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Determination of Peeling Efficiency, Free Fatty Acid, Peroxide Value and Sensory Evaluation of Peeled Pistachio Kernel using Hot Water

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A R T I C L E I N F O

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A B S T R A C T

Pistachio green kernel, is obtained by removing the red testa of around the whole kernel. In this study, the suitable peeling conditions for removing the testa of the kernel were determined using hot water in five termperature levels of 75, 80, 85, 90, and 95°C and diffetent hot water immersion times of 2, 4, 6, 8, and 10 minutes in riped and unripe samples. Quality factors including the number of pistachio green kernels with remained red testa, free fatty acids, and peroxide value were measured at 3 and 6 months after peeling. Sensory evaluations (including appearance, color, taste, and texture) of the best treatments from the previous stage, were measured by 10 trained panelists. Peeling performance were not good using temperatures of 75 and 80°C in both riped and unripe samples. Peeling performance of 100%, was obtained at 85 and 90°C (6, 8 and 10 min) and 95°C (2, 4, 6, 8 and 10 min) kernel immersion in hot water in riped and unripe cultivars. The qualitative factors, free fatty acids and peroxide value, has have increased in both riped and unripe samples during storage. After 6 months of storage, the lowest peroxide value was observed at 90°C (10 min immersion in hot water) and 95°C (2, 4, 6, 8 and 10 min immersion in hot water). The minimum free fatty acid, was observed in riped ripe samples at 90° C (10 min immersion) and in the unripe samples at 95°C (2 and 4 min immersion). According to the comments of trained panelists, the significant differences between treatments were not observed in terms of the sensory characteristics such as taste, texture, color, and appearance at 5% level. In general, with respect to the performance of peeling, free fatty acids, peroxide value, and sensory evaluation, temperature of 95°C (2 min kernel immersion in hot water) can be used for peeling of riped and unripe samples.

Introduction

The Benefits of testa removal include inactivation of enzymes, inhibition of discoloration or even color enhancement (Agüero *et al.*, 2008). Chlorophylls are pigments that are responsible for the green color of

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fruits and vegetables, which rapidly degrade during processing and change the color of food. The main chlorophylls in plants include chlorophyll A and chlorophyll B with a ratio of three to one. The thermal stability of chlorophyll A is lower than that of chlorophyll B (Koca *et al.*, 2007). The stability of chlorophylls decreases at temperatures above 100°C or temperatures around 100°C for a long time (such as the long baking process) (Schwartz & Lorenzo, 1991). The total chlorophyll a and b in pistachios sold as "green brain" is 150mg / kg (Bellomo & Fallico, 2007).

Chlorophyll survival is considered as a qualitative factor for evaluating green color. Peeling inactivates the chlorophyllase enzyme and other kernel-reducing enzymes. However, chlorophyll degradation is accelerated in damaged textures during peeling and other processes (Giuffrida *et al.*, 2006; Koca *et al.*, 2007). Pigment degradation and consequently discoloration during storage have also been reported for pistachios and its kernel products (Gamli & Hayoglu, 2012). Typically, pistachio nuts are commonly used in the food industry to produce products such as pistachio paste, pistachio butter, pistachio spread, pistachio halva and pistachio chocolate (Shakerardekani & Shahedi, 2015; Shakerardekani *et al.*, 2013a, 2013b; Shakerardekani *et al.*, 2013c; Shakerardekani & Karim, 2018; Shakerardekani *et al.*, 2015).

To produce the desired green pistachio paste, it is advisable to remove the testa from the kernel (Gamli & Hayoglu, 2012). To prepare green kernels, the pistachio kernels are usually placed in hot water. Then, by moving the kernels between the two rollers, the testa and kernel are easily separated. The testas are also taken off by the air suction system and will remain green at the end. However, high water temperatures may affect product quality and shelf life. There have been reports of hot water peeling for different products (Gornicki & Kaleta, 2007; Gowen *et al.*, 2007; Kidmose & Martens, 1999; Kowalska *et al.*, 2008; Lentas & Witrowa-Rajchert, 2008; Shivhare *et al.*, 2009). Depending on the degree of adhesion to the kernel, various products are usually peeled at the temperatures of 60 to 100 degrees for 4 to 10 minutes (DiPersio *et al.*, 2007).

