EXTRA VIRGIN OLIVE OIL QUALITY INVESTIGATION OF DIFFERENT BRANDS ACQUIRED IN COMMERCE FROM RIO DE JANEIRO CITY, BRAZIL

INVESTIGAÇÃO DA QUALIDADE DE AZEITES DE OLIVA EXTRAVIRGEM DE DIFERENTES MARCAS ADQUIRIDOS NO COMÉRCIO DA CIDADE DO RIO DE JANEIRO, BRASIL

INVESTIGACIÓN DE LA CALIDAD DE ACEITES DE OLIVA VIRGEN EXTRA DE DIFERENTES MARCAS ADQUIRIDOS EN EL COMERCIO EN LA CIUDAD DE RÍO DE JANEIRO, BRASIL

Rafaelle Franson Alves Coelho¹
Igor Santa Barbara do Nascimento²
Marcela de Souza Coelho³
Emília Akil⁴

DOI: 10.54751/revistafoco.v16n7-034
Recebido em: 12 de Junho de 2023
Aceito em: 11 de Julho de 2023

ABSTRACT
Olive oil is obtained by physical means without the usage of solvents. Different than edible vegetable oils, it can be consumed in the virgin form, also being an oil of a better nutritional quality and stability, since it is mainly composed by monounsaturated fatty acids (oleic acid) as well as many antioxidant compounds. Having its greatest value in raw state, the extra virgin olive oil is the one with best quality in organoleptic aspect. As a result, this kind of oil is the one that shows biggest interest to the population and has the highest commercial value, therefore being more susceptible to adulterations. This paper aims to assess the chemical characteristics which define its classification, chemical quality and possible presence of adulterations in different brands commercialized in Brazil, applying methods described in accordance with identity and quality standards, in conformity with current legislation. This paper consists in bromatological analyzes of quality research related to classification, oxidative state, and adulteration, applying analyzes of acidity, peroxide and iodine. According to the results obtained related to classification and oxidative state, all samples were found within limits of tolerance prescribed by all legislations. Regarding adulterations, based on the iodine

¹ Master's student in Food Science. Universidade Estácio de Sá (UNESA). Rua Paulo Lins, 17, Duque de Caxias, Rio de Janeiro - RJ, CEP: 25071-140. E-mail: rafaellefranson@gmail.com
² Bachelor in Nutrition. Universidade Estácio de Sá (UNESA). Rua Paulo Lins, 17, Duque de Caxias, Rio de Janeiro - RJ, CEP: 25071-140. E-mail: santabaraigor@gmail.com
³ Post-Graduate student in Maternal and Child Health with Emphasis on Breastfeeding. Universidade Estácio de Sá (UNESA). Rua Paulo Lins, 17, Duque de Caxias, Rio de Janeiro, RJ, CEP: 25071-140. E-mail: marcellinha.coelho@gmail.com
⁴ Post-Doctorate in Food Science. Universidade Estácio de Sá (UNESA). Rua Paulo Lins, 17, Duque de Caxias, Rio de Janeiro - RJ, CEP: 25071-140. E-mail: emilia.akil@gmail.com
analyzes, two samples showed higher values determined by legislations and one showed lower value. Values higher than those determined by legislations may show mixtures with lower quality vegetable oils, and lower values may indicate mixture with fats that are rich in saturated fatty acids or a correlation with its oxidative state. Seeing that it is a kind of food that has become a major interest for investigation due to its nutritional benefits, particularly in the prevention of cardiovascular diseases, besides assuring safety to the consumer, this research shows the importance of physicochemical analyzes in the quality of extra virgin olive oils found in the market.

