

Effect of Postharvest Storage Temperatures on the Quality Parameters of Pistachio Nuts

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Abstract

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Pistachios from Italy and Turkey were stored at different temperatures (10, 20, and 30°C) and the moisture of the pistachios, the free fatty acids (FFA) content, the peroxide value, and triacylglycerols (TGs) composition of the extracted oils were evaluated. The content of FFA decreased during storage at 10°C and increased at 20 and 30°C. No differences between the peroxide values were found during storage at 10°C. A significant increase in the peroxide values was observed after 20 days at 20°C and 5 days at 30°C in both the Italian and Turkish samples. The main TGs found in the pistachio oil of both origins were OLO, OLL, OLP, LLL, LLP, OOP, OLLn, and OOO; these accounted for approximately 85% of the total TGs content. A decrease was observed in the amounts of TGs esterified with polyunsaturated fatty acids, such as LLP, OLP, LLL and OLL, and an increase of the relative amounts of TGs with monounsaturated and saturated fatty acids, such as OOO and OOP, with the increasing storage time and temperatures in both samples.

Keywords: oxidative parameters; pistachio oil; triacylglycerols profile

Abbreviation: FFA – free fatty acids; P – palmitic acid; Mo – margaroleic acid; S – stearic acid; O – oleic acid; L – linoleic acid; Ln – linolenic acid; G – gadoleic acid; TGs – triacylglycerols

Pistachio (*Pistacia vera* L.) is one of the most important tree nuts in the world. According to the FAO Statistical Database (FAO 2010), the world production of pistachios is 954 082 tons. Pistachios are mainly cultivated in the Middle East (Iran 446 647 t, Syria 57 471 t), in some Mediterranean countries (Turkey 128 000 t, Italy 9170 t, Greece 8998 t), in the United States of America (236 775 t) and in China (58 000 t) (FAO 2010). The Italian production is very low compared to those of other countries. However, the low production is compensated for by the very high quality (BELLOMO & FALLICO 2007). The Italian pistachio, which comes from Bronte (Southern Italy) and represents approximately 80% of the Italian production with just one variety (Bianca), shows, at ripeness, a red-violet skin while retaining a green nutmeat (BALLISTRERI *et al.* 2009). Usually, it is picked fully ripe and sold as a green product. In

other production areas, in order to have and sell a green product (the consumers' preference), the picking time occurs some weeks in advance, at the end of August or by the beginning of September (BELLOMO & FALLICO 2007).

Pistachio nuts are a rich source of oil and have the lipid content between 40 and 63% (MASKAN & KARATAS 1999; ARENA *et al.* 2007). Triacylglycerols (TGs) constitute the main acylglycerols in pistachio oil (more than 90% of the total glycerolipids) (CHAHED *et al.* 2008). The TGs of pistachio are rich in polyunsaturated fatty acids such as linoleic and linolenic acids, essentials for human diet, and monounsaturated fatty acids such as oleic acid (ANDERSON & SMITH 2005; ARENA *et al.* 2007; BALLISTRERI *et al.* 2010). Lipid oxidation is the major cause of the quality decay in dehydrated food. The high lipid content and the presence of lipids with a high degree of unsatura-

tion affect the lipid oxidation rate and the storage stability of pistachio nuts. Unsaturated fatty acids can easily undergo oxidation, producing a variety of off-flavours and off-aromas (TAVAKOLIPOUR *et al.* 2010). A low temperature and the use of a modified atmosphere improved the storage stability (MASKAN & KARATAS 1998, 1999). Nuts may be held for up to 2–5 years under optimal conditions, but under unsuitable storage conditions, they become inedible within a month because of discolouration, the development of off-flavours and oxidative rancidity (LABUZA 1982; MASKAN & KARATAS 1998).

In the Mediterranean countries, after harvesting, pistachio nuts are undergo a sun-drying process, which is the method most commonly used to reduce the moisture level, and generally, after a short postharvest storage, they nuts are sold. Postharvest storage is usually conducted at ambient temperature and subjected to seasonal variations. The present study evaluated the effect of temperatures on the oxidative parameters and triacylglycerols profile in *Pistacia vera* L. nuts during postharvest storage.

