Use of Rosemary Extract in Preventing Oxidation During Deep-Fat Frying of Potato Chips

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ABSTRACT: The effect of using a rosemary extract on the stability of oil used for frying potato chips has been evaluated. Sliced potatoes were fried intermittently in soybean oil containing a natural extract from rosemary. The conditions used for frying were 185°C for 90 s. Two separate experiments, with and without replenishment of oil, were carried out. Oil samples were taken each day, not only from the frying pans but also by extraction with hexane from the chips. Changes in the induction period of the oil samples (Rancimat method) were determined. The induction period decreased as frying progressed. The reduction in the induction period was higher in the oil free of rosemary extract, and the chips were much darker in color. The oil containing the extract showed greater antioxidant activity, and reduced darkening and rancidity of the oil. Potato chips fried in the oil with added rosemary extract were more acceptable than chips fried in oil containing no extract until the last frying. The free radical scavenging activity of rosemary extract in comparison to other natural antioxidants was also determined by the reduction of $O_2^{\cdot-}$ in a hypoxanthine/xanthine oxidase system.

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KEY WORDS: Antioxidants, frying, induction period, potato chips, rosemary extract.

Deep-fat frying is one of the most commonly used procedures for the preparation and manufacture of foods throughout the world (1). Nearly one-half of all lunch and dinner food orders in restaurants include one or more deep-fried items (2). During deep-fat frying, the oil is exposed to elevated temperatures in the presence of air and moisture. A number of chemical reactions, including oxidation and hydrolysis, occur during this time, as do changes due to thermal decomposition (3). Antioxidants can be used to retard frying oil deterioration.

Antioxidants are used mainly in oil or in oil/water emulsions. Consumers tend to favor the use of additives of natural origin owing to the suspected action of artificial additives as promoters of carcinogenesis or mutagenicity (4). Many plant extracts exhibit various degrees of antioxidant activity in different fats and oils (1,5,6), including spices, herbs, cocoa bean shells, coffee beans, oats, tea, beans, sesame oil, tomatoes, rose hips, osage orange, amla fruit, vegetables (notably onions and peppers), olive leaves, and soybeans (7).

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Rosemary and sage extracts reportedly have very good thermal resistance and strong antioxidative characteristics (8–10). Che Man and Tan (1) studied changes in deodorized palm olein during deep-fat frying of potato chips using oleoresin rosemary and sage extracts as antioxidants. They measured thiobarbituric acid, FFA, PV, iodine value, polymer content, viscosity, color, and specific extinction $E^{1\%}_{1cm}$ at 232 and 238 nm. Unfortunately, no indication of the composition of the herbal extracts used in their work was given and therefore no conclusion could be reached about the antioxidant activity of the compounds. The authors concluded that protection against oxidation was better using rosemary oleoresin than BHA, BHT, or even sage extract.

In another study, 27 compounds in extracts from the *Rosmarinus officinalis* and *Salvia officinalis* were characterized by HPLC coupled with a mass spectrometer equipped with a CI interface and by HPLC coupled with a diode array spectrophotometer (11). Twenty-two of them were identified and comprised mainly phenolic acids, carnosol derivatives, and flavonoids. The extracts showed great variation in their HPLC profiles, and no correlation was apparent between their antioxidant efficiency and their composition (11). The most effective compounds (included in rosemary extract) against oxidation were carnosol, rosmarinic acid, carnosic acid, caffeic acid, rosmanol, and rosmadial (11). Antioxidant performance is dependent on the extraction parameters, with hexane extracts of rosemary showing greater antioxidant properties than methanol extracts (12). However, results from other researchers (11) revealed no clear solvent effect on activity of extracts made with hexane, methanol, and CO_2.

