



## FATTY ACID PROFILE AND ANTIOXIDANT CAPACITY OF *ORYZA sativa* L. (*JAPÔNICA SUBSPECIES*) MARKETED IN ITALY AND BRAZIL: A COMPARISON

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<https://doi.org/10.15414/jmbfs.4842>

### ARTICLE INFO

Received 15. 3. 2021

Revised 19. 5. 2021

Accepted 21. 5. 2021

Published 1. 8. 2021

Regular article



### ABSTRACT

Rice stands out as the most consumed cereal in the world because it is a source of vitamins, minerals, fiber, bioactive compounds, and unsaturated fatty acids. Based on this assumption, the objective of this work was to qualify and quantify fatty acids, in samples consisting of raw, integral, parboiled, and white rice marketed in southern Brazil (Vale do Itajaí) and the Vale do Pó region in northern Italy. The results of this work demonstrate that 95% of the total lipid content, in the respective rice typologies of both countries, is represented by palmitic, oleic, and linoleic acid. These results indicate that the technological processes influence the nutritional and functional quality of the rice grain in these countries. Regarding the content of total polyphenols, the maximum average value obtained was 477 g Eq g<sup>-1</sup> for rice from both countries and the best results for antioxidant activity, using the Photoquem® method with methanolic extract, was 3.43 μM Eq Trolox g<sup>-1</sup> for the Italian rice samples. These results indicate that the technological processes influence the nutritional and functional quality of rice grain from these countries.

**Keywords:** Lipid qualification; Lipid quantification; Antioxidant capacity; Polyphenols; Photoluminescence; Rice benefited

### INTRODUCTION

Rice (*Oryza sativa* L.) belongs to the subgroup *Oryza*, *Gramineae* family (Birla *et al.*, 2017; Wang *et al.*, 2018) and, is consumed worldwide in Africa, the Middle East, and Latin America, in which Brazil represents the third-largest annual producer with more than 12 million tons (Sellapan *et al.*, 2009; Conab, 2015).

Rice consumption is one of the sources of calories and comprises an important source of compounds that our bodies do not synthesize, including vitamins, minerals, fibers, bioactive compounds, and unsaturated fatty acids, such as palmitic acids (16:0), oleic (18:1) - omega 9 and linoleic (18:2) - omega 6, corresponding to approximately 95% of the fatty acids present in total rice lipids. Some rice types (including pigmented rice) are characterized with phenolic acids, flavonoids, anthocyanins, proanthocyanidins, and tocotrienols, besides carbohydrate and fibers (Walter *et al.*, 2008; Dors *et al.*, 2009; Monks *et al.*, 2013; Khoei & Chekin 2015; YU *et al.*, 2016; Melini *et al.*, 2019; Zaupa *et al.*, 2015; Sen *et al.*, 2020).

Rice intake takes the form of whole grain (crude, parboiled and white), flour, and fermented products (Oli *et al.*, 2014). For this reason, this cereal is a promising alternative as a source of energy, nutrients, bioactive compounds, and important antioxidant properties to eliminate free radicals. Polishing is the process in which the rice grain is subjected, and this process can desirable changes in rice properties (Limwachiranon *et al.*, 2019; Qi *et al.*, 2019), and also removes the endosperm, a region in which the phenolic compounds are concentrated in soluble form (conjugated to glycosides) and the insoluble form (complexed to the cell wall components) (Zhou *et al.*, 2004; Wojdylo & Oszmainski, 2007; Mira *et al.*, 2008; Palombini *et al.*, 2013; Kesarwani *et al.*, 2014).

Parboiled rice contains higher amounts of some nutrients than white rice, mainly due to minerals retention and water-soluble vitamins. This commercial rice type is preferred by consumers because it is less sticky than white rice and has better nutritional properties compared to non-parboiled rice (Heinemamm *et al.*, 2005;

Oli *et al.*, 2014; Min *et al.*, 2014). This cereal, regardless of the process conditions, is present in the daily diet of consumers as an important food in healthy diets, rich in phenolic compounds, tocopherols, tocotrienols, and  $\gamma$ -oryzanol (Liu 2007; Gani *et al.*, 2012; Pascual *et al.*, 2013).

The functional and nutritional benefits present in rice stimulate the consumption of brown rice, as its intake helps to regulate and prevent the risk of chronic diseases associated with oxidative damage, cardiovascular diseases, and other diseases. This is due to the tocotrienols, sterols, and  $\gamma$ -oryzanol content with high antioxidant activity, anti-inflammatory properties, and inhibition in the tumor formation (Mira *et al.*, 2008; Butsat & Siriamornpun, 2010; Goufo & Trindade, 2014). Unsaponifiable fraction components of rice, with approximately 50%  $\gamma$ -oryzanol, have an important functional value due to their antioxidant capacity that inhibits or delays oxidative reactions. These effects are associated not only with the unsaponifiable matter composition but also with the saponifiable components present in rice such as fatty acids (Chim *et al.*, 2006; Walter *et al.*, 2008).

