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Antioxidant Evaluation of Coriander Extract and Ascorbyl Palmitate in Sunflower Oil Under Thermoxidation

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Abstract The objectives of this study were to evaluate isolated and synergistic antioxidant effects of coriander extract and ascorbyl palmitate (AP) in sunflower oil subjected to thermoxidation, and to verify their influence on the oxidative resistance of α-tocopherol, which occurs naturally in safflower oil. Sunflower oil samples with 1,600 mg/kg coriander extract, 500 mg/kg AP, and a mixture of those two antioxidants were heated to 180 °C for 30 h. Samples were taken at 0, 10, 20 and 30 h and analyzed to evaluate oxidative stability, total polar compounds, and α-tocopherol content. Results were subjected to variance analyses and Tukey tests at a 5% significance level, in a factorial scheme, to an entirely casual delineation. Coriander extract and AP delayed lipid oxidation and promoted the retention of α-tocopherol when added separately to sunflower oil and subjected to thermoxidation. The mixture of the antioxidants showed a higher antioxidant effect, thereby demonstrating their synergy under these conditions.

Keywords Coriander extract · Ascorbyl palmitate · Oxidative stability · Polar compounds · α-Tocopherol · Thermoxidation

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Abbreviations

RSO	Refined sunflower oil
CE	Coriander extract
AP	Ascorbyl palmitate

Introduction

The application of antioxidants is one of the simplest ways to reduce oil and fat oxidation. Besides delaying oxidation, these substances protect carotenoids, vitamins A and D and other unsaturated compounds [1]. Ascorbyl palmitate (AP) is a synthetic antioxidant that efficiently retards lipid oxidation [2]. It is frequently classified as a natural antioxidant, but this is not entirely correct, since ascorbic acid occurs naturally in many fruits and vegetables, while its palmitoyl ester is not [3]. The Health Ministry in Brazil limits the use of AP to 500 mg/kg [4].

Vegetables [5] and spices [6] are included among the numerous sources of natural antioxidants. Coriander (*Coriandrum sativum* L.), which belongs to the Umbelliferae family, is widely cultivated and is a popular ingredient in many recipes. Many studies confirm its antioxidant action [7, 8]. The antioxidant potential of coriander is attributed to the presence of certain phenolic type phytochemicals.

Deterioration of oil quality and structural modification during heating is largely the result of three agents: moisture from foods, which causes hydrolytic alteration; oxygen, which enters the oil mass through the container surface, making oxidative alteration possible; and high temperature, resulting in thermal alteration [8]. Gordon [1] points out that these three types of alterations may be related. High temperature has a significant effect on development of oxidation products, favoring oxidized and non-oxidized

dimer and polymer formation. Similarly, free fatty acids, which are a product of hydrolysis, are more susceptible to thermal and oxidative alteration than triacylglycerides.

The thermoxidation process is used extensively to simulate the frying process. It consists of subjecting oils and fats to high temperatures without the presence of food. In the absence of moisture and other food borne compounds, temperature and oxygen from the air are the main variables to be considered. Compounds produced during thermoxidation are representative of those originating from frying oils, and they can be formed in better controlled conditions. Several studies have been carried out in order to discover the compounds originating under these conditions [1].

Considering such aspects, the objectives of this study were to evaluate isolated and synergistic antioxidant effects of coriander extract and AP in sunflower oil subjected to thermoxidation, and to verify their influence on the oxidative resistance of α-tocopherol, which occurs naturally in safflower oil.

Experimental Procedures

Materials

Coriander was freshly obtained at a local market. It was washed in flowing water and its roots were removed. Leaves and stems were laid on trays and dried in a forced air oven at 45 °C for 48 h. After dehydration, the leaves and stems were ground, passed through an 80-mesh screen to obtain a uniform powder, placed in polyethylene bags and held at −18 °C during the course of the work.

Coriander extract (CE) was obtained by aqueous extraction as described previously [8]. Dehydrated coriander (10 g) was maintained for 60 min under constant agitation in distilled water (100 mL) at room temperature, and the mixture was centrifuged for 10 min at 4,000 rpm. After transferring the supernatant, the extraction process was repeated and the supernatants were combined. The water was removed under reduced pressure at 60 °C. The dry extract was suspended in 50 mL of distilled water, placed in a closed amber flask under nitrogen, and held at −18 °C for future use.