MATERIAL AND METHODS

Pistachio samples. Twenty-one pistachio samples coming from Bronte, Italy (cv. Bianca) and Gaziantep, Turkey (cv. Siirt) were supplied as green products, but they were picked at two different ripeness stages. The Turkish samples were picked during the 3rd week of August and the Italian samples in the 2nd–3rd week of September. Each sampling was performed from different pistachio producers and importers: 14 Italian samples and 7 Turkish samples. The Italian samples consisted of 1000 kg of pistachio kernels from which 1 kg of pistachio was taken. The Turkish samples were 1 kg each, coming from lots between 1000 and 40 000 kg. All samples were produced and collected in 2010. The pistachio nuts were received after the sun drying process and then immediately stored at controlled temperatures (10, 20, and 30°C). After 5, 10, and 20 days, aliquots of pistachio nuts were sampled for each temperature and immediately analysed.

Moisture, free fatty acids (FFA) and peroxide value determinations. The moisture content (%) of the pistachio powder obtained after crushing kernels in a home grinder was determined. Portions of the powder were used to assess the moisture

content. They were placed in an oven at 105°C until the dry weight was constant. The content of FFA (% oleic acid) and the peroxide value (meq/kg) in the pistachio oil were determined according to standard methods (Commission Regulation No 2568/91 – EEC 1991). All the analyses were conducted in triplicate.

Pistachio oil. For each sample, 500 g of pistachio kernels were shelled and crushed in a home grinder (La Moulinette; Moulinex, Lyon, France); subsequently, the pistachio powder (30 g) was mixed with 50 ml of *n*-hexane (J.T. Baker, Deventer, Holland) and stirred for 30 minutes. The *n*-hexane extract was filtered, and the solvent was evaporated under reduced pressure using a rotavapor (RE 111; Büchi, Flawil, Switzerland).

HPLC analysis of TGs. For HPLC analysis, oil samples were dissolved (1:10, w/v) in acetonitrile: 2-propanol (1:1, v/v) and filtered using a PTFE 0.45 µm filter (Albet). The chromatographic apparatus consisted of an HPLC Spectra System equipped with a P4000 pump with a quaternary gradient pump system, a SCM1000 vacuum membrane degasser, a UV6000LP diode-array UV detector and an AS3000 autosampler (all Thermo Electron Corporation, Waltham, USA). The column was an Alltech Alltima C₁₈ (250 mm × 4.6 mm, 5 µm particle size). The analysis conditions were as follows: 10 µl injection volume, flow rate of 1 ml/min, the spectra were recorded from 200 nm to 300 nm, and UV detection was at 205 nm. The mobile phase and the gradient program were set up according to HOLCAPEK *et al.* (2003). TGs were identified by the correspondence of the retention times and the ECN (equivalent carbon number) with standard compounds. The elution order of TGs is based on the equivalent carbon number increase $ECN = CN - 2DB$ (equivalent carbon number = carbon number – twice the double bond number) (Table 1). The HPLC was connected to the software Chromquest Chromatography Manager 4.2 (Rev. A. 97202) (Thermo Electron, San Jose, USA) to determine the peaks areas and percentages of TGs.

Acetonitrile and 2-propanol were purchased from Lab Scan (Dublin, Ireland) and water from J.T. Baker (Deventer, Holland). All the reagents used were of the required HPLC purity grade. All the triacylglycerol standards used for the study were purchased from Sigma-Aldrich Chemical Co. (St. Louis, USA) and Larodan Fine Chemicals (Malmo, Sweden).

