GRASAS Y ACEITES 70 (1)
January–March 2019, e294
ISSN-L: 0017-3495
https://doi.org/10.3989/gya.0572181

Effects of heating temperature on the tocopherol contents of chemically and physically refined rice bran oil

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Submitted: 11 May 2018; Accepted: 03 September 2018

SUMMARY: The stability of α-, (β+γ)- and δ-tocopherols present in rice bran oil at different heating temperatures has been evaluated. For this purpose, samples of rice bran oil from chemical and physical refining processes in Brazilian industries were studied. The oils were submitted to cabinet drying without air circulation in the absence of light at 100 ºC, 140 ºC and 180 ºC. The samples were taken before heating and after 48, 144, 240, 336, 432, 576, 768, 1008 and 1368h of heating. The analyses of tocopherols were made by high performance liquid chromatography, with a fluorescence detector. It was determined that α-tocopherol was the compound with the fastest degradation rate at the three heating temperatures. The highest degradation rate of tocopherols in both oils occurred at 180 ºC. Among the tocopherols studied, α-tocopherol presented the lowest stability, followed by (β+γ)- and δ-tocopherols.

KEYWORDS*: Antioxidant; Chemical refining; Physical refining; Temperature*

RESUMEN: ***Efecto de la temperatura de refinación química y física de aceites de salvado de arroz sobre el contenido de tocoferoles.*** La estabilidad de los tocoferoles α-, (β + γ) - y δ presentes en los aceites de salvado de arroz a diferentes temperaturas de calentamiento fueron evaluadas. Para ello, se utilizaron muestras de aceite de salvado de arroz proveniente de los procesos de refinación química y física de industrias brasileñas. Los aceites fueron sometidos a 100 ºC, 140 ºC y 180 ºC, en cabinas de secado sin circulación de aire, bajo ausencia de luz. Las muestras fueron tomadas antes de la calefacción y después de 48, 144, 240, 336, 432, 576, 768, 1008 y 1368 h de calentamiento. El análisis de tocoferoles fue realizado por cromatografía líquida de alta eficacia, con detector de fluorescencia. Se observó que el α-tocoferol fue el compuesto con degradación más rápida en las tres temperaturas de calentamiento. La mayor tasa de degradación de los tocoferoles, en ambos aceites, ocurrió a la temperatura de 180 ºC. Entre los tocoferoles analizados, α-tocoferol presentó menor estabilidad, seguido por los (β + γ) - y δ-tocoferoles.

PALABRAS CLAVE*: Antioxidante; Refinación física; Refinación química; Temperatura*

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Citation/Cómo citar este artículo: Bruscatto MH, Pestana-Bauer VR, Otero DM, Zambiazi RC. 2019. Effects of heating temperature on the tocopherol contents of chemically and physically refined rice bran oil. *Grasas Aceites* **70** (1), e294. https://doi.org/10.3989/gya.0572181

1. INTRODUCTION

Rice bran, a by-product of the rice milling process, constitutes about 10% wt of rough rice grain and 18 to 22% oil (saponifiable lipids including glycolipid and phospholipids, and unsaponifiable lipids, including tocopherols, tocotrienols, oryzanol, sterols, and carotenoids), making it the richest oil source from a grain by-product (Salem *et al*., 2014). The antioxidant compounds in rice bran have proven health benefits as well as antioxidant characteristics for improving the storage stability of foods (Azlan *et al*., 2008). Rice bran contains relatively high concentrations of tocopherols compared to other oil seeds, which increases its nutritive value (Ko *et al*., 2008; Salem *et al*., 2014).

α-, β-, γ- and δ-tocopherols, which differ in the number and localization of the methyl groups in the aromatic ring, contain vitamin E. Tocopherols are monophenolic compounds and are characterized by a lateral chain saturated with 3 quiral carbons of asymmetry in positions 2, 4 and 8 (Morrissey and Sheehy, 1999; Cunha, 2006; Flohé, 2006; Rosli *et al*., 2006; Martins, 2006).