Based on the above, this work aimed to study the profile of fatty acids in crude, white and parboiled rice (*Oryza sativa* L.) marketed in Brazil and Italy.

### MATERIAL AND METHODS

Italian rice samples (*Oryza sativa* L.), *Japanese* subspecies, and superfine and long classification were acquired in a rice processing plant in the Vale do Pó, in the region of Ferrara, *Emiglia Romagna*. Brazilian processed rice samples (*Oryza sativa* L.), *Japanese* subspecies, of type 1 - superfine and long classification, were provided by a rice processor from the region of Itajaí Valley, Santa Catarina.

The experimental study was carried out at the Food Chemistry Laboratory, at the Pharmacy Department at the University of Ferrara (UNIFE), and the Food

Processing Laboratory, at the Regional University of Blumenau (FURB). Samples were weighed and previously crushed, being analyzed in triplicate.

#### Determination and quantification of fatty acids

To determine and quantify fatty acids, the lipid content was extracted by the Soxhlet method (AOAC, 2002) with an automatic extractor (VELP SCIENTIFICA, Usmate, Milano), recovered in 3 mL of hexane, and transesterified with 1.5 mL of methanol and sodium hydroxide (5%).

The fatty acid composition was determined by a gas chromatography-mass spectrophotometer (GC-MS). After extraction by Soxhlet, the lipids were diluted in 2 mL of hexane and reserved in a glass tube at -25 °C until analysis time. Fatty acid methyl esters were prepared by transesterification with 1 mL of 5% sodium hydroxide in methanolic solution. The sample was stirred and the supernatant phase with the fatty acids was transferred to a flask with a cap to be injected immediately into GC-MS. The equipment used was a gas chromatograph (GC-Varian 3900) with a *Split-Splitless* injector and mass spectrophotometer (MS-Varian 2100) with electronic impact.

The column used (DB5) had the characteristics: 30 m in length; internal diameter of 0.25 mm and 200 °C of maximum temperature. The injectors had a temperature of 280 °C and the initial pressure of the carrier gas (helium) was 10 psi. The programming started with a temperature of 100 °C for 2 minutes, followed by an increase of 10 °C.min<sup>-1</sup> until reaching 200 °C, where it remained for 25 minutes; injection and acquisition mode: Split and Scan, respectively. The running time for each injected sample (1 µL) was 37 minutes.

#### Total polyphenols determination

The extraction of total phenolic compounds was carried out using 10 g of rice grain samples crushed in 100 mL of a mixture of ethanol and water (50:50, v/v), kept under stirring for 4 hours with a magnetic bar (Santos et al., 2011). An aliquot of the extract between 50 and 100 µL was removed and transferred to a 10 mL flask, in which 2.5 ml of deionized water and 500 µL of the Folin-Ciocalteu reagent were added (Singleton & Rossi, 1965). After the reaction of Folin's reagent with the polyphenols present in the sample, 2 mL of 10% sodium carbonate were added, and the volume was made up with deionized water. The samples remained at room temperature protected from light for 90 minutes and then proceeded to reading on a spectrophotometer (700 nm).

Gallic acid was used as reference, with which the calibration curve was constructed. Total polyphenols were expressed in µg equivalent of gallic acid (EAG) per gram of sample.

#### Sample preparation for antioxidant activity determination

Sample preparation was performed by weighing 5 g of crushed sample in 20 mL of methanol, stirred for 30 minutes. The supernatant was collected and transferred to a volumetric flask. The extraction was repeated with 20 mL of methanol for 30 minutes, and the supernatant was added to the preceding one. The flask contents were rotated at a temperature of 35-40 °C. The extract

recovered with 3 mL of methanol HPLC was kept at 4 °C until the time of analysis.

#### Antioxidant capacity determination by DPPH

The antioxidant capacity was determined with methanolic extract from the analyzed samples following the methodology described by Brand-Williams et al. (1995) modified by Miliauskas et al. (2004), using the DPPH stable radical as standard. The results were expressed in µM equivalent of Trolox per gram of sample.

