 8 weeks storage at 60 ℃ could be seeing in Table 3.

Table 3. Evolution of the index of proxies, K232 and K270 of the virgin olive oils of the varieties Arbequina and Coratina as a function of storage time at 60 ℃

	initial	2	3	4	5	6	7	8	9	10
Arbequina										
Peroxide index	4.4±0.1	14.5±0.5	22.1±0.7	23.8±0.8	34.4±0.3	39.9±0.3	-	-	-	-
K232	1.54±0.15	3.01±0.30	3.69±0.37	3.58±0.36	5.93±0.59	-	-	-	-	-
K270	0.102±0.015	0.145±0.022	0.177±0.027	0.174±0.026	0.242±0.036	0.372±0.056	-	-	-	-
Tocopherols(ppm)	174±9	162±8	166±8	111±6	48±2	0	-	-	-	-
Polyphenols(ppm)	144±7	133±7	104±6	94±6	92±5	87±4	-	-	-	-
Coratina										
Peroxide index	4.2±0.2	7.5±0.3	7.7±0.3	8.5±0.3	8.8±0.5	9.4±0.4	19.5±0.7	22.0±0.7	22.9±0.6	24.8±0.7
K232	1.33±0.13	1.90±0.20	1.98±0.20	2.83±0.28	3.35±0.34	3.36±0.34	-	-	-	-
K270	0.082±0.012	0.166±0.025	0.151±0.023	0.182±0.027	0.154±0.023	0.204±0.031	0.342±0.051	0.326±0.049	-	-
Tocopherols(ppm)	205±10	172±9	164±8	151±8	151±8	136±7	28±1	7±1	-	-
Polyphenols(ppm)	389±19	302±15	197±10	185±9	182±9	210±10	128±6	128±6	-	-

The concentration of polyphenols was always higher in Coratina oil than in Arbequina oil and never disappeared as in Arbequina oil. The same happened with the concentration of tocopherols since in week 6 the Arbequina oil lacked them. These variations of the antioxidant content explain that the Coratina oil is more stable under these conditions.

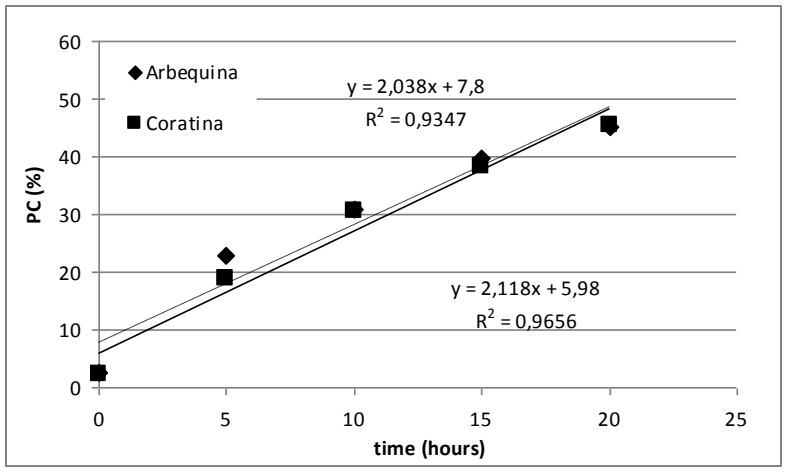
3.4 Thermoxidation with Agitation and Without Air Bubbling

Figure 1a shows the evolution of the content of polar compounds in both oils, as a function of the hours of heating at 180 ℃. Both oils exhibit practically the same behavior at thermoxidation. This was not expected considering the OSI times determined and the deterioration during storage at room temperature and at 60 ℃. This shows that different mechanisms take place for the oxidation of the oils under such different conditions of deterioration.

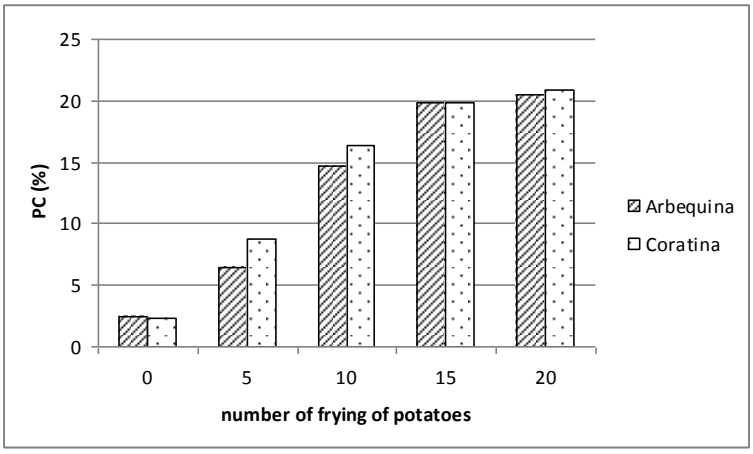
Since tocopherols rapidly deteriorated to 60 ℃ and polyphenols were the most effective antioxidants in virgin olive oil, only the variation of the polyphenol content in the studies at 180 ℃ (thermoxidation and frying of potatoes) was determined (Table 4).