**Keywords:** Extra virgin olive oil; bromatology; quality; classification; adulteration.

RESUMO
O azeite de oliva é obtido do fruto da oliveira (*Olea europaea* L.) por meios físicos, a frio e sem utilização de solventes. Diferente dos outros óleos vegetais alimentares, pode ser consumido na forma virgem, além de ser um óleo de melhor qualidade nutricional e estabilidade, pois é composto majoritariamente de ácidos graxos monoinsaturados (ácido oleico) e diversos compostos antioxidantes. Adicionalmente, tendo seu maior valor em estado bruto, o azeite de oliva extravirgem é o de melhor qualidade no aspecto organoléptico. Diante disso, este óleo torna-se o de maior interesse pela população e apresenta maior valor comercial e, com isso, pode ser alvo de adulterações. Este trabalho tem como objetivo avaliar as características químicas que definem a classificação, a qualidade química e presença de adulterações de azeites de oliva do tipo extravirgem de diferentes marcas comercializados no Rio de Janeiro (Brasil), utilizando métodos descritos de acordo com o padrão de identidade e qualidade de azeite de oliva extravirgem, conforme as legislações vigentes. O trabalho consiste na realização de análises bromatológicas de pesquisa de qualidade relacionadas a classificação, estado oxidativo e adulteração dos azeites de oliva, realizando análises de acidez, peróxido e iodo. De acordo com os resultados obtidos relacionados à classificação e estado oxidativo, todas as amostras se encontram dentro do limite de tolerância preconizado em todas as legislações. Com relação a adulteração, de acordo com as análises de índice de iodo, conforme a classificação de azeite de oliva extravirgem, duas amostras apresentaram valores acima do preconizado pelas legislações e uma amostra apresentou valor abaixo. Valores acima do preconizado pode indicar misturas com óleos vegetais de valores comerciais inferiores e, valores abaixo do preconizado, pode indicar misturas com gorduras que são ricas em ácidos graxos saturados ou uma correlação com o seu estado oxidativo. Visto que se trata de um alimento cada vez mais investigado pelos benefícios nutricionais que promove à saúde, principalmente na prevenção de doenças cardiovasculares, além de garantir segurança ao consumidor, esta pesquisa demonstra para o científico a importância das análises físico-químicas na qualidade dos azeites de oliva do tipo extravirgem encontrados no comércio.

**Palavras-chave:** Azeite de oliva extravirgem; bromatologia; qualidade; classificação; adulteração.

RESUMEN
El aceite de oliva se obtiene del fruto del olivo (*Olea europaea* L.) por medios físicos, en frio y sin el uso de disolventes. A diferencia de otros aceites vegetales alimentarios, puede consumirse en estado virgen, además de ser un aceite de mejor calidad nutricional y estabilidad, ya que está compuesto principalmente por ácidos grasos monoinsaturados (ácido oleico) y diversos compuestos antioxidantes. Además, al tener su mayor valor en estado crudo, el aceite de oliva virgen extra es el de mejor calidad en cuanto a aspectos organolépticos. Ante esto, este aceite se convierte en el de mayor
interés para la población y tiene mayor valor comercial y, por lo tanto, puede ser objeto de adulteraciones. Este trabajo tiene como objetivo evaluar las características químicas que definen la clasificación, calidad química y presencia de adulteraciones de aceites de oliva virgen extra de diferentes marcas comercializados en Río de Janeiro (Brasil), utilizando métodos descritos según el estándar de identidad y calidad de oliva virgen extra. aceite, de acuerdo con la legislación vigente. El trabajo consiste en realizar análisis bromatológicos de investigación de calidad relacionados con la clasificación, estado oxidativo y adulteración de los aceites de oliva, realizando análisis de acidez, peróxidos y yodo. Según los resultados obtenidos en cuanto a clasificación y estado oxidativo, todas las muestras se encuentran dentro del límite de tolerancia recomendado en toda la legislación. En cuanto a la adulteración, según el análisis del índice de yodo, según la clasificación del aceite de oliva virgen extra, dos muestras tenían valores por encima de lo recomendado por la legislación y una muestra tenía un valor por debajo. Valores por encima de lo recomendado pueden indicar mezclas con aceites vegetales de menor valor comercial, y valores por debajo de lo recomendado pueden indicar mezclas con grasas ricas en ácidos grasos saturados o una correlación con su estado oxidativo. Dado que es un alimento cada vez más investigado por los beneficios nutricionales que favorece a la salud, especialmente en la prevención de enfermedades cardiovasculares, además de garantizar la seguridad del consumidor, esta investigación demuestra al científico la importancia de los análisis físico-químicos en la calidad de los aceites de oliva. aceite del tipo virgen extra que se encuentra en el comercio.

Palabras clave: Aceite de oliva virgen extra; bromatología; calidad; clasificación; adulteración.

1. Introduction

The olive oil is a product obtained directly from the olive tree fruit (Olea europaea L.) through a mechanical cold extraction process, extracted by the separation of the natural oil within the olive fruits in the right degree of maturation, preserving the nutritional substances, the original scents, and original flavors. Due to these characteristics, the extra virgin olive oil shows the highest value in its raw state, as it is the best quality oil in nutritional and organoleptic aspect, and different from other edible vegetable oils, it can be consumed in its virgin form (Akil, 2015; Genovese et al., 2015; Gonçalves et al., 2022). However, they are also oils with higher quality and have a better stability as they hold a higher amount of monounsaturated fatty acids (oleic acid) and a range of antioxidant compounds which are not lost, since these oils do not undergo chemical refining (Genovese et al., 2015; Gonçalves et al., 2022).