α-tocopherol is one of the most abundant natural antioxidant in nature, and is found in practically all vegetable oils. It is recognized for exerting biological effects that protect cellular membranes and for increasing the stability of oils and fats. α-tocopherol presents high biological activity as vitamin E, which is twice superior to β- and γ- and 100 times superior to δ-tocopherol (Nolasco *et al*., 2004; Romero *et al*., 2007; Pestana *et al*., 2008a).

Tocopherols are oxidized by oxidizing agents, especially in the presence of heat, light, metals and alkaline mediums. These compounds oxidize slowly in an oxygen-charged atmosphere, in the absence of light, even at temperatures above 200 ºC. However, in the presence of oxygen, the stability of α-tocopherol is reduced by half at each 10 ºC increase when exposed to temperatures higher than 40 ºC (Martins, 2006).

The oxidative degradation of tocopherols is strongly influenced by the oxidation of unsaturated fatty acids. The degradation of tocopherols increases with lipid oxidation, a high concentration of oxygen and the presence of free radicals (Zambiazi, 1997; Pestana, *et al*., 2009). Research carried out by Player, Kim, Lee and Min (2006) to evaluate the stability of α-, γ- and δ-tocopherols during the oxidation of soybean oil at 50 °C demonstrated that α-tocopherol showed higher degradation than γ-and δ-tocopherols. In accordance with the same authors, the degradation of tocopherols increases with the level of oxidation in the oil; α-tocopherol was completely destroyed at 16 days while γ- and δ-tocopherols l were still present after 24 days of heating.

The content and proportion of the tocopherols present in oil depends on a number of factors, such as the oil extraction and purification process, storage time and conditions, as well as the type of refining and conditions, which may be chemical or physical (Martins *et al*., 2006).

Unacceptable materials are separated from crude oils by using a different type of refining process. Chemical refining includes degumming, neutralizing, bleaching, winterizing and, finally, deodorizing stages. In physical refining, the removal of free fatty acids by chemical neutralization is replaced by simultaneous de-acidification/de-odorization (Tasan and Demirci, 2005)

The aim of this study was to evaluate the stability of tocopherols (α, δ- γ) against continuous heating at different temperatures (100 ºC, 140 ºC and 180 ºC) of chemically and physically refined rice bran oil.

2. MATERIALS AND METHODS

2.1. Reagents and samples

The solvents used in the study were isooctane, isopropanol, acetonitrile and acetone (Vetec, Rio de Janeiro, Brazil). Standards of α- tocopherol (99%, Merck, Darmstadt, Germany), γ–tocopherol (> 96%, Sigma) and δ-tocopherol (> 90%, sigma), were also used.

Samples of chemically refined rice bran oil (*Oryza sativa*) were donated by the rice bran oil processing industry (Indústria Rio-Grandense de Óleos Vegetais Irgovel (Pelotas-RS)). The physically refined rice bran oil was donated by the rice bran oil processing industry (Helmut Tessmann (Camaquã/RS)).

2.2. Procedure

Chemically and physically refined rice bran oil was heated in the absence of light. For this purpose, 300 mL of each type of oil were placed separately in open glass recipients with 500 mL capacity. The oils were previously heated until they reached the temperature of the experiment and after that they were placed in the interior of the heater at the predetermined temperature. The experiments were conducted at temperatures of 180 °C ± 2, 140 °C ± 2 and 100 °C ± 2, to simulate the cooking and frying conditions of many food preparations.

The samples were collected at pre-determined time intervals and stored in amber-colored flasks which were frozen at -18 ºC until analysis.