Statistical analysis. The differences between the mean values of the variables reported in Table 2

Table 1. Abbreviations of the fatty acids and triacylglycerols identified in pistachio oil

Fatty acids	Carbon number:double bond	ECN
Palmitic (P)	C16:0	16
Margaroleic (Mo)	C17:1	15
Stearic (S)	C18:0	18
Oleic (O)	C18:1	16
Linoleic (L)	C18:2	14
Linolenic (Ln)	C18:3	12
Gadoleic (G)	C20:1	18
Triacylglycerols	double bond	ECN
POP	1	48
SOP	1	50
PLP	2	46
OOP	2	48
SOO	2	50
OLP	3	46
OOO	3	48
GOO	3	50
LLP	4	44
OLnP	4	44
OLMo	4	44
OLO	4	45
GLO	4	48
LnLP	5	42
OLL	5	44
LLL	6	42
OLLn	6	42
LLLn	7	40

ECN – equivalent carbon number

were tested by the one-way analysis of variance (ANOVA), and the statistical significance of the differences between the samples was determined using the *F*-test. The levels of statistical significance were $P < 0.05$ at a 95% confidence level. Statistical analysis was performed using the software Statgraphic Plus 4.1 (Manugistic Inc., Rockville, USA).

RESULTS AND DISCUSSION

Table 2 shows the moisture content (%) of the pistachio kernels and the FFA level (%) and peroxide value (meq/kg) of the *Pistacia vera* oils, during the postharvest storage at 10, 20, and 30°C.

The initial moisture content (0 days of storage) of the pistachio kernels was very low ap-

Table 2. Moisture of the pistachio kernels, free fatty acids (FFA) and peroxide value of pistachio oils

Origin	Storage temperatures (°C)									
	10			20			30			
Days of storage	0	5	10	20	5	10	20	5	10	20
Italy variety Bianca										
Moisture (%)	4.1 ± 1.3 ^d	4.1 ± 0.5 ^d	4.1 ± 0.2 ^d	4.0 ± 0.3 ^d	3.6 ± 0.7 ^{cd}	3.4 ± 0.2 ^{bcd}	3.3 ± 0.5 ^{abcd}	2.8 ± 1.0 ^{abcd}	2.1 ± 0.8 ^{ab}	1.9 ± 0.7 ^a
FFFA (%)	0.6 ± 0.1 ^a	1.0 ± 0.2 ^{abc}	0.9 ± 0.2 ^{ab}	0.8 ± 0.2 ^a	2.0 ± 0.8 ^{abcd}	2.3 ± 0.3 ^{bcd}	2.4 ± 0.8 ^{cd}	2.5 ± 0.7 ^d	2.6 ± 0.8 ^d	2.8 ± 0.6 ^d
Peroxide value (meq/kg)	1.3 ± 0.1 ^a	1.9 ± 0.4 ^{abc}	1.7 ± 0.4 ^{ab}	1.6 ± 0.5 ^{ab}	2.6 ± 0.2 ^{abcd}	2.8 ± 0.4 ^{bcd}	2.9 ± 0.7 ^{bcd}	3.0 ± 0.8 ^{bcd}	3.1 ± 0.7 ^{cd}	3.3 ± 0.8 ^d
Turkey variety Siirt										
Moisture (%)	3.1 ± 0.4 ^c	3.1 ± 0.2 ^c	3.0 ± 0.1 ^{bc}	3.0 ± 0.9 ^c	2.9 ± 0.6 ^{abc}	2.8 ± 0.1 ^{abc}	2.6 ± 0.1 ^{abc}	1.6 ± 0.1 ^{ab}	1.6 ± 0.1 ^{ab}	1.5 ± 0.2 ^a
FFFA (%)	0.4 ± 0.1 ^a	1.0 ± 0.1 ^a	0.7 ± 0.2 ^a	0.5 ± 0.2 ^a	1.3 ± 0.1 ^a	1.4 ± 0.2 ^a	1.5 ± 0.3 ^a	1.5 ± 0.2 ^a	1.6 ± 1.0 ^a	1.7 ± 0.9 ^a
Peroxide value (meq/kg)	0.7 ± 0.1 ^a	1.5 ± 0.4 ^{abc}	1.4 ± 0.4 ^{abc}	1.3 ± 0.7 ^{abc}	1.9 ± 0.6 ^{abc}	2.0 ± 0.2 ^{abc}	2.1 ± 0.9 ^{bc}	2.2 ± 0.2 ^c	2.3 ± 0.2 ^c	2.5 ± 0.2 ^c