Natural antioxidants are usually used in low-temperature conditions. In foods exposed to high temperatures (i.e., potato chips) little information is available on the effectiveness of natural antioxidants. Potato chips oxidize easily, thus losing commercial value and health properties. The effectiveness of natural antioxidants in reducing or retarding deterioration of refined, bleached, and deodorized palm olein during frying has been reported (1,13). However, owing to health implications, parts of the food industry are replacing palm oils with other vegetable oils such as soybean, sunflower, cottonseed, and canola. All of these oils are more susceptible to oxidation than palm oil because of their higher degree of unsaturation. To our knowledge, no data have been published concerning the stability of the above oils (or their mixtures) used for frying potato chips using natural antioxidants or the stability of the oil absorbed by the chips.

This study had two objectives. The first was to assess the susceptibility to oxidation of a vegetable oil, during intermittent frying of potato chips, treated with a natural extract from rosemary (*R. officinalis* L.). The difference in progress of oxidation also was assessed with and without replenishment with fresh oil. The second objective was to evaluate the oxidative condition of the oil absorbed by the fried chips so as to mesasure indirectly the consumer's intake of harmful pro-oxidation products (free radicals, etc.).

MATERIAL AND METHODS

Materials. RoseMax® (10% rosemary extract dissolved in ethanol), a product of Vioryl Chemical and Agricultural Industry Research S.A. (Athens, Greece), was used in this study. The antioxidant was dissolved in oil at 400 mg/kg. The composition of RoseMax, as declared by Vioryl S.A., is caffeic acid 43%, ferulic acid 7%, carnosic acid 10%, rosmarinic acid 20%, vanillic acid 5%, carnosol 5%, *p*-hydroxy benzoic acid 3%, and ursolic acid 7%.

Preliminary determination of antioxidant activity. The soybean oil (Soyola; Kope, Athens, Greece) used for this determination was purchased in the local market. A preliminary assessment of the antioxidant activity of RoseMax was made with the Rancimat method and with scavenging activity in a hypoxanthine/xanthine oxidase (HPX/XOD) system. The resistance to oxidation of frying or absorbed oils has been measured using the Rancimat method and is expressed in units of time (= induction period). The difference between the induction period of an oil and that of the same oil containing antioxidants is the basis for evaluation of the activity of these antioxidants. The effect of an antioxidant is termed the antioxidant index or protection factor (PF) and is expressed as the ratio of the induction periods for the stabilized and the unstabilized oil (14,15). A protection factor greater than 1 indicates inhibition of lipid oxidation. The higher the value, the better the antioxidant activity (16,17). In using the Rancimat method (18), a quantity of 400 mg of RoseMax per kg of oil was dissolved in 2.5 g of soybean oil, and the sample was placed in the reaction vessel of the Rancimat 679 (Metrohm Ltd., Herisau, Switzerland) along with a sample of soybean oil without antioxidant (control). The induction periods of a sample of soybean oil with 400 mg/kg of α-tocopherol (Sigma Chemicals, St. Louis, MO) and a sample of soybean oil with 200 mg/kg of BHA (Sigma Chemicals Company Ltd.) also were determined. The temperature was set at 90°C and the airflow at 15 L/h.

The second method used, as described by Saint-Cricq de Gaulejac *et al.* (19) determined the scavenging activity of RoseMax by measuring the percentage reduction of $O_2^{\cdot-}$ values in an HPX/XOD system. Caffeic acid, (+)-catechine, ascorbic acid, and *p*-coumaric acid (Sigma Chemicals) were used for comparison.

Frying experiment. The vegetable oil used for frying was a mixture of cottonseed (80%), palm (10%), and sunflower seed oil (10%). Fresh potatoes (Lady Rosetta var.) used for frying were purchased from the local market. The potatoes were peeled and washed about 1 h before use, and sliced into discs 1.1-mm thick, using a stainless steel slicer. They were kept submerged in tap water at room temperature for 1 h maximum before use.

Two methods were used to fry the potatoes: without replenishment (Frying Experiment I) and with frequent replenishment of oil (Frying Experiment II). In both methods, fryings with and without antioxidant were carried out.