Table 4. Variation of the concentration of polyphenols and polar compounds (PC) virgin olive oils of the varieties Arbequina and Coratina at 20 hours of thermoxidation at 180 ℃ and after 20 frying steps

	arbequina		coratina	
	polyphenols (ppm)	PC (%)	polyphenols (ppm)	PC (%)
Initial	129 ±6	3 ±1	389 ±19	2 ±1
20 hours	30 ±2	45 ±1	28 ±1	46 ±1
20 fryings	58 ±3	21±1	45 ±2	21 ±1



a)



b)

Figure 1. Evolution of the content of polar compounds (PC) in the virgin olive oils of the Arbequina and Coratina varieties as a function of a) the hours of heating at 180 ℃; b) the number of frying of potatoes

After 20 hours of thermoxidation, the polyphenol content of the Coratina oil was practically the same as for the Arbequina oil (although initially the Coratina oil had 3 times more polyphenols than the Arbequina oil). This shows that in the thermoxidation the polyphenols were degraded at different rates so that during the process their concentration reached similar values. As a result, the polyphenols failed to protect both oils, which explains that the concentration of polar compounds reached similar values.

This was not expected, according to OSI times and storage trials, in which Coratina oil was much more stable than Arbequina oil (based on increased peroxide index and K232 and K270, Tables 3 and 4). These conclusions are consistent with those of Mancebo-Campos *et al.* (2007) who studied the thermoxidation in a Rancimat equipment, compared with storage at 25 ℃. They found a lack of correlation between both results, in a similar way than in this work.

The results obtained in the present study confirm that the mechanisms of deterioration are different and that the kinetics of peroxide formation at room temperature are not the same as the formation of polar compounds at 180 ℃. As the oils have practically the same composition in fatty acids (their inherent stabilities are similar), these differences of behavior could be due to the accelerated deterioration of the polyphenols during the thermoxidation.

Campanella *et al.* (2008) studied the oxidation under bubbling air at different temperatures (98 ℃ to 180 ℃) and found that the total disappearance of the phenols occurred at shorter and shorter times as the temperature increased. Carrasco-Pancorbo *et al.* (2007) evaluated the influence of the polyphenols composition on the oxidative stability and its deterioration by thermoxidation at 180 ℃. Although olive oil extra virgin used in both studies, their results can t́ be compared with this study because they determined the peroxide index of oils and not the content of polar compounds.

3.5 Discontinuous Frying of Potatoes in Frying Pan

Figure 1b shows the increase in the content of polar compounds in the oils used for the frying of potatoes, depending on the number of frying made with them.

As fried potatoes were made, the content of polar compounds increased for both oils. After frying No. 15, a slowdown in the formation of polar compounds for both oils was observed. The decrease in the formation rate of the polar compounds when increasing the number of fryings can be due to the degradation of molecules already altered (polar). In general, Coratina oil appeared to be more unstable than Arbequina oil. This was not expected from the determined OSI times, demonstrating that the mechanisms followed for the deterioration of the oils in these two different deterioration conditions are different.

Considered only de first 15^{th} frying steps (before the slowing of the formation of polar compounds), is possible see that the polar compound content of Coratina was higher than that of Arbequina oil, and both oils exhibited similar rates of deterioration.

About the total content of polyphenols after 20 potato fryings in both oils (Table 4), for approximately the same content of polar compounds, the polyphenol content was slightly higher in the Arbequina oil than in the Coratina oil (starting from a Coratina oil with 3 times the content of polyphenols than the Arbequina oil). It follows that Arbequina oil reduced its polyphenol concentration to 45 % while Coratina reduced it to 12 %. This indicates that the polyphenols of the Coratina oil were degraded at a higher rate than the polyphenols of the Arbequina oil (phenomenon similar to the one found in this work for the temoxidation). This degradation indicates that the protection coming from them was reduced drastically with the number of fryings. Possibly because of this, both oils simultaneously reached the same % polar.

Casal *et al.* (2010) studied the frying of potatoes at 170 ℃. The phenols disappeared after a few hours of frying (between 6 and 9 hours), the results are not completely compatible with the present study since the methodology used for the measurement of the phenols was not the same.

3.6 Comparison of the Four Processes of Deterioration

The peroxide index increased much more rapidly in the oil at 60 °C than at room temperature (Tables 2 and 3). This is expected according to the acceleration caused by the increase in temperature.

On the other hand, at week 40 at room temperature, the ratio of the peroxide index of the Arbequina oil to that of the Coratina oil was 41.23/36.98 = 1.1 while at week 6 at 60 ℃ the ratio was 39.94/9.41 = 4.2. This means that the acceleration of deterioration due to temperature increase was not the same for both oils.

Both tocopherols and polyphenols deteriorated more slowly in 5 weeks at room temperature than at 60 ℃. This justifies that shelf-life under accelerated conditions is so much shorter than room temperature.