Data expressed as the mean ± standard deviation; ^{a-d} values with different letters in the rows are significantly different ($P < 0.05$)

proximately 4 and 3% for the Italian and Turkish samples, respectively. A low moisture content is important for maintaining the quality and shelf life of seeds because it decreases the probability of microbial growth, unwarranted fermentation and premature seed germination (KUCUKONER & YURT 2003; VENKATACHALAM & SATHE 2006; ARENA *et al.* 2007). Moreover, pistachio seeds with a water content above 6.5% are not suitable for the market (CEE 2004).

The moisture content, significantly decreased ($P < 0.05$), during postharvest storage, after 10 and 5 days of storage at 30°C, for the Italian and Turkish pistachios, respectively.

The initial oxidative parameters (0 days of storage) of the *Pistacia vera* oils were the following: FFA contents of 0.6 and 0.4% for the Italian and Turkish samples, respectively, and peroxide value of 1.3 and 0.7 meq/kg for the Italian and Turkish samples, respectively.

The FFA contents showed a similar trend with the sampling of both origins, decreasing at 10°C and increasing at 20 and 30°C, reaching the highest values after 20 days of storage at 30°C (2.8 and 1.7% for the Italian and Turkish samples, respectively) (Table 2).

The one-way ANOVA results displayed no significant changes ($P > 0.05$) of the peroxide values with the sampling of both origins with respect to the initial ones (0 days of storage) during postharvest storage at 10°C and also after 5 days of storage at 20°C. Significant increases ($P < 0.05$) were observed after 10 and 20 days of storage at 20°C for the Italian and Turkish samples, respectively. There were no significant differences of the peroxide values ($P > 0.05$) between the samples stored at 20 and 30°C (Table 2). The increases in the peroxide values may be due to the lipoxygenase activity and lipase enzymes. Moreover, chlorophyll of a pistachio nuts can act as a sensitizer (LABUZA 1971; FAKOURELIS *et al.* 1987; BONVEHI & COLL 1993). MASKAN and KARATAS (1998) did not find any significant change in the peroxide value of pistachio nuts during 6 months of storage under ambient conditions.

The main constituents of pistachio lipids are triacylglycerols (TGs). In fact, they account for more than 90% of the total glycerolipids content (CHAHED *et al.* 2008). The TGs of pistachio oil have been separated by HPLC according to their degree of unsaturation and their total number of carbon atoms in the three fatty acyl chains (HOLCAPEK *et al.* 2003; BALLISTRERI *et al.* 2010).

By comparing the retention times and equivalent carbon numbers to those of standard compounds, 18 TGs were identified. They were, in the order of elution, the following: LLLn, LLL, OLLn, LnLP, OLL, LLP, OLnP, OLMo, OLO, OLP, PLP, GLO, OOO, OOP, POP, GOO, SOO and SOP.

Table 3 reports the percentage distribution of the TGs during the postharvest storage. The main TGs in the pistachio oil of both origins (Italy and Turkey) were OLO, OOO, OLL, OLP, OOP, LLL, and LLP. According to other authors (DYSZEL & PETTIT 1990; HOLCAPEK *et al.* 2003; BALLISTRERI *et al.* 2010), they accounted for 85.6 and 83% of the total TGs of the Italian and Turkish samples, respectively. The most abundant TGs were OLO and OOO; together, they accounted for approximately 36 and 34% of the total TGs of the Italian and Turkish pistachios, respectively. The TGs profiles of the two oils were very similar, with the exception of the OOO contained in the Bianca variety, which accounted for 17.4% of the total TGs, and in the Siirt variety, where it accounted for 15.9% of the total TGs.