#### Photochem®

The determination was carried out using the Photochem® instrument with the ACL kit (Analytikjena, Jena, Germany), and following the procedure described by Popov and Lewin (1999). Two or three mL reagent 1 (solvent and dilution reagent), 200 µL reagent 2 (buffer solution), 25 µL reagent 3 (photosensitizer) and 10 µL of standard or solution were mixed and measured. Trolox was used as standard to obtain a calibration curve (0.5–2 nM). The light emission curve was measured at λ<sub>max</sub>=350 nm during 180 s, using the inhibition of superoxide anion radicals as the parameter to evaluate antioxidant effect. The antioxidant capacity was determined by using the area under the curve. The results were expressed as µmol Trolox equivalents (TEs) per g sample. Antioxidant capacity was determined replacing standard by diluted samples. Determinations were performed with 3 replicates of each sample. All reagents were purchased from Sigma-Aldrich (Milan, Italy). The luminol PCL assay was carried out using the Photochem® instrument with the ACL kit (Analytikjena, Jena, Germany).

#### Statistical analysis

Analysis of variance (ANOVA) was performed employing Tukey Test, and the statistical significance was defined at a level of p < 0.05. Data analysis was carried using Statistica Windows, version 7.0, Statsoft. All determinations were conducted in triplicate, and the data were presented as mean values ± standard deviation.

## RESULTS AND DISCUSSION

The oil extracted from rice samples (*Oryza sativa* L.), marketed in Brazil and Italy, has a heterogeneous fatty acid composition among samples of Italian rice types (crude, brown, parboiled, and white) as well as Brazilian rice (crude, integral, parboiled and white) with gradual reduction of monounsaturated, polyunsaturated and saturated (Deepa et al., 2008) as can be seen in Table 1. Crude rice oil consists of 90 to 96% saponifiable lipids (triacylglycerols, diacylglycerols, monoacylglycerols, free fatty acids, and waxes) and 3-5% unsaponifiable (sterols, tocopherols, tocotrienols, triterpene alcohols) (Paucar-Menacho et al., 2007; Yoshida et al., 2011).

**Table 1** Fatty acid content of rice (*Oryza sativa* L.) Crude, White, Parboiled, and Integral Marketed in Brazil and Italy per gram of lipid extract

| Fatty Acid          | CR (g.100g <sup>-1</sup> ) | BR (g.100g <sup>-1</sup> ) | PR (g.100g <sup>-1</sup> ) | WR (g.100g <sup>-1</sup> ) |
|---------------------|----------------------------|----------------------------|----------------------------|----------------------------|