As for commercialization and distribution, the olive oil shelf life is limited by oxidation reactions. During the olive oil degradation process, a series of chemical reactions involving unsaturated fatty acids, light, humidity, and oxygen
occur, in which these undesirable alterations are called hydrolytic and oxidative rancidity (Botti, 2014; Houshia, 2014; Gonçalves et al., 2022). By virtue of this, in Brazil, the olive oil regulation is done mainly by the Ministry of Agriculture, Livestock and Food Supply (MAPA) via instructive norms which aim to categorize the product based on identity and quality requirements, simultaneously to defining the sampling, the presentation mode and the marking or labeling of the packages, according to the categorization of the product (BRASIL, 2012).

The frequent consumption of olive oil is associated to various benefits to human health, particularly to the reduction of cardiac diseases due to a higher concentration of monounsaturated fatty acids present in its composition (oleic acid), to a lower concentration of saturated fatty acids and to a high content of antioxidants and vitamins. Such composition supports not only the decrease of inflammatory processes and, therefore, reducing the risk of chronic diseases, but also results in a reduction of LDL plasmatic cholesterol levels, preserving the level of HDL, and helping in cholesterol control (Donat-Vargas et al., 2021; Guasch-Ferré et al., 2022).

As a result of these benefits of olive oil to human health, the Food and Drug Administration (FDA) proposes that the substitution of foods rich in saturated fat by monounsaturated lipids, such as the olive oil, can reduce the risk of coronary heart diseases. Thus, the commercialization of olive oil has increased in a global level for its assurance of nutritional properties beneficial to health (Gonçalves et al., 2022; Guasch-Ferré et al., 2022). According to the International Olive Council (2019), the world’s production of olive oil has tripled in the past sixty years and Brazil is the third country with most importations.

According to the legislation (Brasil, 2012; Codex Alimentarius, 2015), for the olive oils to be commercialized, they must be in all cases within the current standards, based on physicochemical analyses. Additionally, in the extra virgin olive oil, any mixture of other oils or virgin olive oil is not allowed. These mixtures modify the sensorial and nutritional qualities, stimulate the loss of antioxidant properties, and reduce its effects that are beneficial to health (Akil et al., 2015; Genovese et al., 2015; Aued-Pimentel, 2017). The increased demand of extra virgin olive oils by the customers makes them hold a higher commercial value
and, consequently, be more susceptible to frauds, for instance the mixture with other vegetable oils with lower commercial value (Houshia et al., 2014; Ferreira, 2016; Aued-Pimentel, 2017).

For that matter, this paper intended to verify if the main labels of extra virgin olive oils sold in Brazilian commerce are in accordance with the current standards of Brazilian law, through physicochemical analyses (acidity, iodine and peroxide index). In addition, it aimed to investigate possible tampering according to the olive oil classification, as well as evaluate the oxidation state and quality parameters.

2. Materials and Methods

2.1 Acquisition and Preparation of the Samples

The samples have been obtained from twenty-five different brands of extra virgin olive oil, which have been purchased in several markets located in the city of Rio de Janeiro, Brazil. Three units of the same manufacturing batch of each brand have been acquired, on which were applied sampling methods in order to obtain reliable aliquots of those sample in each batch. The samples were stored in amber glass bottles, kept from light, in nitrogen atmosphere and in temperature of -18ºC until the execution of the analyses. The twenty-five brands of extra virgin olive oil examined were classified by numbers (1 to 25).

2.2 Definition of Quality Standards of the Extra Virgin Olive Oils

The quality standards of the extra virgin Olive Oils were determined by the acidity index, IP and iodine index (II). The analyses were made following the AOCS (2004) methods as described below. For a higher consistency of the results, three analyses on blank test were carried out and the results were expressed with mean and standard deviation.

2.3 Acidity Value

The definition of acidity value (AV) is based on the neutralization of free fatty acids up to the point of equivalence by an alkaline solution, with the usage of an indicator. This analysis establishes the amount of free fatty acids existent
in the olive oil samples. The analysis was made using titration of an alkaline solution of sodium hydroxide (NaOH) 0,1M with phenolphthalein indicator 1% and with previously dissolved samples in alcohol-ether solution (1:2 v/v). The acidity is equivalent to the number of milliliters of alkaline solution necessary to neutralize the free fatty acids existent in 100g of oil or fat, expressed by a percentage of oleic acid (Method Ca 5-40, AOCS, 2004).

2.4 Peroxide Value

Peroxide value (PV) indicates the level of oxidation of olive oils. Due to spontaneous oxidation, the organic peroxides produced in the beginning of the rancidity process act on the potassium iodide and release iodine. The analyses were made in accordance with the AOCS (Method Cd-8-53, 2004), titration with factored sodium thiosulfate 0,01M, with the samples previously diluted in solution of acetic-chloroform (3:2 v/v) with further addition of saturated solution of potassium iodide and starch solution to 1%. The results of PV were expressed in milliequivalents (mEq) of active oxygen per kilogram of sample (mEq O₂/kg).