Shakerardekani examined suitable conditions for the preparation of pistachio green kernels in the whole sample, and the immersion of whole pistachio kernels in hot water at 90°C for 7.5 minutes (Shakerardekani *et al.*, 2012). They reported the quality characteristics of the product immediately after peeling. There is no further report on the production of green kernel using hot water.

In this study, we tried to immerse the pistachio kernel in hot water by applying different times and temperatures, to remove the testa on ripe and unripe samples. Then the green kernels were evaluated for 6 months during storage to determine the suitable conditions for pistachio kernel peeling with hot water.

Materials and Methods

Preparation of Pistachio Kernel

In this study, dried pistachio nuts cv. Ohadi (ripe and unripe samples) was used. The shells of pistachio nuts were separated in the laboratory and those with the same size and color and without damage (4.9% moisture content) were used.

Preparation of Samples

Ripe and Unripe pistachio were harvested from Pistachio Research Center (Station No. 2, Rafsanjan) at 5 August and 20 September 2016, respectively. In the first experiment, 500 pistachio kernels were used for each treatment. The basket containing the samples was placed in hot water. Sample to hot water ratio of 1:10 was considered for water circulation in the bath (Hughey *et al.*, 2011). The factors studied included hot water temperature (75, 80, 85, 90 and 95°C) and time of the kernel immersed in hot water (2, 4, 6, 8 and 10 minutes). The factorial experiment was conducted in a completely randomized design. It should be noted that the temperature was maintained by using hot and cold water at different times. After immersion treatments, the samples were immersed in cold water at 0 to 4°C for three minutes for cooling (Agüero *et al.*, 2008). After removing the membrane of the kernel by hand, the samples were placed in an oven at 70°C for 2 hours to dry (Nair, 2003).

Measuring Quality Factors

Qualitative factors measured included the count of pistachio nuts with remained testa, free fatty acid and peroxide value and according to the method described in National Iranian Standard No. 4631 (ISIRI, 2008) 0 (control), 3 and 6 months after peeling.

Pistachio Nuts with Remained Testa

The number of kernels with remained testa was counted in 500 kernels and percentage of unpeeled kernels was calculated. The percentage of unremoved testa was considered zero in the kernels whose testa was completely separated.

Peroxide Value (PV)

To extract pistachio oil, the dried pistachio powder was poured into filter paper and weighed. Then 120 ml of n-hexane was poured on each sample and after 48 hours the filter paper was placed in a desiccator for 48 h to prevent moisture absorption and evaporation. The mixture of oils and solvent was also poured into a rotary evaporator (model RV8, Germany) and the pure oil extracted from the solvent (Wrolstad *et al.* 2001).The kernel oil sample (5.00 ± 0.05 g) was placed in a 250 ml-glass flask. Then, 30 ml of 3:2 acetic acid/chloroform solution was added and stirred in the flask until the oil was dissolved. Half a milliliter of saturated potassium iodide was added to the glass flask. The solution remained in the dark for 1 min and was shaken frequently. Then, 30 ml of distilled water was added to the flask along with a standardized amount of 0.1 N sodium thiosulfate which contained 0.1 N sodium carbonate (Na_2CO_3). These steps were taken for the titration of the solution until the yellow color almost disappeared. The total added sodium thiosulfate volume was recorded. During the titration, the mixture was shaken constantly and vigorously. Then, 0.5 ml of 1% (w/v) starch solution was used as an indicator of the titration. The titration was continued by adding sodium thiosulfate solution that contained 0.1 N sodium carbonate (Na_2CO_3) drop by drop until the violet color disappeared (Wrolstad *et al*. 2001).

$$PV = ((S-B)\times N\times 1000)/W$$

S= the sodium thiosulfate volume (ml) needed to titrate the sample

B= the sodium thiosulfate volume (ml) needed for the blank

N= normality of the standardized sodium thiosulfate solution

W= the sample weight (g)

Free Fatty Acid (FFA) Content

The kernel oil sample (3.5 g) was dissolved in 100 ml neutralized alcohol, preheated to 60°C and then to 65°C, which was subsequently added to 1 ml solution of 1% (w/v) phenolphthalein. The mixture was stirred to make sure the solution mixed thoroughly. Titration was immediately carried out with 1 N sodium hydroxide solution which was vigorously stirred throughout the titration. The solution was allowed to reach a permanent pink color. The used volume of sodium hydroxide solution was recorded (Wrolstad *et al.*, 2001).