The fryings were performed using two different pans of 22 cm diameter. Temperature was monitored with two IKA Labortechnik ETS-D4 fuzzy (Staufen, Germany) digital thermometers. Peeled and sliced potatoes were divided in two lots and deep-fried independently (one lot in oil with antioxidant and the other in oil without antioxidant). From each lot, batches of 150 g were withdrawn at intervals and fried in about 2 L of oil.

A batch, about 150 g, of sliced potatoes was put in oil when the temperature reached 185°C and fried for 90 s. Repeated fryings were carried out at 1-h intervals. The total number of fryings, which was done for five consecutive days, was nine (three on the first day, two on the second, one on the third, two on the fourth, and one on the last day). The pans were left uncovered during the frying period but covered at the end of the day until the beginning of fryings the next day. Between fryings the heat was turned off. Before the beginning of fryings each day, a 30-g sample (blank) of oil was removed from each fryer and stored at 0°C in a brown bottle under nitrogen. The quantity of potatoes fried was reduced to about 110 g after the seventh frying to avoid the increasing the frying time (due to the reduction in the oil/potatoes ratio) (Frying Experiment I).

With the second frying method (Frying Experiment II), a quantity of fresh oil (with and without antioxidant), approximating the percentage amount removed during frying of potato chips (usually about 18 g), was added back to the pans after each frying. Replenishment of oil is a standard operating procedure in industry. Its purpose is to stabilize the ratio of oil/potatoes during continuous frying, since a quantity of oil is absorbed by potato chips. This ratio determines the time of frying and therefore the sensory properties of the final product. In experiments with added antioxidant, the oil that was added to the frying pans contained 400 mg/kg RoseMax. In total, four fryings per oil (with and without RoseMax) were carried out in one day (Frying Experiment II).

Sensory evaluation and analysis of fried potato chips. After the end of each frying, the chips were placed in plastic dishes for evaluation of their sensory quality. Fifteen panelists were selected from the laboratory staff. Each sample was coded with a three-digit number. Panelists were required to evaluate the overall acceptability of each sample using a numerical scale of 1 to 9 (1 = not acceptable, 9 = extremely good). They were also asked to state which chips they preferred the most if they could distinguish any difference (overall preference). This overall preference meant that they had to take into account any flavor of rancidity and undesirable taste.

After the sensory panel, the portions of chips were separately placed in 250 mL of *n*-hexane in conical flasks for 30 min to extract the lipid phase. Then the hexane with the extracted lipid phase was removed from the flasks and evaporated under vacuum using a rotary evaporator. The collected lipid phase was kept in brown vials under nitrogen at 0°C until their induction period was measured. The efficiency of oil extraction was 95–100%. For the determination of the induction period, 2.5 g of oil was weighed into each of the reaction vessels of the Metrohm Rancimat 679. The temperature was set at 100°C and the airflow rate at 20 L/h.

The quantity of chips not subjected to extraction was packed in bags (made of commercial laminated foil) under nitrogen, sealed, and stored at room temperature for 60 d. After this period the bags were opened, and sensory evaluation of the chips was carried out.

RESULTS AND DISCUSSION

Evaluation of antioxidant activity. The antioxidant activity of RoseMax, determined using the Rancimat method, is shown in Table 1. The results indicate that the samples of soybean oil containing 400 mg/kg of RoseMax showed the least oxidation. Therefore, RoseMax seems to be a better antioxidant than α-tocopherol at the same level of addition. Also, its protective action is higher than that of BHA (added to the oil at the maximum legally permitted level of addition, 200 mg/kg). Other researchers (1) have observed similar results in palm olein during frying of potato chips.