2.5 Iodine Value

The effectuation of iodine value (IV) in olive oils identifies a possible adulteration by mixture with other vegetable oils. The result is obtained in accordance with the level of unsaturation of the fatty acids and it is expressed by the number of centigrams of iodine absorbed by a gram of the sample (% of absorbed iodine). Each oil holds a specific range in IV value. The iodine reacts on the double reactions of fatty acids, therefore, the higher the number of unsaturations, the higher the IV (Pascue et al., 2008; Rodriguez et al., 2014). The analyses were made by the Wijis method, titration with sodium thiosulfate 0,01M, with the samples previously solubilized and homogenized with chloroform, Wijs solution, potassium iodide and starch indicator to 1% (AOCS, Method Cd 1b-87, 2004).

2.6 Statistical Analyses

Descriptive statistics was performed for all variables in order to calculate
means, medians, standard deviation, and to estimate data normality. Results were expressed as mean ± standard deviation considering three independent replicates. Multifactor analysis of variance (MANOVA) was used for comparisons between means; significant differences between pairs of means were determined by the Fisher’s test. \( P \) values less than 0.05 were considered statistically significant. All statistical analyses were performed using the Statistica 8.0 software (StatSoft®, Oklahoma, USA).

3. Results and Discussion

3.1 Acid Value

Acid value represents the content of free fatty acid in the samples extracted from the triglyceride oxidation. The olive oil is highly predisposed to rancidity, since in its composition are predominant unsaturated fatty acids that are more susceptible to degradation. The process of decomposition modifies the concentration of hydrogen ions, that being both by oxidation and hydrolysis, and by fermentation. Although, during the processing and stocking chemical and enzymatic reactions occur (hydrolytic rancidity), due to lower trace of water present in the lipid that reacts with triacylglycerol and removes the fatty acid, which acidifies the surroundings, hence the more free fatty acids there are, the more acidified is the environment. This acidification alters the olive oil sensory characteristics, such as flavor and odor, in addition to promote nutritional loss. The main issue of having more free fatty acids is that it becomes susceptible to oxygen - oxidative rancidity (Akil et al., 2015; Clements & Decker, 2019). The free fatty acids acidify the environment by changing the oil’s physicochemical characteristics and this decomposition is accelerated by light and heat. Thus, the acidity analysis is fundamental for the conservation status and quality assessment of the oil (Clements & Decker, 2019).

Besides the hydrolytic rancidity, many other elements influence the acidity, such as the growth with the olive quality, if its damaged, fermented or infested by plagues; the maturation degree, the enzymatic action and the olive’s storage; and the method of acquisition and extraction of the extra virgin olive oil (Scherer et al., 2018). The assessment of the composition of free fatty acids in olive oils is of
EXTRA VIRGIN OLIVE OIL QUALITY INVESTIGATION OF DIFFERENT BRANDS ACQUIRED IN COMMERCE FROM RIO DE JANEIRO CITY, BRAZIL

great importance, not only as a study for the evaluation of hydrolytic rancidity condition that the product is in, but also to validate its classification and to provide more accurate identification of these frauds (Aued-Pimentel, 2017).

The extra virgin olive oil must have its acidity expressed in oleic acid lower or equal to 0.80%, according to the Codex Alimentarius (2015). On Table 1 the results obtained by the AV analyses of the twenty-five brands of extra virgin olive oil are represented.

Table 1. Acid value (% oleic acid) in all extra virgin olive oils brands.

<table>
<thead>
<tr>
<th>Brands</th>
<th>Acid value</th>
<th>Brands</th>
<th>Acid value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.28 ± 0.01</td>
<td>14</td>
<td>0.18 ± 0.02</td>
</tr>
<tr>
<td>2</td>
<td>0.16 ± 0.00</td>
<td>15</td>
<td>0.22 ± 0.02</td>
</tr>
<tr>
<td>3</td>
<td>0.29 ± 0.02</td>
<td>16</td>
<td>0.20 ± 0.00</td>
</tr>
<tr>
<td>4</td>
<td>0.18 ± 0.02</td>
<td>17</td>
<td>0.15 ± 0.02</td>
</tr>
<tr>
<td>5</td>
<td>0.21 ± 0.02</td>
<td>18</td>
<td>0.38 ± 0.03</td>
</tr>
<tr>
<td>6</td>
<td>0.19 ± 0.02</td>
<td>19</td>
<td>0.21 ± 0.05</td>
</tr>
<tr>
<td>7</td>
<td>0.21 ± 0.02</td>
<td>20</td>
<td>0.17 ± 0.03</td>
</tr>
<tr>
<td>8</td>
<td>0.25 ± 0.02</td>
<td>21</td>
<td>0.20 ± 0.00</td>
</tr>
<tr>
<td>9</td>
<td>0.26 ± 0.00</td>
<td>22</td>
<td>0.35 ± 0.02</td>
</tr>
<tr>
<td>10</td>
<td>0.29 ± 0.00</td>
<td>23</td>
<td>0.23 ± 0.02</td>
</tr>
<tr>
<td>11</td>
<td>0.16 ± 0.00</td>
<td>24</td>
<td>0.20 ± 0.00</td>
</tr>
<tr>
<td>12</td>
<td>0.20 ± 0.00</td>
<td>25</td>
<td>0.10 ± 0.00</td>
</tr>
<tr>
<td>13</td>
<td>0.31 ± 0.02</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Results are expressed as mean ± standard derivation of triplicates.
Source: From the author