The collection of samples was carried out every 48 h until 432 h of heating for oil at 180 °C. The oil samples heated at 140 ºC were collected at the same intervals until 432 h of heating, and the samples were collected every 72 h until 576 h, and after each 120 h until 1008 h of heating. The same procedure was followed for the oil heated at 100 °C until 1368 h of heating. The final point of sample collection at different temperatures was defined when α-tocopherol was absent from the oil sample.

2.3. Quantification of tocopherols

The analysis of tocopherols was carried out in accordance with the methodology described by Pestana *et al*., 2008b. Approximately 250 mg of rice bran oil were weighed and diluted in acetone to the volume of 5mL. The mixture was centrifugated for 6 minutes at 9000 rpm in a micro-centrifuge (NT800 Nova Técnica, Piracicaba, Brazil), and the organic phase was removed to a vial with a 1.5 mL capacity. Aliquots of 20 to 40 μL were injected into the liquid chromatograph.

The HPLC separations were performed at 25 ºC with a constant flow rate of 1 mL·min^{-1}. Fluorescent detection, with excitation and emission wavelengths set at 290 and 330 nm, was used for the tocopherols. The initial and final mobile phases were 50:40:10 (A) and 30:65:5 (B) acetonitrile-methanol-isopropanol mixtures (v/v/v), respectively. Separation was carried out with an isocratic elution of phase A for 5 min., changing by a linear gradient for 10 min. to phase B, followed by 5 min. of isocratic elution with phase B and then returning to phase A in 5 min. The time of analysis was 15 min. Class-VP software was used to acquire and process the data. Standards of α-, γ- and δ- tocopherols were used for external calibration curves.

2.4. Statistical analysis

The design was completely randomized in a 2x10 bi-factorial scheme, with two forms of refining and ten times of evaluating. To analyze the data, the means and respective standard deviations were performed, as well as the analysis of variance ($p < 0.05$). For the quantitative variables that presented significance, regression analysis was performed; while for the qualitative analysis, the T test ($p < 0.05$) was performed. All analyses were performed in triplicate.

3. RESULTS

α-tocopherol was the major tocopherol found in the chemically refined rice bran oil (OCR) as well as in the physically refined rice bran oil (OPR), followed by (β+γ)- and δ-tocopherols. The content of (β+γ)- and δ-tocopherols was practically the same in both oils. However, the chemically refined oil showed the highest level of α-tocopherol (time zero, Table 1)

The content of α-tocopherol in the OCR showed a gradual reduction until 432 h of heating at 100 ºC, reaching a 28,65% loss in this period. After this period its degradation was more intense and in the period of 1368 h it presented total degradation.

The content of α-tocopherol in OPR showed a lower degradation rate, reaching a loss of only 8.53% in the period of 432 h of heating. During the period from 432 h to 1008h of heating, the tocopherol showed a loss of 47.56%; therefore, the loss was lower to that presented by the chemically refined oil. The loss in α-tocopherol was only 63.69% upon completing 1368 h of heating, also lower than that presented by the chemically refined oil. Therefore, at 100 ºC, the loss in α-tocopherol in chemically refined oil was lower than in physically refined oil.

Table 1. Tocopherol contents (n=3, mean ± SD), in chemically refined rice oil and physically refined oil subjected to a temperature of 100 °C