Commercial AP (Grindox^{TM} 562), provided by Danisco S/A, was a blend of 10% of AP (vitamin C palmitate), 90% propylene glycol, and a food grade emulsifier.

To carry out this study, refined sunflower oil without added synthetic antioxidants and citric acid was used. A mono-diglyceride emulsifier (Grindsted Mono-Di Ca 52-B) was also utilized to combine the coriander extract with the sunflower oil (1%). The sunflower oil was provided by Bunge Alimentos S/A, Gaspar-SC, and the mono-diglyceride was provided by Danisco S/A.

Four treatments were submitted to thermoxidation, which were carried out in two replicates. The four treatments were refined sunflower oil (RSO, control), RSO plus 1,600 mg/kg of coriander extract (RSO + CE), RSO plus 500 mg/kg of ascorbyl palmitate (RSO + AP), and a mixture of coriander extract (1,600 mg/kg) and AP (500 mg/kg) in RSO (RSO + M).

Heating was conducted on a hot plate in 50 mL beakers. Addition of treatments (30 mL) in the beakers resulted in a surface to volume ratio of 0.4 cm^{-1}. The samples were heated at 180 ± 5 °C, which is typical for frying by immersion. The frying was carried out using a discontinuous approach involving 10 h of heating per day. Samples were taken at time intervals of 0, 10, 20 and 30 h and stored in amber flasks at −18 °C under nitrogen until needed for the analyses.

Methods

Quantification of total phenolic compounds present in the coriander extract was determined by the colorimetric method described below. Samples submitted to thermoxidation were analyzed to determine oxidative stability, total polar compounds and α-tocopherol content.

Total Phenolic Compounds

Total phenolic compounds were quantified using the Singleton and Rossi method [9]. This method utilizes Folin–Ciocalteau reagent. The blue color produced by reduction of Folin–Ciocalteau reagent by phenolics was measured spectrophotometrically at 765 nm. A standard curve was established using gallic acid at concentrations from 0 to 500 mg/L; the determination coefficient was $r = 0.9981$, and the results were expressed as g gallic acid equivalence (GAE) per 100 g extract.

Oxidative Stability

Oxidative stability was determined by the AOCS-proposed method Cd 12b-92 [10], which is based on the electric conductivity of volatile product degradation. These analyses employed the Rancimat and were conducted at 100 °C with an air flow of 20 L/h, using 3 g of sample and 60 mL of distilled water in the electrode flasks. Electrical conductivity vs. time was automatically registered during the reaction and also during the test, and the period of induction expressed in hours.

Total Polar Compounds

This method is based on adsorption chromatography, which separates the sample into two different polarities

that can be determined gravimetrically. The chromatographic method proposed by Dobarganes, Velasco, and Dieffenbacher [11] was used.

α-Tocopherol Content

AOCS Ce 8-86 [12] was used to determine α-tocopherol content. An HPLC, with a fluorescence detector using the following conditions: 125 × 4 mm silica gel column with 5 μm pore; detection using λex = 292 nm, and λem = 326 nm; the mobile phase was 98.6% *n*-hexane, 1.2% ethyl acetate, and 0.2% isopropanol at a flow rate of 1.5 mL/min. Concentrations were calculated based on excitation peak area, and expressed in mg/100 g.

Statistical Analysis

The coriander extraction and total phenolic compound quantification were conducted in two replicates. Thermoxidation was carried out in factorial scheme 4 × 4 (Treatments = RSO, RSO + CE, RSO + AP, RSO + M; heating periods = 0, 10, 20 and 30 h), in a completely randomized design, with two replicates [13]. The mean results obtained from the oxidative stability, total polar compounds and α-tocopherol content, in duplicate, were subjected to analysis of variance, and to the Tukey test at 5% significance level using the program ESTAT (System for Statistical Analyses, version 2.0) [14].

Results and Discussion

Extract yield was 58.4% and phenolic compounds quantification resulted in 0.92 g GAE per 100 g extract. Aqueous extraction exhibited a significant yield, confirming the solvent efficiency. Total phenolic compounds content was similar to the previously reported [7], where 1.06 g GAE per 100 g extract of coriander leaves aqueous extract was found.