As shown on table 1, the twenty-five brands which were tested are in accordance with the legislation (Codex Alimentarius, 2015; BRASIL, 2012), which values are within the limits of tolerance advocated, in which the lowest value found was of 0.10%, referring to the sample 25 and the highest value was of 0.38% regarding the sample 18, demonstrating that the processing and storage were possibly executed correctly.

The increase of free acidity occurs mainly in consequence of the enzymatic activity caused by damages on the olive tissue (Manai et al., 2007). By analyzing the conventional quality parameters and classifying 47 samples of extra virgin
olive oils from Greece, collected in the period of harvest during a year, Karabagias et al. (2013) identified 10 samples with acidity index slightly high, in which the values were expressed in percentages of oleic acid, where the lowest value was 0.25% and the highest 4.71%. This variation may be explained by the method of harvesting, since in that region the olive trees grow more than the usual and, for that matter, the usual method of collecting olives with the hands or with the assistance of brushes are impracticable. In that case, the harvest is done using plastic nets spread on the soil and that leads to an oxidation of the oil and an increase on its acidity.

In the study of Pardo et al. (2010), by analyzing the potential and real qualities of extra virgin olive oils of four different province denominations in Spain, under physicochemical parameters (free acidity and peroxide index) according to the Commission Regulation CEE/2568/91 by the Official Journal of European Communities (EUC,1991) and sensory parameters (median of defects, median of fruity and ranking test panel). From the twelve samples collected, all the olive oils analyzed showed very low values in all physicochemical quality parameters assessed, from which the lowest value of index acidity found was of 0.10% and the highest a value of 0.23%. These low values attest the high quality of these oils, and thus classified as extra virgin in accordance with (EUC,2003).

The sensory and physicochemical characteristics of the olive oil are modified according to crop conditions, the fruit maturation state, and harvest techniques (INMETRO, 2010). However, external factors such as inadequate storage conditions may interfere on the properties of the oil ready for consumption, causing loss of quality and nutritional value (Stefanoudaki et al., 2010).

Souza et al. (2020), by analyzing the stability of extra virgin olive oil samples during the storage in packing which allowed the passage of oxygen and light and kept under the light during fifty-one days, verified the increase on the acidity content, since the initial acidity of the sample was of 0.35% and by the 51st day the acidity had increased up to 0.54%. These results corroborate with those reported by Pristouri et al. (2010) e Dabbou et al. (2011), who analyzed the effect from package that allows the passage of oxygen and light on the stability and
quality of the olive oil and who also observed loss in quality, evidencing the influence that the package has on the exposition, degradation, and liberation of fatty acids during the storage.

3.2 Peroxide Value

Peroxide value indicates the level of oxidation of a lipid, and it is one of the most used methods for measuring the oxidation state (Moretto & Fett, 1998). The oxidative rancidity is mainly related to unsaturated fatty acids, where the reactive oxygen reacts on the fatty acid unsaturation double bonds, therefore the more unsaturation, the highest is the reactivity and the more unsaturated is the fatty acid, the more susceptible it is for rancidification (Scherer et al., 2018).

According to Akil et al. (2015), the oxidative rancidity takes place in three stages: initiation, when by being catalyzed by light and heat, the fatty acids lose an atom of hydrogen to the reactive oxygen, forming free radicals; propagation: the free radicals that were formed react with the atmospheric oxygen and form the peroxides, which in turn react with the free fatty acids producing primary compounds (hydroperoxides). This reaction occurs until all the unsaturated fatty acids are consumed. The third stage is called termination: the collected hydroperoxides react with one another and decompose, forming several secondary compounds, including aldehydes, ketones, alcohols, and hydrocarbons. Not only do these compounds alter both the sensory characteristics such as color, flavor and odor and nutritional characteristics and, thus reducing the olive oil’s lifespan, but are also harmful to human health.