In addition to the Rancimat method, which provided information about the protection of the oil against oxidation, the HPX/XOD system was used to determine the scavenging activity on $O_2^{\cdot -}$ of RoseMax. Oxidation at high temperatures is initiated by free radicals and $O_2^{\cdot -}$ dissolved in oil or fat or that may be present in the plant tissue (potato slice). RoseMax showed the greatest reduction of $O_2^{\cdot -}$, in a HPX/XOD system, in comparison with the other antioxidants tested (Table 2). RoseMax, in both concentrations (50 and 75 mg/kg), showed higher $O_2^{\cdot -}$ scavenging activity than caffeic acid, which was considered to be one of the most potent $O_2^{\cdot -}$ scavengers. The synergistic effects between chemical constituents present in RoseMax can explain this higher value. As Chen *et al.* (12), stated, the level of protection against oxidation is different between rosemary extracts and depends on the method of extraction. This observation suggests that the antioxidant protection can vary according to different compounds and the synergistic effects between them. However, the mechanism of this synergy is still unknown.

Effects of RoseMax on the stability of frying oil. (i) Experiment I (with no replenishment of oil). Figures 1 and 2 illustrate the changes in the induction period of the frying oils and the oils extracted from chips, respectively. Induction period measurements showed that RoseMax improved the resistance to oxidative rancidity not only of the frying oils but also of the oils absorbed in potato chips. Induction periods of the absorbed oils appeared to be lower than those of the frying oils. The inhibition of oxidation not only of the frying oil but also of the oil absorbed by the potato chips is very important. Absorbed

TABLE 1
Antioxidant Activity of RoseMax as Determined Using the Rancimat Method at 90°C and Airflow of 15 L/h

Sample	Induction period[a] (h)	Protection factor[b]
Soybean oil (SB) [control]	35.1 (0.8)	—
SB + 400 mg/kg RoseMax	65.3 (0.9)	1.86
SB + 400 mg/kg α-tocopherol	36.5 (0.8)	1.04
SB + 200 mg/kg BHA	41.7 (0.6)	1.19

[a]Values are means (SD) (n = 3).
[b]Protection factor = (induction period for stabilized oil)/(induction period for unstabilized oil).

TABLE 2
Percentage Reduction[a] of $O_2^{\cdot -}$ Values in an HPX/XOD System by Various Antioxidants and RoseMax

Antioxidant	50 mg/L	75 mg/L
Caffeic acid	57 (2)	67 (2)
(+)-Catechine	54 (3)	60 (2)
Ascorbic acid	19 (1)	28 (1)
p-Coumaric acid	23 (2)	31 (2)
RoseMax	71 (3)	88 (3)

[a]Values are means (SD) (n = 3). HPX/XOD, hypoxanthine/xanthine oxidase.

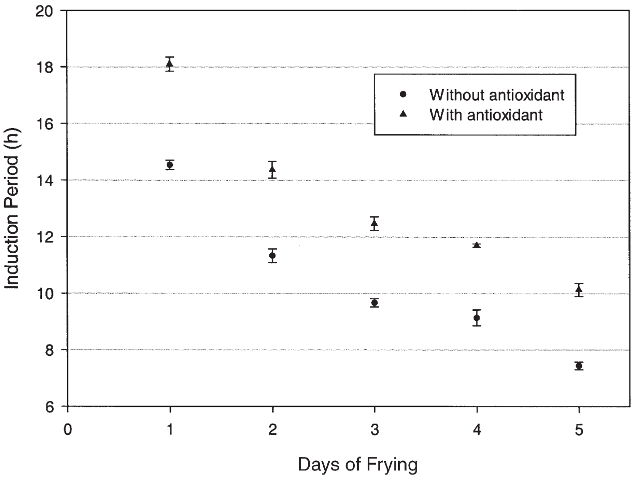

FIG. 1. Changes in induction period of the frying oils without replenishment of oil (Frying Experiment I).