|                     | I/B                        | I/B                        | I/B                        | I/B                        |
| Miristic (C14:0)    | 0,37 ± 0.07 <sup>b</sup>   | 0,33 ± 0.04 <sup>b</sup>   | 0,70 ± 0.11 <sup>a</sup>   | 0,48 ± 0.10 <sup>b</sup>   |
|                     | 0,61 ± 0.11 <sup>ab</sup>  | 0,55 ± 0.05 <sup>ab</sup>  | 0,44 ± 0.07 <sup>b</sup>   | 0,66 ± 0.11 <sup>a</sup>   |
| Palmitic (C16:0)    | 17,65 ± 0.88 <sup>a</sup>  | 15,75 ± 1.63 <sup>a</sup>  | 44,14 ± 1.47 <sup>a</sup>  | 25,27 ± 0.48 <sup>a</sup>  |
|                     | 32,7 ± 1.58 <sup>a</sup>   | 27,60 ± 2.29 <sup>a</sup>  | 28,21 ± 0.79 <sup>a</sup>  | 27,91 ± 2.90 <sup>a</sup>  |
| Palmitoleic (C16:1) | 0,21 ± 0.04 <sup>b</sup>   | 0,18 ± 0.04 <sup>b</sup>   | 0,26 ± 0.01 <sup>a</sup>   | 0,19 ± 0.04 <sup>c</sup>   |
|                     | 0,19 ± 0.03 <sup>b</sup>   | 0,31 ± 0.06 <sup>b</sup>   | 0,19 ± 0.03 <sup>b</sup>   | 0,15 ± 0.06 <sup>a</sup>   |
| Stearic (C18:0)     | 2,64 ± 0.81 <sup>bc</sup>  | 1,98 ± 0.04 <sup>c</sup>   | 5,46 ± 0.51 <sup>a</sup>   | 3,44 ± 0.48 <sup>b</sup>   |
|                     | 05,04 ± 0.13 <sup>b</sup>  | 4,67 ± 0.79 <sup>b</sup>   | 5,61 ± 0.85 <sup>b</sup>   | 9,32 ± 1.73 <sup>a</sup>   |
| Oleic (C18:1)       | 43,98 ± 0.83 <sup>a</sup>  | 42,75 ± 0.65 <sup>a</sup>  | 41,64 ± 0.16 <sup>a</sup>  | 44,58 ± 2.12 <sup>a</sup>  |
|                     | 49,25 ± 1.75 <sup>ab</sup> | 52,28 ± 1.00 <sup>a</sup>  | 46,83 ± 2.42 <sup>b</sup>  | 37,84 ± 1.15 <sup>c</sup>  |
| Linoleic (C18:2)    | 34,69 ± 0.93 <sup>a</sup>  | 37,27 ± 3.01 <sup>a</sup>  | 0,90 ± 0.10 <sup>c</sup>   | 20,27 ± 2.63 <sup>b</sup>  |
|                     | 08,47 ± 0.33 <sup>a</sup>  | 11,54 ± 0.62 <sup>b</sup>  | 14,45 ± 1.60 <sup>a</sup>  | 07,35 ± 0.33 <sup>c</sup>  |
| Saturated           | 20,64 ± 0.45 <sup>b</sup>  | 18,07 ± 0.44 <sup>b</sup>  | 47,79 ± 0.53 <sup>a</sup>  | 29,19 ± 0.28 <sup>c</sup>  |
|                     | 38,36 ± 0.46 <sup>a</sup>  | 32,82 ± 0.79 <sup>a</sup>  | 34,26 ± 0.43 <sup>a</sup>  | 47,89 ± 1.20 <sup>a</sup>  |
| Monounsaturated     | 43,98 ± 0.83 <sup>a</sup>  | 42,75 ± 0.65 <sup>a</sup>  | 41,64 ± 0.16 <sup>a</sup>  | 44,58 ± 2.12 <sup>a</sup>  |
|                     | 49,25 ± 1.75 <sup>ab</sup> | 52,28 ± 1.00 <sup>a</sup>  | 46,83 ± 2.42 <sup>b</sup>  | 37,84 ± 1.15 <sup>c</sup>  |
| Polyunsaturated     | 34,69 ± 0.93 <sup>a</sup>  | 37,27 ± 3.01 <sup>a</sup>  | 0,90 ± 0.10 <sup>c</sup>   | 20,27 ± 2.63 <sup>b</sup>  |
|                     | 08,47 ± 0.33 <sup>a</sup>  | 11,54 ± 0.62 <sup>b</sup>  | 14,45 ± 1.60 <sup>a</sup>  | 07,35 ± 0.33 <sup>c</sup>  |