The postharvest conditioning treatments also affect the PV, along with the process of extraction affects together with the initial oxidation and rancidification of the oil as well as the deterioration which may occur on natural antioxidants such as tocopherols and polyphenols (Cardoso et al., 2010). Besides its composition facilitate the oxidation, by being exposed to certain conditions, the olive oil becomes even more susceptible to this process. Factors such as: oxygen, which the more contact with the oxygen, the higher will be the process of degradation; light, which favors the oxygen reaction with unsaturated fatty acids; enzymes, by increasing the acidity; metals, since metallic ions are self-
oxidation catalysts and may cause alterations in flavor; and temperature, as the heat is a great catalyst and promotes oxidation. Therefore, it is of extreme importance to control the storage conditions of the oil to prevent undesirable reactions and, thus, preserve its quality (Gonçalves et al., 2022; Aued-Pimentel et al., 2017; Scherer et al., 2018)

According to the Codex Alimentarius (2015), the PV is measured in terms of milliequivalents (mEq) of active oxygen per kg of fat, being the limit for extra virgin olive oils equal or less than 20 mEq O₂/Kg. On table 2 are represented the results obtained by the analyses of PV of the twenty-five brands of extra virgin olive oil.

<table>
<thead>
<tr>
<th>Brands</th>
<th>Peroxide value</th>
<th>Brands</th>
<th>Peroxide value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12.6 ± 0.33</td>
<td>14</td>
<td>5.18 ± 0.20</td>
</tr>
<tr>
<td>2</td>
<td>9.74 ± 0.28</td>
<td>15</td>
<td>10.3 ± 0.00</td>
</tr>
<tr>
<td>3</td>
<td>6.93 ± 0.27</td>
<td>16</td>
<td>3.11 ± 0.10</td>
</tr>
<tr>
<td>4</td>
<td>10.8 ± 0.61</td>
<td>17</td>
<td>7.22 ± 0.57</td>
</tr>
<tr>
<td>5</td>
<td>7.11 ± 0.09</td>
<td>18</td>
<td>4.60 ± 0.40</td>
</tr>
<tr>
<td>6</td>
<td>5.20 ± 0.40</td>
<td>19</td>
<td>6.52 ± 0.50</td>
</tr>
<tr>
<td>7</td>
<td>4.41 ± 0.60</td>
<td>20</td>
<td>5.57 ± 0.49</td>
</tr>
<tr>
<td>8</td>
<td>6.67 ± 0.40</td>
<td>21</td>
<td>5.50 ± 0.11</td>
</tr>
<tr>
<td>9</td>
<td>3.01 ± 1.01</td>
<td>22</td>
<td>9.31 ± 0.86</td>
</tr>
<tr>
<td>10</td>
<td>6.82 ± 0.21</td>
<td>23</td>
<td>6.35 ± 0.04</td>
</tr>
<tr>
<td>11</td>
<td>4.56 ± 0.01</td>
<td>24</td>
<td>4.40 ± 0.20</td>
</tr>
<tr>
<td>12</td>
<td>5.40 ± 1.01</td>
<td>25</td>
<td>0.21 ± 0.40</td>
</tr>
<tr>
<td>13</td>
<td>8.04 ± 0.60</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Results are expressed as mean ± standard derivation of triplicates. Source: From the author

As shown in table 2, all the twenty-five brands tested are in conformity with the legislations, which values are within the limits of tolerance prescribed and which the lowest value found was of 3.01 mEq O₂/Kg referring to the sample 9 and the highest was of 12.6 mEq O₂/Kg from sample 1.

The results found in the twenty-five samples validate the relation between the fact that the samples were new and were under correct storage, since the
change in PV is due to the contact of the samples with unfavorable conditions, such as exposition to light and oxygen, and when they are stored in recipients that favor the passage of oxygen. The oxygen easily reacts with the free carbon of the lipid molecule, forming a peroxide radical. The peroxide radicals hold great energetic amount, removing an atom of hydrogen of the lipidic molecule, thus the peroxil radical turns into a hydroperoxide molecule, producing another lipidic radical. Such process may repeat several times in brief time (Kamal-Eldin & Pokorny, 2005).

According to Dabbou et al. (2011), when analyzing the effect of the material of the packages such as inox, jar, transparent polyethylene terephthalate (PET), transparent glass and dark glass bottle over the quantity of the oil with respect to its storage time from 0 to 12 months, the peroxide value showed an increase in data in the sixth month, circa 7 times more than the control at the end of storage. The inox, PET, transparent glass and dark glass materials showed similar tendencies to the material of the bottles, although with little variability after the ninth month. For these stored oil samples, a raise of around two to three times was detected. It can be observed that in the plastic packages exposed to light during its storage, the oil shows a higher peroxide value than in the dark glass bottles, since with time, the oxygen may enter the plastic packages due to its permeability, starting the oxidation. Therefore, time may affect the quality of the oil due to this oxidation process.