Oxidative Stability

Throughout the heating process, the sunflower oil exhibited a significant decrease in oxidative stability. This was expected, since it was free of added synthetic antioxidants. Samples containing antioxidants also showed a decrease in oxidative stability throughout the heating periods (Table 1). For each heating time, the induction period of the oil with the antioxidant mixture was the longest, followed by AP. The oil with the coriander extract had lower oxidative stability values than other antioxidant treatment until the 20 h heat treatment (Table 1). However, the induction time of the oil with coriander extract were significantly longer than sunflower oil.

Yanishlieva et al. [15] evaluated the addition of ethanolic extract from summer savory to sunflower oil heated to 180 °C for 50 h, and based on oxidative stability results at 100 °C, observed the efficiency of the natural extract on

Table 1 Oxidative stability and polar compounds and α-tocopherol contents in thermally oxidized sunflower oil with and without antioxidants

Treatments	Heating periods (hours)			
	0	10	20	30
Oxidative stability (hours)				
RSO	08.71 ± 0.09^{aD}	1.72 ± 0.01^{bD}	0.38 ± 0.01^{cC}	0.50 ± 0.00^{cC}
RSO + CE	09.81 ± 0.05^{aC}	3.53 ± 0.02^{bC}	1.46 ± 0.01^{cB}	2.65 ± 0.01^{bB}
RSO + AP	21.62 ± 0.09^{aB}	4.90 ± 0.41^{bB}	2.26 ± 0.05^{cB}	2.59 ± 0.22^{cB}
RSO + M	23.44 ± 0.16^{aA}	6.02 ± 0.87^{bA}	5.08 ± 0.01^{bcA}	4.22 ± 0.01^{cA}
Polar compounds (%)				
RSO	3.48 ± 0.03^{dA}	20.22 ± 0.06^{cA}	40.08 ± 0.39^{bA}	54.84 ± 0.43^{aA}
RSO + CE	4.70 ± 0.09^{dA}	16.45 ± 0.28^{cB}	31.23 ± 0.55^{bB}	48.24 ± 1.02^{aB}
RSO + AP	4.68 ± 0.03^{dA}	10.22 ± 0.08^{cC}	26.28 ± 0.26^{bC}	41.00 ± 0.78^{aC}
RSO + M	4.54 ± 0.01^{dA}	08.52 ± 0.01^{cC}	22.20 ± 0.91^{bD}	37.47 ± 2.76^{aD}
α-tocopherol (mg/100 g)				
RSO	63.33 ± 0.04^{aA}	07.31 ± 0.01^{bD}	000.20 ± 0.01^{cD}	0.10 ± 0.01^{cC}
RSO + CE	61.92 ± 0.71^{aB}	16.53 ± 0.08^{bC}	02.74 ± 0.01^{cC}	2.46 ± 0.01^{cB}
RSO + AP	61.44 ± 0.14^{aB}	21.81 ± 0.08^{bB}	04.52 ± 0.01^{cB}	3.89 ± 0.01^{cA}
RSO + M	61.67 ± 0.01^{aB}	27.89 ± 0.22^{bA}	13.74 ± 0.05^{cA}	4.12 ± 0.02^{dA}

RSO, refined sunflower oil; *RSO + CE*, RSO + 1,600 mg/kg of coriander extract; *RSO + AP*, RSO + 500 mg/kg of ascorbyl palmitate; *RSO + M*, RSO + 1,600 mg/kg of coriander extract + 500 mg/kg of ascorbyl palmitate

Means followed by the same lower case letter are not significantly ($P > 0.05$) different over time (*line*). Means followed by the same upper case letter are not significantly ($P > 0.05$) different between treatments (column)

the protection of the oil. Gámez-Meza et al. [16] found that grape bagasse extract with total phenolics concentrations of 0.1, 0.3 and 0.5%, BHA at 0.02%, and TBHQ at 0.02%, were added to soybean oil and submitted to the oven test at 60 °C for 21 days. All extract concentrations exhibited significant oxidative stability differences between treatments ($P < 0.05$). Extracts had higher antioxidant activity than BHA, but lower than TBHQ, except for phenolic compounds concentration of 0.5%, which exhibited a higher induction period than the synthetic antioxidant TBHQ.