	α-tocopherol (mg·100g^{-1})		γ-tocopherol (mg·100g^{-1})		δ-tocopherol (mg·100g^{-1})	
Time (h)	**OCR***	**OPR****	**OCR***	**OPR****	**OCR***	**OPR****
0	32.84 ± 1.5^{a}	25.67 ± 1.9^{b}	9.91 ± 1.1^{a}	9.22 ± 0.8^{a}	0.77 ± 0.1^{a}	0.71 ± 0.1^{a}
48	32.17 ± 2.0^{a}	25.15 ± 1.9^{b}	8.84 ± 0.3^{a}	8.54 ± 0.9^{a}	0.77 ± 0.1^{a}	0.63 ± 0.1^{b}
144	31.51 ± 2,9^{a}	25.01 ± 0.8^{b}	8.59 ± 0.5^{a}	7.09 ± 0.8^{b}	0.73 ± 0.1^{a}	0.63 ± 0.1^{a}
240	26.88 ± 2.3^{a}	23.93 ± 1.2^{b}	8.13 ± 0.8^{a}	6.85 ± 0.4^{b}	0.69 ± >0.1^{a}	0.53 ± 0.1^{b}
336	25.77 ± 0.8^{a}	23.83 ± 1.0^{a}	8.10 ± 0.2^{a}	6.71 ± 0.3^{b}	0.69 ± >0.1^{a}	0.52 ± 0.1^{b}
432	23.43 ± 2,6^{a}	23.48 ± 0.9^{a}	7.99 ± 0.3^{a}	6.37 ± 0.6^{b}	0.64 ± >0.1^{a}	0.52 ± >0.1^{a}
576	18.43 ± 1,4^{a}	20.49 ± 1.8^{a}	6.82 ± 1.1^{a}	5.60 ± 0.2^{b}	0.61 ± >0.1^{a}	0.49 ± >0.1^{a}
768	14.46 ± 1.3^{b}	20.45 ± 1.7^{a}	6.07 ± 0.5^{a}	5.51 ± 0.3^{a}	0.60 ± >0.1^{a}	0.48 ± >0.1^{a}
1008	6.29 ± 1.1^{b}	13.46 ± 0.5^{a}	4.16 ± 0.6^{a}	3.70 ± 0.4^{a}	0.53 ± >0.1^{a}	0.42 ± 1.0^{a}
1368	Nd	9.32 ± 0.6^{a}	2.00 ± 0.2^{a}	2.38 ± 0.4^{a}	0.51 ± >0.1^{a}	0.28 ± 1.0^{b}

Values followed by lowercase letters between the columns (OCR and OPR) do not differ from each other at 5% significance by the T test t ($p > 0.05$).
Nd- not detected
*OCR: chemically refined oil
**OPR: physically refined oil

The content of (β+γ)-tocopherol in the chemically refined oil showed a degradation of 19.37% in the period of 432 h of heating, reaching losses of 58.02% at 1008 h of heating. The highest degradation rate of the (β+γ)-tocopherol occurred at the end of the heating period (1.368 h), when its content presented a reduction of 79.82%.

In the physically refined oil, the reduction of (β+γ)-tocopherol was also greater, 30.91% at 432 h of heating. However, the highest percentage of degradation occurred in the period of 1008 h (59.87%) and at the end of the heating period (1368 h), the reduction of the (β+γ)-tocopherol (74.19%) was lower when compared to the chemically refined oil.

The content of δ-tocopherol in the chemically refined oil showed a reduction of 16.88% in the period of 432 h and 37.77% at the end of the heating period (1368 h). In the physically refined oil, the content of this tocopherol showed a more intense decrease than the content of δ- tocopherol in the chemically refined oil, with a reduction of 26.76% in the period of 432 h and of 60.56% at the end of the heating period (1368 h).

Thus, at the heating temperature of 100 ºC, it was observed that tocopherols present in the physically refined oil remained more stable than the tocopherols present in the chemically refined oil, which can be observed in Figure 1a.

The content of α-tocopherol in the chemically refined oil heated at 140 ºC (Table 2) showed a degradation of 32.19% at 432 h and its degradation was 100% at 1008 h of heating. Once again, the content of α-tocopherol in physically refined oil presented a reduction of only 59.80% at the end of the period of 1008 h.

The OCR heated at 140 ºC showed a gradual reduction in the (β+γ)-tocopherol in all heating periods, presenting a degradation of 87.08% at the end of the heating period (1008 h). The (β+γ)-tocopherol in OPR presented a reduction of 59.65% compared to the 41.57% reduction in (β+γ)-tocopherol in the chemically refined oil during the same period, which means that more than half of its initial content had already been degraded.