As stated by Hijawi (2021), when analyzing the oil content, peroxide values and acidity, fatty acid profile and total phenolic content, the old olive trees located in different climatic regions of the Palestine during the years of 2008 up to 2010, through the systems of Soxhlet and Abencor. The values of acid and peroxide were determined using the standard methods. The study showed that in 2008 the results of peroxide index were not significantly different among the many indicated locations, although in 2009 and 2010 considerable variations were found. In 2009, the highest peroxide value found was of 8.6 mEq O₂/Kg, in Bedjah, and the lowest was of 5.4 mEq O₂/Kg. In 2010, the highest value was of 12.1 mEq O₂/Kg in Beit Anan as the lowest was of 3.4 mEq O₂/Kg in Sourief. The results of this study showed a large range of peroxide values for different samples.
of oil from different regions and different years of harvest, as the highest and lowest values were of 12.1 mEq O$_2$/Kg in Beit Anan in 2010 e 3.4 mEq O$_2$/Kg in Sourief in 2010, respectively.

When the oil has low peroxide index and when it is kept closed during storage, it makes possible the preservation of important chemical compounds which are antioxidant, such as the level of α-tocopherol. These compounds function as “shields” in the olive oil’s nutritional and sensorial preservation, as they are the first compounds to suffer the oxidative process, preserving the unsaturated fatty acids. On the other hand, if the product is frequently opened, it considerably loses antioxidants, especially the α-tocopherol for being abundant in olive oils and, therefore, it is of great importance to be cautious during the domestic usage of the oils in order to preserve its characteristics (Akil et al., 2015; Marques et al., 2016; Rios et al., 2022).

3.3 Iodine Value

Iodine value determines the level of unsaturations of oils and fats for it quantifies the number of double bonds present in the lipid’s fatty acids. This index is directly connected to the lipid’s oxidation, since the unsaturations are the target of oxidation, and therefore the decrease of IV in a sample shows an increase of its degradation (Barradas et al. 2015; BRASIL, 2012).

This process follows a halogenation reaction, where the iodine is added to the fatty acids unsaturations in the form of iodine monochloride (ICl), succeeded by an addition reaction and, after that, by the titration with sodium thiosulphate for iodine quantification (Ferreira, 2016). That is a conventional and quick analysis in which any adulteration resulted of the mixture with other vegetable oils can be identified. As the iodine reacts with the fatty acids which have carbon-carbon double bonds, the higher the number of unsaturations, the higher will be the IV (Pascuet et al., 2008; Rodriguez et al., 2014; Barradas et al. 2015).

On one hand, this analysis enables to identify an adulteration caused by the mixture with other vegetable oils considering that the range of the values referred to the IV is particular for each fat. On the other hand, this index does not consider the structural differences present in the fatty acids, such as the position,
the number, or the nature of the double bonds (Rodriguez et al. 2014, Ferreira, 2016). The olive oils of the type of extra virgin and virgin must not be subjected to any mixture with other types of oil in its composition, this being allowed only to the olive oil, which is obtained by mixing the refined olive oil with either virgin or extra virgin olive oil in equal parts or in a higher proportion of the better-quality oil. As a result, the values of IV of the extra virgin olive oil must be expressed within the values of 75 to 94g I\(^2\)/100g (BRASIL, 2012; Codex Alimentarius, 2015).

On table 3 the results of II of the twenty-five samples of extra virgin olive oil are represented.

Table 3. Iodine value (I\(^2\)/100 g) in all extra virgin olive olis brands.

<table>
<thead>
<tr>
<th>Brands</th>
<th>Iodine value</th>
<th>Brands</th>
<th>Iodine value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>94.86 ± 4.40</td>
<td>14</td>
<td>84.24 ± 1.37</td>
</tr>
<tr>
<td>2</td>
<td>76.24 ± 0.21</td>
<td>15</td>
<td>81.35 ± 2.27</td>
</tr>
<tr>
<td>3</td>
<td>80.03 ± 0.72</td>
<td>16</td>
<td>80.83 ± 0.58</td>
</tr>
<tr>
<td>4</td>
<td>68.37 ± 0.04</td>
<td>17</td>
<td>83.06 ± 0.25</td>
</tr>
<tr>
<td>5</td>
<td>75.63 ± 2.06</td>
<td>18</td>
<td>81.67 ± 0.30</td>
</tr>
<tr>
<td>6</td>
<td>77.71 ± 0.99</td>
<td>19</td>
<td>77.05 ± 0.82</td>
</tr>
<tr>
<td>7</td>
<td>76.82 ± 0.19</td>
<td>20</td>
<td>79.30 ± 1.93</td>
</tr>
<tr>
<td>8</td>
<td>103.4 ± 2.85</td>
<td>21</td>
<td>78.82 ± 2.40</td>
</tr>
<tr>
<td>9</td>
<td>90.65 ± 0.72</td>
<td>22</td>
<td>80.71 ± 1.84</td>
</tr>
<tr>
<td>10</td>
<td>78.07 ± 2.31</td>
<td>23</td>
<td>78.00 ± 0.17</td>
</tr>
<tr>
<td>11</td>
<td>75.80 ± 6.14</td>
<td>24</td>
<td>78.28 ± 1.47</td>
</tr>
<tr>
<td>12</td>
<td>79.24 ± 2.34</td>
<td>25</td>
<td>91.38 ± 4.68</td>
</tr>
<tr>
<td>13</td>
<td>80.15 ± 0.78</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Results are expressed as mean ± standard derivation of triplicates.
Source: From the author