In the present study, oxidative stability results have indicated that coriander extract and AP have the ability to better increase sunflower oil's period of induction when antioxidants were used together, rather than separately. However, the mixture was not considered synergistic except at the 20 h sampling period.

Total Polar Compounds

Total polar compounds are considered to be nonvolatile compounds having a higher polarity than triacylglycerols, resulting from thermal, hydrolytic, and oxidative alteration [11]. The concentration of byproducts resulting from oxidative alteration of the oil increased as a function of frying, limiting the usefulness of the oil. In many countries, an upper limit of 25% total polar compounds has been established [17], since the higher the polar fraction is, the worse the oil quality will be.

In all treatments, the total polar compounds content significantly increased throughout the study period. Initially, there was no significant difference between polar compound levels between any of the evaluated treatments. However, with each heating period, polar compounds were significantly lower in the antioxidant mixture and AP treatments than the other treatments (Table 1).

It is important to emphasize that all antioxidants delayed the formation of polar compounds throughout heating, but with different levels of efficiency. After 30 h of heating, coriander extract, AP and the mixture of antioxidants had reduced polar compound formation by 12, 25.2, and 31.7%, respectively. Once again indicating the higher efficiency of antioxidants when applied together rather than separately.

The polar compounds limit value of 25%, as regulated by some countries, was reached at heating time intervals of 10–20 h for refined sunflower oil samples with no antioxidants, with coriander extract and with AP. The upper limit was reached at 20–30 h for the treatment containing the antioxidant mixture, reinforcing the higher activity of this mixture (Table 1).

Barrera-Arellano et al. [18] have verified tocopherol loss and degradation product formation in purified soybean oil subjected to heating at 180 °C. After 10 h, they found 26.5% total polar compounds in purified soybean oil, and 23.1% for the same oil with 500 mg/kg of α-tocopherol. Rosa mosqueta shell extract in canola oil subjected to 180 °C for 18 h prevented the formation of polar compound as compared to the control [19].

α-Tocopherol Content

One way to monitor oil quality during the frying process is to determine the concentration of antioxidants occurring in the oils, especially tocopherols [20]. The content of α-tocopherol in all treatments drastically decreased throughout all heating study periods (Table 1). At 20 h, there were no significant differences between the treatments, except for that with the antioxidant mixture. At 30 h, the antioxidant mixture sample still had a significantly higher level of tocopherols than the others.

At 0 h, that there was no significant difference in tocopherol levels among any of the treatments. However, as heating progressed, differences in α-tocopherol retention levels were observed, with the best results observed with the antioxidant mixture. At 30 h heating time, the oil with AP presented similar results.

For evaluation of food antioxidants, Decker et al. [21] indicated that antioxidant effectiveness, among other ways, can be expressed as the loss and retention percentage after time under standardized conditions. To facilitate the analyses, the results from Table 1 are presented as residual α-tocopherol percentage on Table 2.

Table 2 shows that, at the 10-h heating time, α-tocopherol degradation was significant, with a reduction of more than 50% in all treatments. Residual α-tocopherol in sunflower oil with coriander extract during heating is higher than in sunflower oil. However, the oils with AP and with the antioxidants mixture exhibited better efficiency in retaining tocopherols.

At the end of heating there was a pronounced α-tocopherol degradation in all treatments, with residual α-tocopherol

Table 2 Residual α-tocopherol content (%) in sunflower oil with antioxidants addition

Treatments	Heating periods (hours)			
	0	10	20	30
RSO	100	11.5	tr < 0.3	nd < 0.2
RSO + CE	100	26.7	4.4	4.0
RSO + AP	100	35.5	7.4	6.3
RSO + M	100	45.2	22.3	6.7

RSO, refined sunflower oil; *RSO + CE*, RSO + 1,600 mg/kg of coriander extract; *RSO + AP*, RSO + 500 mg/kg of ascorbyl palmitate; *RSO + M*, RSO + 1,600 mg/kg of coriander extract + 500 mg/kg of ascorbyl palmitate

tr traces, *nd* not detected

levels of less than 7%. Moreover, it was demonstrated that sunflower oil exhibited a drastic α-tocopherol loss, while the oils with AP and the antioxidant mixture exhibited a higher α-tocopherol retention.

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