CR: Raw Rice; BR: Brown Rice; PR: Parboiled Rice; WR: White Rice. I: Italian; B: Brazilian. Different lower case letters on the same line indicate a significant difference at a 5% level of significance by Tukey test.

Unsataponifiable material content in rice varies according to the intensity and the processing method to which the rice is subjected. However, crude oil has an average content of 4% when compared to other vegetable oils that present around 1% (Wu et al., 2011; Tanigawa et al., 2011; Bruscatto et al., 2012; Wang et al., 2014).

The main fatty acids present in rice include palmitic acids (16:0), oleic acid (18:1), and linoleic acid (18:2), representing about 95% of the fatty acids present in total lipids. Among these fatty acids, unsaturated ones have important functions in several physiological processes, but they need to be introduced into the diet, as they are not synthesized by the human body (Deepa et al., 2008; Yoshida et al., 2011; Orsavova et al., 2015; Lilei et al., 2016).

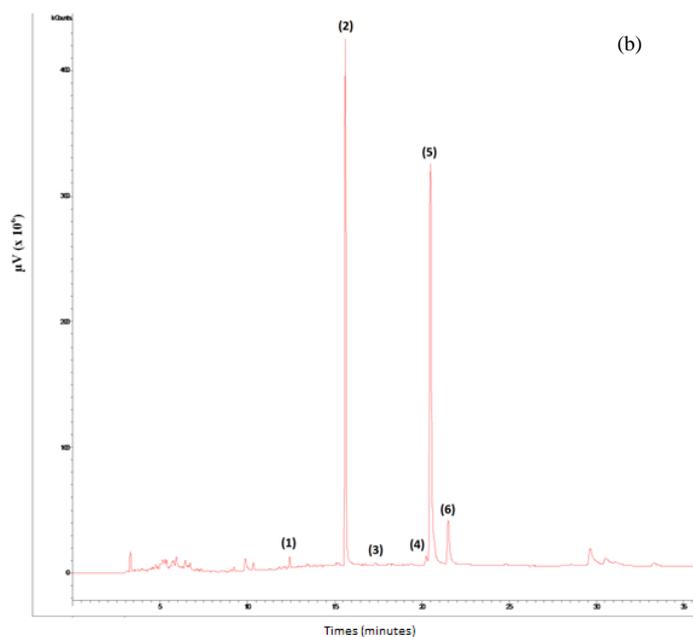
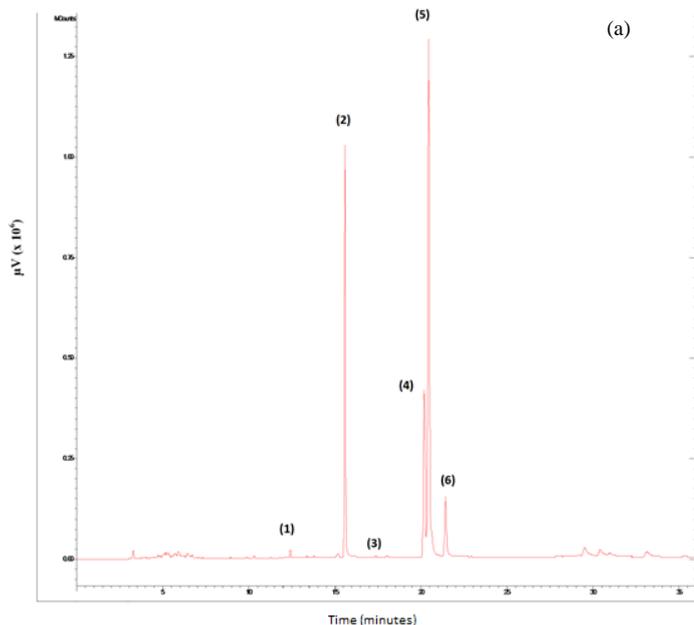
The lipid fraction of Italian rice samples with the highest percentage of palmitic, oleic, and linoleic acid, represented more than 80% of the total fatty acids. Among saturated acids, palmitic (16:0) represents a percentage between 15.75% (brown rice) to 44.14% (parboiled rice). As for unsaturated acids, oleic acid (18:0) is present in significant amounts from 42.75% (brown rice) to 44.58% (white rice) and linoleic acid (18:2), omega 6, ranging from 37.27% (brown rice) to 0.9% (parboiled rice).

When analyzing the grains after the parboilization process, it can be seen that the polyunsaturated fatty acids concentration decreased with hydrothermal treatment and grain polishing, probably due to the amylose complexation specifically with linoleic acid, which can lead to a slight increase in saturated and monounsaturated rice (Pestana et al., 2008; Dharmaraj & Malleschi 2011; Phatanayindee et al., 2012; Thammapat et al., 2016).

A decrease in polyunsaturated levels may be due to processing and heating, which can cause protein degradation in the membrane structure, phospholipid release, and polyunsaturated substances oxidation, which predominate in phospholipids (Min et al., 2014; Massarolo et al., 2016; Thammapat et al., 2016). In general, polyunsaturated fatty acids differ significantly ( $p \leq 0.05$ ) from saturated ones, for Italian rice, indicating that acids containing double bonds are more unstable to heat when compared to acids with single bonds. This reduction can also be attributed to the fatty acids degradation, as well as the unsaturated fatty acids of the macadamia nuts studied by Phatanayindee et al. (2012).

For Brazilian white rice, the linoleic acid content was lower than brown rice and to parboiled rice, different from Italian rice whose parboiled rice had a lower linoleic acid concentration than white rice, which indicates that this acid is unstable when subjected to the parboiling process, probably more intense, followed by polishing (Thammapat et al., 2016; Wu et al., 2016). A similar situation was reported by Kitta et al. (2005) when presenting similar results to those found in the samples of Italian and Brazilian rice, indicating that the percentage of linoleic acid decreases with the parboiling process, consequently increasing the percentage of palmitic acid. The average percentage of 43.23% for oleic acid in Italian rice samples in all conditions presented is similar, which indicates that this acid is a stable molecule to the different processes including parboiling (Pornpisanu et al., 2016).

In Figure 1(a), it can be seen that Brazilian parboiled rice is the one with the highest oleic acid percentage (52.28%), while Italian parboiled rice (b) stands out palmitic (44%), indicating that each country parboiling process can influence the results of the analyzed samples differently. This difference can also be related to the planting location, grain variety as well as climatic conditions (Dors et al., 2009; Thammapat et al., 2016; Massarolo et al., 2016).