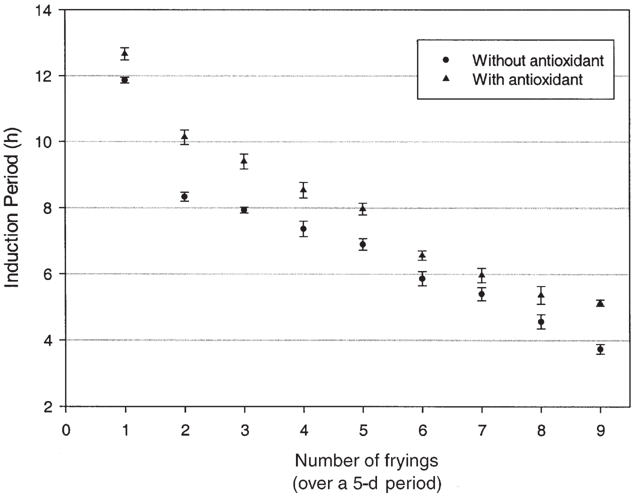

FIG. 2. Changes in induction period of the oils extracted with hexane from chips without replenishment of oil (Frying Experiment I).

TABLE 3
Results of Sensory Evaluation of Fried Chips

	Overall acceptability (1 to 9)[a]		Overall preference (% of panelists)[b]			Overall preference after 60 d (% of panelists)		
Number of fryings	Without antioxidant	With antioxidant	Without antioxidant	With antioxidant	Could not distinguish	Without antioxidant	With antioxidant	Could not distinguish
Frying Experiment I (without replenishment of oil)								
1	9 (0.0)	9 (0.0)	2	8	90	12	31	57
2	9 (0.0)	9 (0.0)	2	10	88	10	39	51
3	9 (0.0)	9 (0.0)	11	15	84	8	52	40
4	7 (1.3)	8 (1.3)	13	29	58	5	63	32
5	6 (1.8)	8 (1.2)	17	55	28	4	76	20
6	5 (1.5)	7 (1.3)	20	68	12	3	95	2
7	5 (1.7)	6 (1.8)	15	75	10	3	97	0
8	3 (1.0)	6 (2.1)	11	82	7	2	98	0
9	3 (1.3)	5 (1.4)	10	87	3	0	100	0
Frying Experiment II (with frequent replenishment of oil)								
1	9 (0.0)	9 (0.0)	1	1	98	15	35	50
2	9 (0.0)	9 (0.0)	2	3	95	10	49	41
3	8 (1.0)	9 (0.0)	3	7	90	9	58	33
4	7 (1.1)	8 (1.4)	6	10	84	5	75	20
5	6 (1.9)	8 (1.2)	7	15	78	5	81	14

[a]1 = not acceptable, 9 = extremely good. Values are means of a single determination by 15 panelists; SD are given in parentheses.
[b]Numbers represent the percentage of panelists who expressed their preference for a particular sample.

oil continues to be oxidized even when potato chips are packed under nitrogen, leading to an unacceptable product. The sensory results of this effect were detected by the panelists after 60 d of storage (Table 3).

(ii) Experiment II (with frequent replenishment of oil). Figure 3 illustrates the changes in induction period of the frying oils. Induction period measurements showed that RoseMax improved the resistance to oxidative rancidity of the frying oils. The induction period of the oil containing RoseMax remained stable during the repetitive fryings, indicating that the newly added fresh antioxidant (dissolved in the replenishment oil) compensated for the loss of protection against oxidation. This loss mainly occurred either from the absorption by chips or from the chemical reactions that occurred during the scavenging of free radicals. The final result was a steadiness of the induction period and hence in the oxidative state of the oil. The induction periods of the absorbed oils followed the same trend. Additionally, they appeared to be lower than those of the frying oil (Fig. 4).