Sensory evaluation

Ten trained assessors (6 males and 4 females) performed sensory tests of taste, color, texture and appearance on the selected samples. Appearance, in addition to color, can also include residual testa on the kernel, oily spots, kernel size, and so on. In this study, panelists were selected based on their health, interest, and diagnostic ability and were trained for 12 hours (6 sessions each lasting 2hours) on how to identify and evaluate the specimens. The samples were disposed of using single-digit containers encoded with 3-digit random table numbers. The samples were then submitted to panelists at room temperature. For each sensory evaluation, a 15cm line was used for each feature, with both ends indicating very low to very high intensities. The evaluators marked the desired intensity on the line, which was then measured with a ruler and converted to a quantitative number (Stone *et al.*, 2012).

Statistical analysis

The factorial experiment was conducted in the form of a completely randomized design. Analysis of variance (ANOVA) was used for statistical analysis that was performed by Minitab version 16.1. The Tukey test was used to compare means of ripe and unripe pistachio kernels peeled with different methods. Each treatment was repeated three times.

Results

The Amount of Pistachio Kernel with Remained Testa

According to the results, the highest amount of remained testa after peeling was observed in unripe samples at 75°C for 2 minutes immersed in hot water (Table 1). There was no significant difference between the amount of remained testa on the kernel at 75°C in the unripe sample at 2 and 4 minutes immersion and the sample obtained at 2 minutes immersion at 5% level. According to the results, 100% peeling yield (zero percent remained testa) was obtained in both ripe and unripe samples at temperatures of 85 and 90°C and immersion times of 6, 8 and 10 minutes in hot water and 95°C, with no significant difference at the 5% level.

Table 1. Mean of remained testa percentage in different temperature per immersion time intraction

Temperature (ºC)	Immersion time (min)	Mean remained testa (%)	
		Riped	Unripe
75	2	24 ab	28 a
75	4	20 bc	24 ab
75	6	12 d-f	16 cd
75	8	10 e-g	14 d-f
75	10	5 g-i	10 e-g
80	2	17 cd	20 bc
80	4	10 e-g	14 d-f
80	6	2 hi	6 gh
80	8	2 hi	5 g-i
80	10	2 hi	5 g-i
85	2	15 c-e	20 bc
85	4	5 g-i	9 fg
85	6	0 i	0 i
85	8	0 i	0 i
85	10	0 i	0 i
90	2	6 gh	10 e-g
90	4	2 hi	6 gh
90	6	0 i	0 i

Table 1. Continued.

90	8	0 i	0 i
90	10	0 i	0 i
95	2	0 i	0 i
95	4	0 i	0 i
95	6	0 i	0 i
95	8	0 i	0 i
95	10	0 i	0 i

In each column, the mean of non-letter letters was significant at the 5% level.

Free fatty acid

Based on the results obtained from both ripe and unripe samples, free fatty acid increased over time, but this increase was more pronounced at temperatures of 75 and 80°C (Table 2). At the end of shelf life (after 6 months), the lowest free fatty acid in the sample was observed at 95°C (2 minutes immersion) and in the unripe sample at 95°C (2 and 4 minutes immersion).