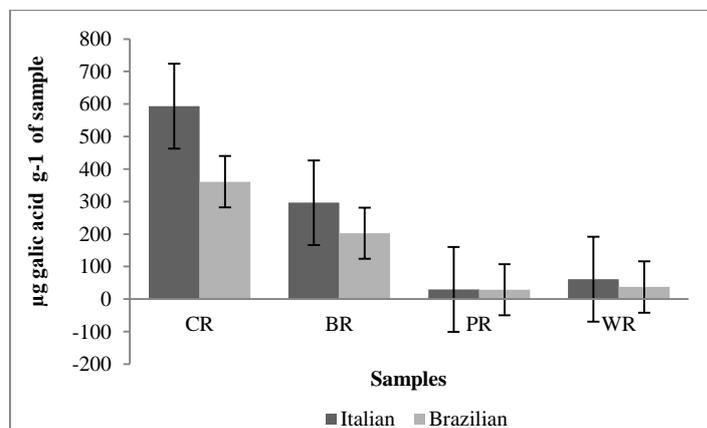


**Figure 1** (a) Fatty acid chromatogram (GC) from Brazilian parboiled rice samples (1) C14:0 (myristic acid); (2) C16:0 (palmitic acid); (3) C16:1 (palmitoleic acid); (4) C18:0 (stearic acid); (5) C18:1 (oleic acid); (6) C18:2 (linoleic acid) and (b) Fatty acids chromatogram (GC) from Italian parboiled rice samples. (1) C14:0 (myristic acid); (2) C16:0 (palmitic acid); (3) C16:1 (palmitoleic acid); (4) C18:0 (stearic acid); (5) C18:1 (oleic acid); (6) C18:2 (linoleic acid).

### Total antioxidant and phenolic properties

Recent studies report that a large part of the world population consumes rice as a source of calories and nutrients to promote satiety. However, these benefits go further and point out that this cultivar is an important phenolic compounds making them stable and beneficial to human health, due to the antioxidant action developed by such compounds, which can prevent cell damage, chronic diseases, cardiovascular and in some cases also cancer (Mira et al., 2008; Okater, Liu, 2010; Sumczynski et al., 2016; Magalhães et al., 2017). Among the foods under study is rice, in which the greatest antioxidant activity is present in whole grains due to the concentration of polyphenols found in the rice husk (Pauca-Menacho et al., 2007; Quagliariello et al., 2016). To elucidate the knowledge about antioxidants in rice and to identify a methodology that is more practical and quick, analyzes of total phenols and total antioxidant capacity were performed using the Photochem® and DPPH methods. Although the practice of different methodologies is known due to the different types of free radicals and their forms of action (Alves et al., 2010).

When evaluating the content of total polyphenols (Figure 3), it was found that the Brazilian samples show similar results to the Italian samples, when compared to the typology and related to the industrial technological treatment to which they were submitted to the samples. Thus, it is believed that both polishing and hydrothermal treatment significantly impact the amount of polyphenols present in the grains (Zhang et al., 2015; Thammapat et al., 2016).



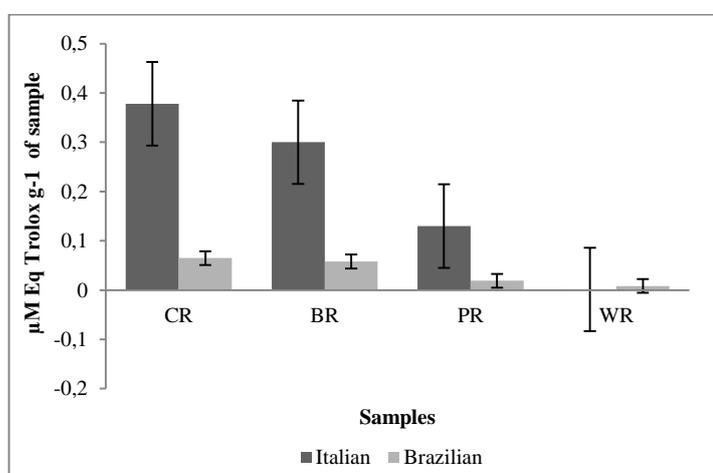
**Figure 3** Total polyphenols content ( $\mu\text{g}$  of gallic acid  $\text{g}^{-1}$  of sample) in the types of Italian and Brazilian rice ( $\text{CV}\% \leq 2$ ). CR: Raw rice; BR: Brown Rice; PR: Parboiled rice; WR: White Rice.

When comparing the results of raw rice in relation to the total polyphenol content for both countries studied with brown, parboiled and white rice, there is an average reduction of 477; 249; 29; 49  $\mu\text{g}\cdot\text{g}^{-1}$  respectively, mainly for the last two treatments. Thus, it is observed that polyphenols are sensitive to heat in the parboiling process, as well as the presence of oxygen and light (Roberto *et al.*, 2010; Setyaningsih *et al.*, 2016).