Both at room temperature and at 60 ℃, the highest deterioration rate of polyphenols (pending the respective trend lines) corresponds to Coratina oil (which has the highest initial polyphenol content). As a result, the rate of deterioration of each polyphenol depends on its initial concentration, so higher initial concentration, higher rate of deterioration, as indicated by Gómez-Alonso *et al.* (2007).

In the tests at 180 ℃ (thermoxidation and frying of potatoes) the behavior of the oils was very different: both deteriorated at the same rate (according to the formation of polar compounds).

Under conditions of thermoxidation at 180 ℃ (in the absence of food) or during repeated frying of potatoes at 180 ℃, the formation of polar compounds determines their possibility of re-use. This follows very different mechanisms from the primary oxidation (peroxide formation) of oil stored under ambient conditions or at 60 ℃.

These differences in behavior are also related to the deterioration of the polyphenols present. The polyphenols (ppm) content of both oils are shown in Figure 2 for the four tests performed: after 40 weeks storage at room temperature, after 6 weeks storage at 60 ℃, after 20 hours of thermoxidation at 180 ℃ and after 20 frying of potatoes at 180 ℃.

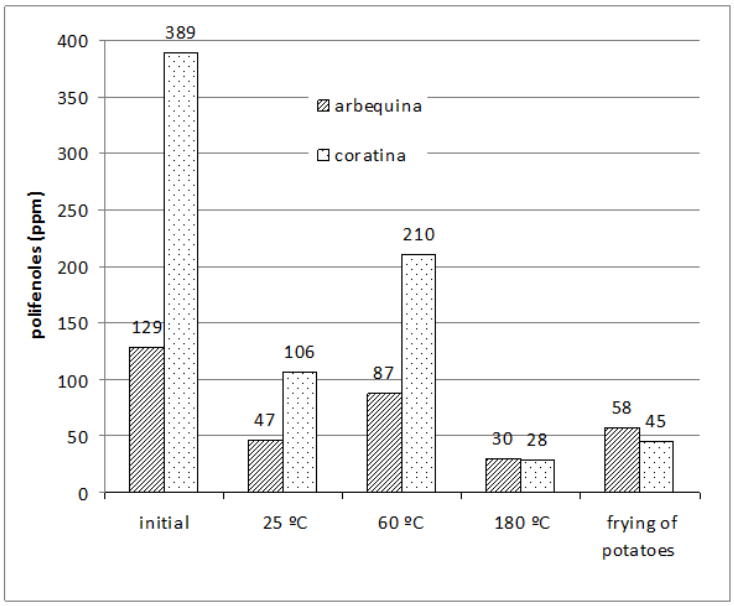


Figure 2. Polyphenol content (ppm) of the virgin olive oils of the Arbequina and Coratina varieties for the four tests performed: after 40 weeks of storage at 25 °C, after 6 weeks of storage at 60 °C, after 20 hours of thermoxidation at 180 °C and after 20 frying of potatoes at 180 °C

The 20 frying of potatoes (each of 4 minutes) at 180 ℃ correspond to a total of 80 minutes. The thermoxidation of the oil at 180 °C was 20 hours. Although the final content of polyphenols was slightly higher in the oil used for frying potatoes, given the very large difference in heating times it can be deduced that the deterioration of polyphenols is bigger when there is potato (frying) than in their absence (thermoxidation). These results are consistent with those found by Silva *et al.* (2010) because they found that all the polyphenols components decreased their concentration with the heat treatment and that decrease was drastic in the presence of food.

There is a noticeable difference in behavior between oils stored at room temperature and at 60 ℃ with oils kept at 180 °C (thermoxidation) or used in frying potatoes at 180 ℃. Coratina oil with a high content of polyphenols is more protected against oxidation (depending on, for example, its peroxide index) at relatively low temperatures than at high temperatures where polyphenols degrade and fail to protect it (with a mechanism of preponderant polar formation deterioration and not of peroxide formation). At moderate temperature conditions, OSI index is indicative of the stability of the oil, but in similar conditions to frying of foods, tocopherols and polyphenols which deteriorate rapidly, stops being.

4. Conclusions

The OSI times do not reflect the order of stability of the oils under thermoxidation conditions at 180 ℃ or in the frying of potatoes at the same temperature, where the formation of polar compounds determines their use. In contrast, OSI times are indicative for comparison of shelf-life of oils where the mechanisms of formation of

primary oxidation compounds predominate. However, without air bubbling and at these low temperatures (20-30 ℃) with respect to the OSI test temperature (110 ℃) the quantitative stability ratios are not maintained.

The antioxidants are deteriorated at very different rates depending on the experimental conditions. Thus, at high temperatures, in the absence or presence of food, antioxidants disappear quickly, failing to protect oils. Therefore, the initial antioxidant content of an extra virgin olive oil has little relevance to its use in repeated frying of food (the fatty acid composition of the oil is probably more important, so an olive oil will be more stable than other more polyunsaturated oils).

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