Table 2. Mean free fatty acid during 6 months of storage in different hot water treatments

Temperature (ºC)	Time (min)	Ripe			Unripe		
		0	3	6	0	3	6
75	2	0.185 a	0.455 e-h	1.415 de	0.145 a	0.425 h-l	1.400 ef
75	4	0.135 a	0.475 c-f	1.435 b-d	0.135 a	0.445 f-j	1.415 de
75	6	0.135 a	0.495 b-d	1.455 a-c	0.145 a	0.475 c-f	1.430 c-e
75	8	0.135 a	0.515 ab	1.485 a	0.155 a	0.495b-d	1.455 a-c
75	10	0.155 a	0.535 a	1.485 a	0.155 a	0.515 ab	1.465 ab
80	2	0.155 a	0.425 h-l	1.310 ij	0.135 a	0.405 k-m	1.290 j
80	4	0.155 a	0.445 f-j	1.325 hi	0.145 a	0.420 i-l	1.305 ij
80	6	0.155 a	0.465 d-g	1.335 hi	0.145 a	0.445 f-j	1.315 ij
80	8	0.155 a	0.485 b-e	1.355 gh	0.145 a	0.465 d-g	1.335 hi
80	10	0.155 a	0.505 a-c	1.375 fg	0.155 a	0.485 b-e	1.355 gh
85	2	0.135 a	0.405k-m	0.805 no	0.135 a	0.380 m	0.785 op
85	4	0.135 a	0.425 h-l	0.825 mn	0.135 a	0.405 k-m	0.805 no
85	6	0.135 a	0.445 f-j	0.845 lm	0.135 a	0.420 i-l	0.825mn
85	8	0.135 a	0.465 d-g	0.865 kl	0.135 a	0.445 f-j	0.845 lm
85	10	0.145 a	0.485 b-e	0.885 k	0.135 a	0.465 d-g	0.865 kl
90	2	0.135 a	0.395 l-m	0.785 op	0.135 a	0.375 m	0.765 pq
90	4	0.130 a	0.415 j-l	0.805 no	0.135 a	0.395 l-m	0.785 op
90	6	0.140 a	0.435g-k	0.825 mn	0.135 a	0.415 j-l	0.805 no
90	8	0.145 a	0.450 f-i	0.845 lm	0.135 a	0.430 h-k	0.825mn
90	10	0.145 a	0.465 d-g	0.865 kl	0.135 a	0.445 f-j	0.845 lm
95	2	0.135 a	0.415 j-l	0.725 rs	0.135 a	0.395 l-m	0.705 s
95	4	0.135 a	0.435 g-k	0.745 qr	0.135 a	0.415 j-l	0.725 rs
95	6	0.145a	0.455 e-h	0.765 pq	0.135 a	0.430 h-k	0.745 qr
95	8	0.145 a	0.475 c-f	0.785 op	0.135 a	0.445 e-h	0.765 pq
95	10	0.155 a	0.495 b-d	0.805 no	0.135 a	0.475 c-f	0.785 op

In each column, the mean of non-letter letters was significant at the 5% level.

Peroxide Value

During the storage period, the peroxide value in both ripe and unripe samples increased over time (Table 3). Also, different immersion times for 4, 6, 8 and 10 minutes did not show any significant difference in terms of peroxide value obtained from different treatments. Only during immersion for 2 minutes, a significant difference was observed in peroxide value, with the highest value wasobtained in the ripe sample at 75°C and the lowest value in the unripe sample at 95°C.

According to the results, a significant difference was observed in the peroxide value of the ripe and unripe sample during hot water treatment ($p \leq 0.05$). The highest peroxide value was observed after 6 months of storage. Also in both ripe and unripe samples, the peroxide number decreased in most cases as the hot water temperature increased. Therefore, the highest peroxide value was observed at 75°C and the lowest at 95°C.