According to **Walter and Marchesan** (2011) the total phenols percentage in rice grains has been commonly associated with antioxidant activity. Probably because these different antioxidant classes substances can act to inhibit lipid peroxidation and lipoxygenase (Sousa *et al.*, 2007; Morais *et al.*, 2009).

The antioxidant capacity determination can be defined by several methods, among them the Photochem<sup>®</sup> method that uses methanolic extract and lipid extract (Soxhlet), while the DPPH method uses only the methanolic extract. These two methodologies were tested in order to compare them in terms of results, practicality and speed.

When determining the antioxidant capacity by the DPPH method (methanolic extract, Figure 5) and Photochem<sup>®</sup> (lipid extract, Figure 4), it is observed that the processing of Brazilian and Italian rice, significantly influences the total antioxidant capacity of the grains. This is shown in Figure 4, where the Italian crude rice, when transformed into brown rice, reduces the initial value by about 20%. From this to the parboiled, the reduction approaches 57% and from the parboiled to the white, there is a significant reduction of 99% of the total antioxidant capacity of the grain.



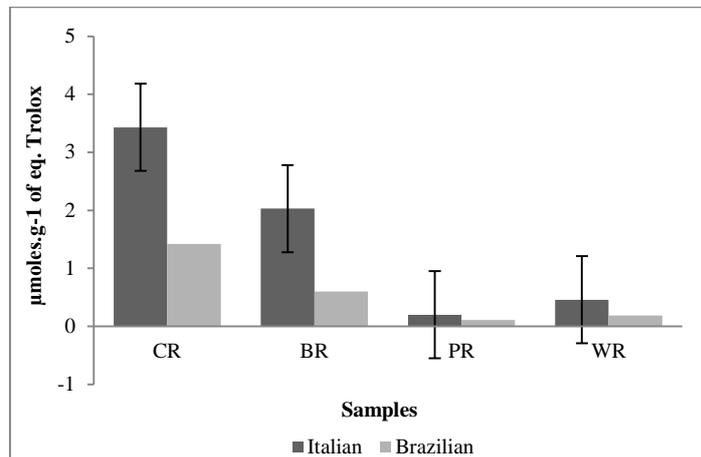
**Figure 4** Total antioxidant capacity ( $\mu\text{M}\cdot 10^{-1}$  Eq. Trolox  $\text{g}^{-1}$  of sample) of the lipid extract of the Italian and Brazilian rice types, using the Photochem<sup>®</sup> method ( $\text{CV}\% \leq 2$ ). CR: Raw Rice; BR: Brown Rice; PR: Parboiled Rice; WR: White Rice.

The Brazilian and Italian cultivars analyzed showed that brown rice contains about 10% of the husk and approximately 2.5% of oil, important from a nutritional and functional point of view, which makes it more attractive when compared to white and parboiled rice, whose process retains trace elements when migrating into the rice, but does not allow the maintenance of fat-soluble substances, such as tocopherols and  $\gamma$ -oryzanol, due to the influence of the time and temperature of the process (Kim *et al.*, 2007; Walter, *et al.*, 2011; Oluremi *et al.*, 2013; Zhang *et al.*, 2015). The components of the unsaponifiable fractions of rice, with approximately 50%  $\gamma$ -oryzanol, have an important functional value due to their antioxidant capacity that inhibits or delays oxidative reactions (Chim *et al.*, 2006; Walter *et al.*, 2008).

These effects are associated not only with the composition of unsaponifiable matter, but also with the saponifiable components present in rice such as fatty acids. Reports in the literature have shown that the use of high temperatures can lead to the formation of new compounds with greater antioxidant power. In this context, the Maillard reaction generates several products (MRPs - Maillard Reaction Product) with antioxidant power resulting from the thermal processing or prolonged storage of some foods (Yoshida *et al.*, 2011; Bastos *et al.*, 2011; **Shibao & Bastos**, 2011; **Vhangani & Wyk**, 2016; Lilei *et al.*, 2016).

Upon realizing that the antioxidant activity is not only related to fat-soluble compounds, but also to a heterogeneous set of substances, the total antioxidant capacity of the methanolic extract was determined using the Photochem<sup>®</sup> and DPPH method.