The levels of TGs reported in this study (Table 3), were similar to those reported in the literature. The ranges of the main TGs reported in the literature varied from 16.9% to 25.2% for OLO, from 4.7% to 24.8% for OLL, from 5.2% to 11.8% for OLP, from 1.3% to 7.9% for LLP, from 1.0% to 11.7% for LLL, from 1.0% to 2.7% for OLLn, and from 8.9% to 47.0% for OOO (DYSZEL & PETTIT 1990; HOLCAPEK *et al.* 2003; BALLISTRERI *et al.* 2010, 2011a,b). The high variability of the TGs distribution in *Pistacia vera* oil was ascribed both to the origin and the variety of pistachios as well as to different years of harvesting (DYSZEL & PETTIT 1990; HOLCAPEK *et al.* 2003; BALLISTRERI *et al.* 2010, 2011a,b).

During postharvest storage, variation of the TGs distribution was observed. TGs, such as OLO, OLL, OLP, LLL, LLP, OLLn, PLP, OLnP, LnLP, LLLn, GLO, rich in polyunsaturated fatty acids decreased during storage in both pistachio samples (Table 3). Among the main TGs, OLP and LLP decreased more than the others in Italian pistachios. In particular, LLP revealed the highest reduction during the postharvest storage. At 10°C, it decreased from approximately –1% to approximately –65% after 5 and 20 days of storage, respectively, and at the highest temperatures, 20 and 30°C, from approximately –44% to approximately –66% after 5 and 20 days of storage, respectively. The OLP its content decreased up to –53% during storage at 10°C

Table 3. Content (%) of the most relevant triacylglycerols types in pistachio oil during storage

Origin		Storage temperatures (°C)									
		10			20			30			
Days of storage	0 ^a	5	10	20	5	10	20	5	10	20	
Italy variety Bianca											
85.6%	OLO	18.6	18.7	11.9	10.4	11.3	9.6	8.1	11.4	9.9	8.4
	OOO	17.4	17.3	31.2	31.0	30.5	30.9	29.8	29.7	31.9	31.2
	OLL	13.9	13.9	8.4	7.5	7.8	6.8	5.7	7.9	6.8	5.8
	OLP	10.7	10.6	5.7	5.0	5.7	5.0	4.2	5.7	5.0	4.3
	OOP	9.0	8.7	21.3	21.0	21.8	22.3	20.6	19.1	21.7	21.5
	LLL	8.6	8.5	4.8	4.1	6.2	5.1	3.4	6.0	4.4	3.7
	LLP	7.4	7.3	3.0	2.6	4.1	3.5	2.5	4.2	3.6	2.5
	OLLn	2.4	2.4	0.9	0.7	0.8	0.5	0.4	0.9	0.7	0.5
14.3%	PLP	2.1	2.1	0.6	0.5	1.0	0.7	0.5	1.0	0.8	0.5
	SOO	2.1	3.0	4.5	7.7	4.0	6.2	7.1	5.8	6.2	6.8
	POP	1.8	1.2	4.4	5.8	2.3	5.4	13.4	3.5	5.0	10.7
	OLnP	1.4	1.4	0.5	0.4	0.6	0.5	0.4	0.9	0.5	0.4
	LLLn	1.2	1.2	0.6	0.3	0.9	0.7	0.3	0.8	0.5	0.3
	GOO	0.9	0.9	0.7	1.2	0.5	0.7	1.2	0.9	1.0	1.7
	LnLP	0.8	0.8	0.5	0.3	0.4	0.3	0.2	0.4	0.3	0.3
	GLO	0.6	0.5	0.1	0.0	0.2	0.1	0.1	0.2	0.1	0.0
	SOP	0.5	0.3	0.3	0.8	0.2	0.6	1.3	0.3	0.5	0.7
	OLMo	0.4	1.3	0.6	0.4	1.5	1.1	0.8	1.4	1.2	0.6
Turkey variety Siirt											
83.0%	OLO	17.8	18.2	10.9	9.9	9.7	8.8	8.3	10.5	9.1	8.4
	OOO	15.9	16.1	28.2	30.8	30.4	30.0	31.8	25.9	28.8	30.2
	OLL	14.4	14.5	8.2	7.6	7.1	6.7	6.3	7.6	6.7	6.3
	OLP	10.2	10.7	5.4	4.9	5.2	4.8	4.5	5.5	4.9	4.5
	LLL	9.1	9.1	4.9	4.3	5.9	5.6	5.0	6.1	4.3	3.9
	OOP	7.9	5.7	28.2	28.0	28.1	30.8	30.3	26.1	29.3	28.8
	LLP	7.7	7.9	3.4	3.0	4.0	3.8	3.7	4.4	3.8	3.6
17.0%	OLLn	3.1	3.1	1.4	1.1	0.7	0.6	0.5	1.3	1.1	0.9
	PLP	2.2	2.2	0.6	0.5	0.4	0.4	0.4	1.0	0.8	0.5
	SOO	2.0	2.0	2.9	3.2	3.0	3.2	3.2	3.4	3.6	4.9
	POP	1.6	1.1	0.7	1.6	0.3	0.3	1.2	0.4	1.0	2.1
	OLnP	2.0	1.9	0.7	0.6	0.5	0.4	0.4	0.7	0.6	0.5
	LLLn	1.5	1.5	0.9	0.6	1.2	1.1	0.7	1.3	0.8	0.7
	GOO	0.8	0.8	0.7	1.1	0.7	0.8	1.1	0.5	1.0	1.5
	LnLP	1.6	1.5	0.9	0.7	1.0	0.6	0.3	1.1	0.8	0.6
	GLO	0.8	0.7	0.1	0.1	0.0	0.0	0.0	0.2	0.1	0.1
	SOP	0.5	0.3	0.8	1.0	0.6	1.0	1.4	0.8	1.0	1.4
	OLMo	0.9	2.7	1.2	0.8	1.1	0.8	0.8	3.0	2.4	8.4