As shown on table 3, within the twenty-five brands tested, the lowest value found was of 68.37 g I\(^2\)/100 g regarding sample 4 and the highest was of 103.4 g I\(^2\)/100 g regarding sample 8. Sample number 8 had been found superior to the value predicted by legislation and sample 4 lower than the value predicted by legislation, as it was earlier mentioned. A lower value shows a possible degradation of the oil and thus reducing the level of unsaturation of these samples, as can be marked by the IP value of these samples on table 3 (10.8
mEq O$_2$/kg). In that case, sample number 4 was the second one which showed the highest PV values among the twenty-five samples, even though it was according to legislation, with PV lower only than sample number 1, justifying its low IV value. As it was earlier demonstrated, the PV is the main index which shows the beginning of oxidative rancidity, in which occurs the degradation of unsaturations of the fatty acids. If there is a high PV value on the sample, it shows that there is a high number of unsaturated fatty acids subjected to oxidation thus increasing the level of unsaturation on the sample.

The same correlation between PV and IV was observed on Cardoso et al. (2010), when they analyzed the physicochemical characteristics, such as IV, and the profile of the fatty acids present on olive oils from five different kinds of olives, they identified in one of the samples a value of 51.80 I$_2$/100 g, being that much lower than the standards of IV, and showing an PV higher than standard (25.50 mEq O$_2$/kg), being those the most different values among the five types analyzed, indicating a possible degradation of this oil and undesirable oxidations during the process of extraction.

On the other hand, the high IV values, as can be seen on sample number 8, may indicate a possible addition of a lower quality vegetable oil since when such fraud occurs the physicochemical and organoleptic characteristics suffer modifications, which were not noticeable during the analysis. The level of unsaturations of vegetable oils is higher when compared to that of extra virgin olive oil (Rios et al., 2013; Andrade et al., 2017). The vegetable oil most consumed in Brazil is the Soy, which shows a range of IV between 124 g and 139 g I$_2$/100 g (MAPA, 2006).

Yan et al. (2020), performed an investigation to identify the vulnerabilities for fraud throughout the productive chain of extra virgin olive oils among twenty-eight companies. It was noticed that any vulnerability for fraud depends largely on the motivations and opportunities that the fraudsters have, due to some failures in the production process which allow the occurrence of fraud. The factors related to technical opportunities during the production were classified as high risk for adulterations since the liquid state of the oil facilitates adulteration by the addition of either vegetable oils or lower quality olive oils in its composition.
In conclusion, any fraud on olive oils tampered with any vegetable oil will increase the olive oil’s level of unsaturation as occurred in the two samples. However, a deeper analysis is necessary using gas chromatography (GC), for being considered the main responsible to identify the composition of lipids (Visentainer, 2012), which quantifies the composition, profile, and number of fatty acids present in the sample, and therefore precisely indicating which vegetable oil was added and its concentration.

4. Conclusion
This paper was able to assure that among the twenty-five brands of extra virgin olive oil acquired in the market of a Brazilian city, most of them were found within the limits of identity and quality standards of current legislations, except for the Iodine Index of some samples, which could indicate possible frauds by the addition of some cheaper vegetable oil. From the foregoing, the relevance of this paper is explained by the increasing consumption of olive oil in Brazil, which by the nutritional perspective is exceptional, due to the uncountable benefits associated with its frequent ingestion.

ACKNOWLEDGMENTS

We thank UNESA (Duque de Caxias, RJ), which provide all materials support to analysis. The financial support of CNPq (Brazil), Franson R. was a recipient of an scientific research.

REFERENCES


HOUSHIA, O. et al. Effect of olive oil adulteration on peroxide value, delta-K and...


BRASIL. Instrução Normativa 1 de 30 de janeiro de 2012. Diário Oficial da União, Seção 1, 30/01/2012.