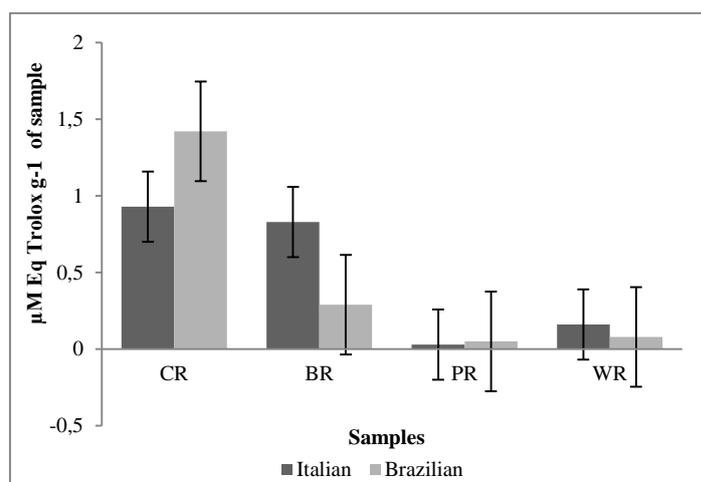
For the Photochem<sup>®</sup> method in the methanolic extract, the values varied between 3.43 to 1.42  $\mu\text{M}$  Eq Trolox  $\text{g}^{-1}$  of sample in Italian and Brazilian rice (Figure 5) when compared to the lipid extract 3.78 to 0.65  $\mu\text{M} \cdot 10^{-1}$  Eq Trolox  $\text{g}^{-1}$  of sample in Italian and Brazilian rice (Figure 4). These values were significantly higher ( $p < 0.05$ ), suggesting that the antioxidant action of phytochemicals in the lipid fraction of rice is much lower than the total antioxidant capacity of this cereal. It is believed that the high extraction temperature of the lipid component (by means of automatic Soxhlet at 130 °C) may have influenced the reduction of the total antioxidant capacity.



**Figure 5** Total antioxidant capacity ( $\mu\text{M}$  Eq. Trolox  $\text{g}^{-1}$  of sample) of the methanolic extract of the Italian and Brazilian rice types, using the Photochem<sup>®</sup> method ( $\text{CV}\% \leq 2$ ). CR: Raw rice; BR: Brown Rice; PR: Parboiled rice; WR: White Rice.

The results obtained for both extracts indicate the industrial processes influence on the antioxidant activity of rice (Walter *et al.*, 2011; Zhang *et al.*, 2015). For the Brazilian rice types, the total antioxidant activity values of the methanolic extract of the samples are easily correlated to the content of total polyphenols, while the results of the antioxidant capacity obtained from the lipid extract do not correlate to these when analyzed for the influence of technological treatments on the composition of rice.

When evaluating the antioxidant capacity of Brazilian and Italian samples using the DPPH method (Figure 6), in relation to the industrial treatment to which they were submitted and the analysis methodologies, it was found that there was variation in the different types of rice.



**Figure 6** Total antioxidant capacity ( $\mu\text{M}$  Eq. Trolox  $\text{g}^{-1}$  of sample) of the methanolic extract of Italian and Brazilian rice, using the DPPH method, ( $\text{CV}\% \leq 2$ ). CR: Raw Rice; BR: Brown Rice; PR: Parboiled rice; WR: White Rice.

Despite this method being widely used by several authors to evaluate the methanolic extract antioxidant capacity of the analyzed samples, has as principle the inhibition of the stable radical 2,2-diphenyl-1-picrylhydrazyl (DPPH •) by antioxidants (**MOON & Shibamoto**, 2009; **Scherer & Godoy**, 2009; Deng *et al.*, 2011; **Kedare & Singh**, 2011).

Regardless of the method used for the analysis of the methanolic extract, it can be seen that brown rice had a more favorable total antioxidant capacity when compared to parboiled rice, whose value is lower, probably due to the heat treatment and/or polishing process to the which were submitted. Such processes considerably reduce the antioxidant activity of phytochemicals present in rice. A similar situation was also reported by Hu *et al.* (2017) when they found that the phenols level present in parboiled rice also changed, possibly due to the different conditions of the hydrothermal treatments to which the product was subjected, as well as to the different analytical methodologies used.

## CONCLUSION

The sample analysis of processed rice, Italian and Brazilian (crude, integral, parboiled and white), demonstrated the influence of industrial technological processes on the quality and quantity of fatty acids, total polyphenols and total antioxidant capacity of the analyzed grains.

The main fatty acids present in rice in all types are palmitic acids, oleic acid and linoleic acid. The quantification analyzes of the total polyphenols and the total antioxidant capacity, using methanolic extract (DPPH and Photochem<sup>®</sup>) demonstrated the same negative influence of reduction of these compounds when the rice is submitted mainly to the thermal treatment, different from the analyzes with lipid extract (Photochem<sup>®</sup>) reported the lowest values for white rice grains.

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