Effects of RoseMax on potato chips and sensory evaluation. In both experiments the overall acceptability of the potato chips was more or less the same between treatments (with and without antioxidant) (Table 3). As shown in both frying experiments, the acceptability started to decrease from the fourth or fifth frying, but the difference between the two treatments was not significant. This meant that the potato chips were equally acceptable with or without antioxidant, especially in the first three or four fryings. In Frying Experiment I acceptability decreased noticeably as the number of fryings increased.

When panelists were asked to discriminate between the two treatments (with and without antioxidant) for overall preference, they showed a preference for potato chips fried with the antioxidant (Table 3). This was more pronounced after the fourth or the fifth frying in both experiments.

The darkening of the potatoes fried in the oil with antioxidant was negligible during fryings and was much lower compared to that for potatoes fried in pure oil (without antioxidant). The color and flavor of fried potatoes are produced mainly by the Maillard reaction. RoseMax acted as an antioxidant and seemed not only to reduce oxidation but also to block, indirectly, the Maillard reaction. This resulted in a reduction of the dark color of chips during frying. When varieties of potatoes

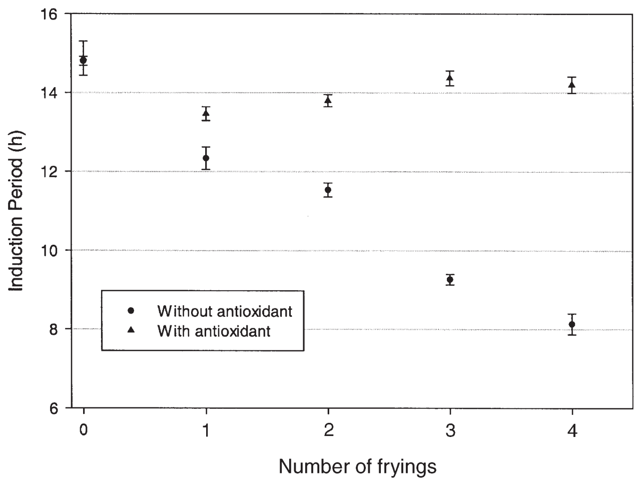

FIG. 3. Changes in induction period (h) of the frying oils with replenishment of oil (Frying Experiment II).

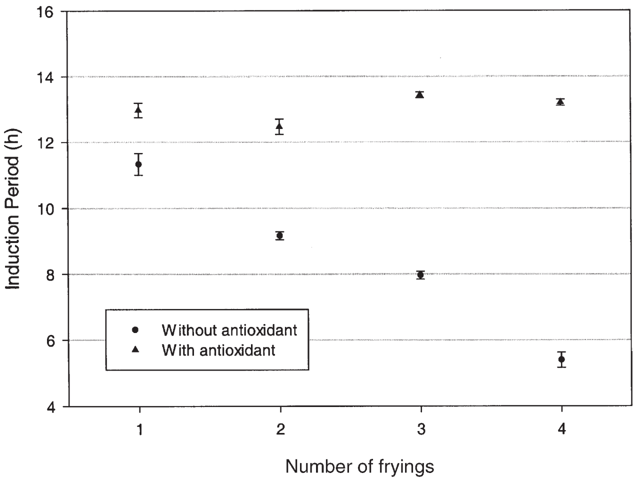

FIG. 4. Changes in induction period of the oils extracted with hexane from chips with replenishment of oil (Frying Experiment II).

with high levels of free sugars are used, darkening during frying is observed mainly due to the reactions between the free sugars and amino acids. This point is of great importance for the potato chip industry. The typical flavor of potato chips is due to compounds formed *via* the Maillard reaction. The flavor of chips fried in the oil containing RoseMax was found to be less intense but generally preferable by the sensory panel (Table 3). During the progressive frying of the chips, more and more members of the sensory panel could distinguish a difference in flavor between the chips fried in oil with and without antioxidant. Potato chips fried in oil without RoseMax had a pungent taste contributed by the oxidation of the absorbed oil in the chip. Until the last day of storage, panelists preferred the chips fried in oil with antioxidant (Table 3).

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