Table 3. Mean peroxide value during 6 months of storage in different hot water treatments

Temperature (ºC)	Time (min)	Ripe			Unripe		
		0	3	6	0	3	6
75	2	0.45 a	2.35 a-c	4.75 ab	0.35 a	2.15 c-g	4.55 b-f
75	4	0.45 a	2.25 b-e	4.75 ab	0.35 a	2.05 d-h	4.55 b-f
75	6	0.45 a	2.25 b-e	4.70 a-c	0.35 a	2.05 d-h	4.50 b-g
75	8	0.45 a	2.15 c-g	4.70 a-c	0.35 a	1.95 f-j	4.50 b-g
75	10	0.50 a	2.20 b-f	4.70 a-c	0.35 a	2.00 e-i	4.50 b-g
80	2	0.45 a	2.45 ab	4.85 a	0.35 a	2.25 b-e	4.65 a-d
80	4	0.45 a	2.35 a-c	4.85 a	0.40 a	2.35 a-c	4.65 a-d
80	6	0.50 a	2.30 a-d	4.70 a-c	0.40 a	2.10 c-g	4.50 b-g
80	8	0.50 a	2.20 b-f	4.70 a-c	0.40 a	2.05 d-h	4.55 b-f
80	10	0.55 a	2.30 a-d	4.70 a-c	0.45 a	2.20 b-f	4.60 a-e
85	2	0.35 a	1.90 g-k	4.60 a-e	0.30 a	1.80 h-l	4.50 b-g
85	4	0.35 a	1.75 i-l	4.50 b-g	0.30 a	1.65 k-m	4.40 d-i
85	6	0.35 a	1.80 h-l	4.50 b-g	0.30 a	1.70 j-m	4.45 c-h
85	8	0.35 a	1.65 k-m	4.35 e-j	0.35 a	1.55 l-n	4.25 g-k
85	10	0.35 a	1.70 j-m	4.35 e-j	0.35 a	1.60 l-n	4.30 f-k
90	2	0.35 a	1.65 k-m	4.35 e-j	0.35 a	1.55 l-n	4.25 g-k
90	4	0.35 a	1.65 k-m	4.35 e-j	0.35 a	1.55 l-n	4.25 g-k
90	6	0.35 a	1.65 k-m	4.35 e-j	0.35 a	1.55 l-n	4.25 g-k
90	8	0.35 a	1.55 l-n	4.30 f-k	0.35 a	1.45 mn	4.20 h-l
90	10	0.35 a	1.55 l-n	4.20 h-l	0.35 a	1.45 mn	4.10 j-l
95	2	0.40 a	1.55 l-n	4.20 g-l	0.40 a	1.45 mn	4.15 i-l
95	4	0.45 a	1.65 k-m	4.20 g-l	0.40 a	1.55 l-n	4.15 i-l
95	6	0.45 a	1.65 k-m	4.15 i-l	0.45 a	1.55 l-n	4.05 kl
95	8	0.45 a	1.55 l-n	4.15 i-l	0.45 a	1.45 mn	4.05 kl
95	10	0.50 a	1.45 mn	4.05 kl	0.45 a	1.35 n	3.95 l

In each column, the mean of non-letter letters was significant at the 5% level.

Sensory evaluation

Table 4 shows the sensory evaluation of the best peeling treatments in the two ripe and unripe samples selected from previous experiments.

Table 4. Sensory evaluation of selected peeling treatments in two riped and unripe samples.

Sample	Temperature (ºC)	Immersion time (min)	Flavor*	Texture	Color	Appreence
Ripe	95	2	13.5 a**	12.4 a	12.5 a	12.6 a
Unripe	95	2	13.6 a	12.6 a	12.5 a	12.5 a
Unripe	95	4	13.6 a	12.6 a	12.5 a	12.5 a

*A 15-cm linear scale (zero: minimum score and 15: maximum score) was used for evaluations.
**In each column, the mean of non-letter letters was significant at the 5% level.

These treatments were carried out at 95°C (2 minutes immersion in hot water) in the riped sample and 95°C (2 and 4 minutes immersion in hot water) in the unripe sample. According to the opinions of the trained evaluators, no significant differences were observed between treatments in terms of the sensory characteristics such as taste, texture, color, and appearance.

Discussion

In general, the higher the temperature of hot water, the greater would be the degree of membrane detachment from the Kernel. These results are in line with the findings of Shakerardekani *et al.* (2012) on pistachio kernel peeling with hot water. Castruccio (1923) reported that, the time of exposure of the nuts to higher temperatures must be reduced as the danger of cooking is more in such high temperatures. Also, although the yield of peeling was lower than that of unripe sample, it was not significant at 5% level.