Once again, the content of (β+γ)-tocopherol in the physically refined oil presented a more rapid degradation during the heating period than in the chemically refined oil. However, at the end of the exposure time to heating, it presented very similar reduction percentages.

The content of δ-tocopherol in the chemically refined oil showed a gradual reduction until reaching the period of 432 h of heating (29.87%). After this period its degradation was more intense, reaching a reduction of 44.16% upon completion of

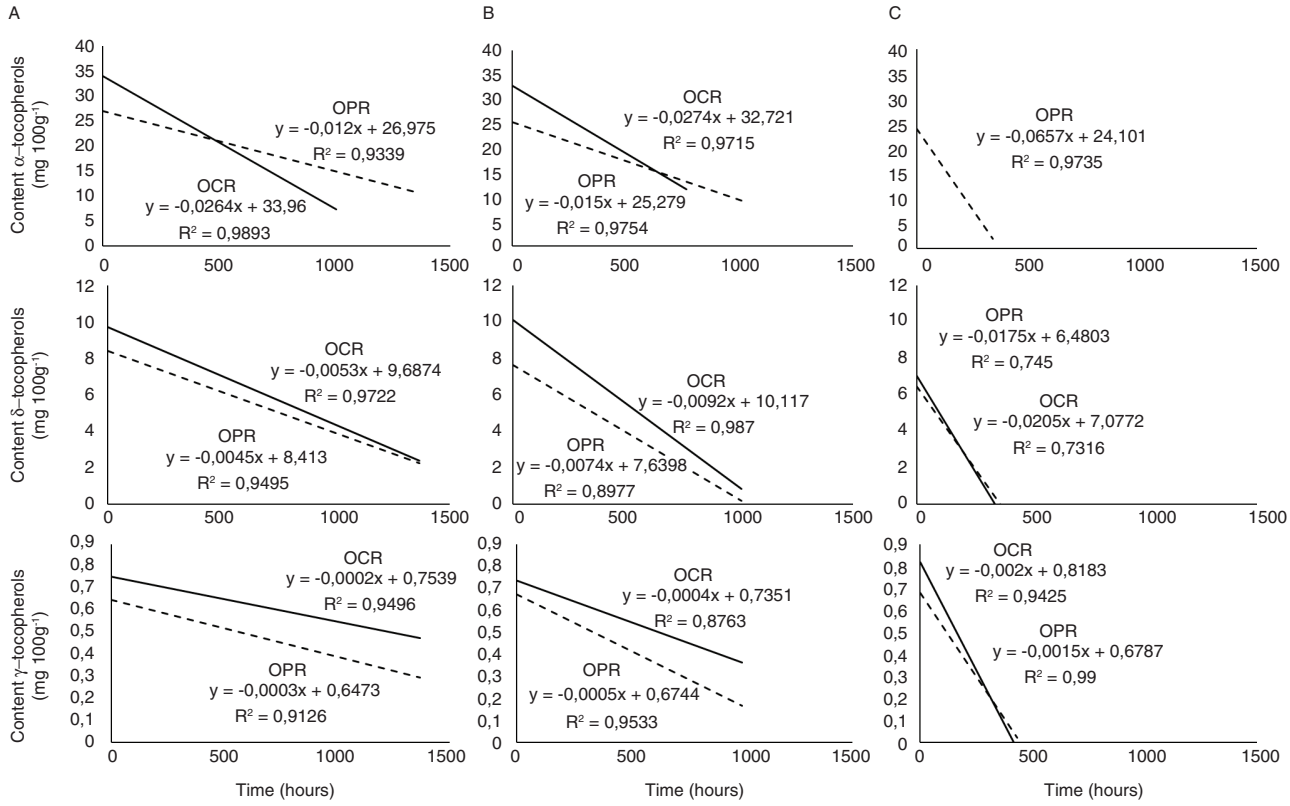

FIGURE 1. Regression analysis of α, δ and γ tocopherols in chemically (___) and physically refined rice oils (----) in relation at the different analysis temperatures, where: (a) 100 °C; (b) 140 °C and (c) 180 °C.

Table 2. Tocopherol contents (n=3, mean ± SD) in chemically refined rice oil and physically refined oil submitted to a temperature of 140 ºC

	α-tocopherol (mg·100g^{-1})		γ-tocopherol (mg·100g^{-1})		δ-tocopherol (mg·100g^{-1})	
Time (h)	**OCR***	**OPR****	**OCR***	**OCR***	**OPR****	**OCR***
0	32.84 ± 1.2^{a}	25.67 ± 1.6^{b}	9.91 ± 0.3^{a}	9.22 ± 0.3^{b}	0.77 ± 0.2^{a}	0.71 ± >0.1^{a}
48	31.19 ± 1.8^{a}	24.27 ± 1.2^{b}	9.88 ± 0.3^{a}	7.66 ± 0.4^{b}	0.75 ± 0.1^{a}	0.70 ± >0.1^{a}
144	28.58 ± 1.1^{a}	23.05 ± 0.9^{b}	9.45 ± 0.5^{a}	6.25 ± 0.4^{b}	0.73 ± 0.2^{a}	0.59 ± >0.1^{a}
240	25.05 ± 0.9^{a}	21.15 ± 1.4^{b}	7.93 ± 0.3^{a}	5.01 ± 0.2^{b}	0.61 ± 0.1^{a}	0.53 ± >0.1^{a}
336	22.46 ± 0.9^{a}	20.95 ± 1.0^{b}	6.69 ± 0.3^{a}	4.57 ± 0.5^{b}	0.54 ± 0.1^{a}	0.48 ± 0.1^{a}
432	22.27 ± 1.1^{a}	18.50 ± 0.7^{b}	5.79 ± 0.2^{a}	3.72 ± 0.3^{b}	0.54 ± 0.1^{a}	0.41 ± >0.1^{a}
576	18.98 ± 1.3^{a}	17.12 ± 1.2^{b}	4.59 ± 0.35^{a}	2.81 ± 0.2^{b}	0.49 ± >0.1^{a}	0.37 ± >0.1^{a}
768	10.19 ± 0.7^{a}	11.26 ± 0.3^{a}	2.87 ± 0.3^{a}	1.97 ± 0.3^{a}	0.44 ± >0.1^{a}	0.26 ± >0.1^{a}
1008	Nd	10.32 ± 0.8^{a}	1.28 ± 0.3^{a}	1.27 ± 0.2^{a}	0.43 ± >0.1^{a}	0.23 ±>0.1^{a}

Values followed by lowercase letters between the columns (OCR and OPR) do not differ from each other at 5% significance by the T test ($p > 0.05$).
Nd- not detected
*OCR: chemically refined oil
**OPR: physically refined oil

Table 3. Tocopherol contents (n=3, men ± SD), in chemically refined rice oil and physically refined oil submitted to a temperature of 180 ° C

	α-tocopherol (mg·100g^{-1})		γ-tocopherol (mg·100g^{-1})		δ-tocopherol (mg·100g^{-1})	
Time (h)	**OCR***	**OPR****	**OCR***	**OCR***	**OPR****	**OCR***
0	32.84 ± 1.8^{a}	25.67 ±0.5^{a}	9.91 ± 0.5^{a}	9.22 ± 0.4^{b}	0.77 ± 0.06^{a}	0.71 ± 0.04^{b}
48	21.75 ± 0.6^{a}	18.77± 0.7^{a}	5.68 ± 0.4^{a}	4.34 ± 0.4^{b}	0.74 ± 0.06^{a}	0.59 ± 0.04^{b}
144	3.27 ± 0.4^{b}	15.55 ± 0.8^{a}	1.76 ± 0.3^{b}	2.28 ± 0.1^{a}	0.66 ± 0.07^{a}	0.44 ± 0.05^{b}
240	Nd	7.56 ± 0.8^{a}	0.39 ± 0.1^{b}	1.17 ± 0.1^{a}	0.28 ± 0.01^{a}	0.28 ± 0.02^{a}
336	Nd	2.52 ± 0.4^{a}	0.20 ± 0.03^{b}	0.68 ± 0.1^{a}	0.08 ± 0.01^{b}	0.19 ± 0.02^{a}
432	Nd	Nd^{a}	0.14 ± 0.03^{a}	0.15 ± 0.04^{a}	0.03 ± 0.01^{a}	0.03 ± 0.06^{a}