According to Iranian National Standard No. 4631 (ISIRI, 2008), the amount of pistachio kernel with testa can be at maximum 2%. This means that in addition to the treatments with 100% peeling yield, the ripe sample treatments at 80°C (the immersion for 6, 8 and 10 minutes) and 90°C (the immersion for 4 minutes) can also be among the choices.

According to our results, the immersion at 75°C was not suitable for peeling. Also 100% peeling yield (zero percent residual testa) was observed in both ripe and unripe samples at 85 and 90°C (the immersion in hot water for 6, 8, and 10 min) and 95°C (all immersion times). Although the peeling efficiency was lower in unripe samples than in the ripe samples, they were not significantly different at 5% level.

Although free fatty acid increased in both ripe and unripe samples during storage, this increase was higher at 75 and 80°C. The reason for this is that the blanching has not been fully processed at these two temperatures and the activity of the enzymes has led to an increase in the release of fatty acids. Buranasompob *et al.* (2007) reported that short-time heat treatments, retard the development of oxidative rancidity, and reduce the shelf-life of walnuts and almonds during distribution and storage.

At the end of storage (after 6 months), the lowest free fatty acid content was observed in the sample immersed at 95°C (for 2 minutes) and in the unripe sample immersed at 95°C (for 2 and 4 minutes). These three treatments, performed at 95°C, are recommended as the best treatmentswhich lead to the complete inactivation of the enzymes at 95°C.

Cam and Kilic (2009) have also presented similar results regarding the retention of peeled hazelnut meal. Enzymes present in tree nuts include lipase, peroxidase, and lipoxygenase, which can play an important role in oxidation reactions (Bonvehí & Rosüa, 1996; Seyhan *et al.*, 2002).

Lipase and peroxidase have been reported to negatively affect fruit quality during storage (Bonvehí & Rosüa, 1996; Mortazavi *et al.*, 2015). In addition, the oxidation stability of tree nuts was inversely correlated with lipoxygenase activity (Pershern *et al.*, 1995). Lipase hydrolyzes triglycerides to free fatty acid, resulting in hydrolytic rancidity. The lipoxygenase enzyme also prefers free fatty acid over its esterified form (Patterson, 1989).

Ory *et al.* (1992) stated that if lipoxygenase has been active in the peanuts, even though the kernels show no visible signs of damage, oxidized fatty acids can still be present in the kernels and will affect flavor.

Immersing the pistachio kernel in hot water at temperatures above 85 °C has the advantage of proper peeling and also inactivating destructive enzymes and thus increasing the shelf life of the resulting pistachio product. Angelo *et al.* (1977) suggested that the peanut kernels in water blanching are placed at 86°C water for 1-1.5 minutes, and the testa are then mechanically removed.

In general, however, the peroxide value range is a small range of 4-5 after 6 months of storage. Blanching was not completely treated at 75 and 80 °C and these treatments could not be selected as the best treatments. In terms of peroxide value, the best treatments for ripe and unripe samples (with the lowest peroxide value after 6 months of storage) were performed at 90°C (immersion for 10 minutes in hot water) and at 95°C (immersion for 2, 4, 6, 8, and 10 minutes in hot water). Similarly, Sanders and Bett (1995) reported that the peroxide value in the blanched peanut was lower than in the unbleached peanut. Branch *et al.* (1987) also reported that the peroxide value of peanuts immersed in hot water (79°C) for 1.5 min was less than that of peanut not immersed.

The results of this study showed that the oxidative stability of pistachio was affected by the blanching process. Several researchers reported similar results for different nuts such as cashew (Chandrasekara & Shahidi, 2011), peanuts (Angelo *et al.*, 1977; de Camargo *et al.*, 2016; Sanders *et al.*, 1999), and almonds (Valdés *et al.*, 2015).

Conclusions

Considering all the quality factors measured in this study, in order to obtain maximum performance for pistachio kernel peeling, it is recommended to immerse pistachio kernels at 95 °C hot water for 2 minutes. These conditions can be applied to both ripe and unripe samples.

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