Values followed by lowercase letters between the columns (OCR and OPR) do not differ from each other at 5% significance by the T test ($p > 0.05$).
Nd- not detected
*OCR: chemically refined oil
**OPR: physically refined oil

1008 h of heating. The δ-tocopherol present in the physically refined oil presented higher losses than those which occurred in the chemically refined oil, reaching a loss of 42.25% in the period of 432 h and of 67.61% at 1008 h of heating.

Thus, such as occurred at the heating temperature of 100 ºC, it was observed that the tocopherol content in the physically refined oil was more stable than the tocopherol content present in the chemically refined oil when heated at 140 ºC (Figure 1b).

The chemically refined oil heated at 180 ºC (Table 3) showed a rapid reduction in its content of (β+γ)-tocopherol, reaching a percentage of degradation of 96.06% in 240 h of heating. At the end of the heating period, the percentage of degradation was 98.59%. At this temperature, the degradation of the (β+γ)-tocopherol of the physically refined oil was similar to that which occurred in the chemically refined oil.

The δ-tocopherol of the chemically refined oil heated at 180 ºC showed a gradual degradation throughout the period of exposure of the rice bran oil to heating, reaching a reduction of 96.10% at the period of 432 h. The physically refined oil showed a reduction in δ-tocopherol content similar to that which occurred in the physically refined oil, reaching the percentage of degradation of 95.77% at the end of the heating period (432 h).

The same occurred at heating temperatures of 100 ºC and 140 ºC. It was observed that the tocopherols present in the physically refined oil showed higher stability than the tocopherols present in the chemically refined oil when heated at 180 ºC (Figure 1c).

A greater reduction in the content of α-tocopherol in the oil was observed both in the chemically and physically refined oil as it was heated at higher

temperatures. However, at all temperatures, it was observed that the content of α-tocopherol in the chemically refined oil showed a higher degree in the reduction of its content than in the physically refined oil, probably due to a greater concentration of γ-oryzanol in the physically refined oil.

For all treatments a significant R^2 regression (> 0.7) was observed. It was possible to observe that as a function of time, all the tocopherols had their contents reduced and with the increase in temperature, the curve of decrease was more accentuated (Figure 1).

4. DISCUSSION

In accordance with Kalucka, Korczak, Elmadfa and Wagner (2005) and Player *et al*., (2006), the rapid degradation in α-tocopherol resulted in secondary reactions of the radical tocoferoxil with hydro-peroxides or fatty acids which were not oxidized to generate more radicals. However, the initial tocopherol molecule may have also reacted with hydro-peroxides to form radical peroxil. In accordance with the same authors, both reactions accelerated lipid oxidation reactions.

As observed in α-tocopherol, as the temperature increased, a higher degradation rate of the (β+γ)- and δ-tocopherols occurred. Once again, the (β+γ)- and δ-tocopherols present in the physically refined oil showed higher stability than the (β+γ)- and δ-tocopherols present in the chemically refined oil.

Therefore, α-tocopherol showed lower stability when compared with the other tocopherols, which is in agreement with the results found by Player *et al*., (2006) and Lampi and Kamal-Eldin (1998). The order of degradation at 100 ºC for the physically refined oil was: (β+γ)- > α-> δ-tocopherol, and at 140 ºC the order of degradation was: (β+γ)- > δ- > α-tocopherol. Only at 180 ºC the order of the degradation rate was: α- > (β+γ)- > δ-tocopherol, also in agreement with the results found by Player *et al.,* (2006) and Lampi and Kamal-Eldin (1998).

The highest stability shown by δ-tocopherol may be due to its lack of capacity to donate its phenolic hydrogen to the free radicals. According to Kalucka *et al.,* (2005), the high stability of the δ-tocopherol can be associated with its smaller anti-oxidant effect when compared to α-tocopherol, which is oxidized more rapidly into the tocopherol radical and participates in chain reactions that result in the acceleration of oxidation. Thus, δ-tocopherol is more stable because it does not participate so easily as α-tocopherol in secondary reactions with hydro-peroxides, mainly at higher temperatures.

According to Steel *et al*., (2005), the rate of tocopherol degradation demonstrates that α- and γ-tocopherols are destroyed more rapidly than β- and δ-tocopherols present in soybean oil heated at 180 ºC for 10 h.

However, the physically refined oil showed higher tocopherol stability in all temperatures when compared to the chemically refined oil, indicating that the oryzanols and other compounds present in the oil may have an influence on the extension of the oxidative induction period and consequently, in the stability of the oil subjected to heating.

These important natural antioxidants (tocopherols) are decreased during each step of refining and markedly reduced during deodorizing, a process of chemical refining (Chu and Lin, 1993). Some investigators (Tasan and Demirci, 2005; Alpaslan *et al.*, 2001; Ferrari *et al.*, 1996) reported similar observations to ours on total tocopherol loss in oil obtained from the chemical refining process. In physical refining, the steam distillation stage causes the greatest overall reduction in total tocopherol content. In contrast to physical refining, the degumming-neutralizing stage causes the greatest overall reduction in total tocopherol content during chemical refining. In the refining process, it is especially important to maintain appropriate control during the deodorizing/distillation and degumming-neutralizing stages.

Ko *et al.,* (2003), observed that short periods of heating of rice bran oil, both in a microwave oven as well as an electric oven, heated at temperatures of 170 ºC, 180 ºC and 190 ºC caused losses in tocopherols in heating periods over 20 min, 5 min and 3 min, respectively.

In a study carried out by Rennick and Warner (2006), evaluating the degradation of the α-tocopherol in soybean and sunflower oils, it was observed that the content of α-tocopherol presented a high reduction level at the beginning of the heating period at 180 ºC in oils enriched with α-tocopherol. After 30 h of heating, α-tocopherol had already been totally degraded, while the soybean oil, without the addition of α-tocopherol, still showed 7% of its initial concentration.

The concentration of α-tocopherol in samples of olive oil was monitored during thermal oxidation at 60 ºC and 100 ºC (Nissiotis and Tasioula-Margari, 2002). Under these conditions, the authors observed that at the end of 100 h of heating at 100 ºC, α-tocopherol had been totally degraded and during the same period at 60 ºC, 60.36 $mg \cdot kg^{-1}$ of α-tocopherol were detected in the oil.

5. CONCLUSIONS

At temperatures of 100, 140 and 180 ºC the degradation of tocopherols occurred, which increased considerably with the increase in heating temperature in both oils. There was a higher degradation of tocopherols in chemically refined oil than in physically refined oil at all heating temperatures.

Through this study, a loss in natural antioxidants during the use of rice oil in the preparation of food was evaluated and the loss in natural antioxidants

in rice oil as a function of the refining process was verified.

ACKNOWLEDGMENTS

National Council – Scientific and Technological Development and the Coordination of Upper Level Personal Perfecting of Brazil, Indústria Riograndense de Óleos Vegetais and to Helmut Tessmann, Brazil.

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