^acontent (%) of triacylglycerols before storage

and from approximately –47% to approximately –60% after 5 and 20 days of storage, respectively, both at 20 and 30°C.

In the Turkish samples, OLO, OLL, OLP, LLL, and LLP the highest reduction occurred during storage. At 10°C, OLP and LLL decreased from approximately –47% to approximately –53% after

10 and 20 days of storage, respectively. At 10°C, the levels of LLP and OLL were reduced up to –61% and –47%, respectively, at the end of the storage. However at the highest storage temperatures, 20 and 30°C, OLL and OLP revealed the highest decreases among the main TGs and had similar trends. In fact, at the end of the postharvest stor-

age (20 days), both OLL and OLP were decreased up to –56%. There was a similar trend for LLL which showed a reduction of approximately –45% and –57% after 20 days of storage at 20 and 30°C, respectively. The content of LLP and OLO were reduced their contents up to –53% after 20 days of storage, both at 20 and 30°C.

Among the minor TGs, the contents of OLLn, PLP, OLnP, LLLn, LnLP and GLO were reduced by more than 50% both in the Italian and Turkish samples. Generally, these TGs had a high degree of unsaturation and often contained linolenic acid. During pistachio storage, a proportionally larger amount of linolenic acid was lost by oxidation compared to that of linoleic acid (MASKAN & KARATAS 1998).

The decrease of TGs with polyunsaturated fatty acids resulted in an increase of the relative amounts of TGs with monounsaturated and saturated fatty acids such as OOO, OOP, SOO, POP, GOO, SOP, and OLMo. Among the main TGs, only OOO and OOP increased with the storage time in both the Bianca and Siirt varieties. The temperatures did not seem to affect the variation of these TGs levels.

The OOO level in the Italian samples increased by more than 70% after 20 days of storage at 10, 20, and 30°C. In the Turkish samples, during the same storage time, OOO increased by more than 90%. A similar trend was found with OOP. In the Italian samples, it increased by more than 130%, while in the Turkish ones, it increased by more than 250%. The decline in the TGs containing linoleic and linolenic acids and the strong increase in the TGs containing oleic acid reflect the observed increase of oleic acid and the decreases of the linoleic and linolenic acids during pistachio storage (MASKAN & KARATAS 1998).

Generally, the temperature of postharvest storage is not considered to have an effect on the quality of pistachio nuts, most likely, because of the short time of this stage as compared to the long shelf-life of the pistachios. In this study, the importance of the temperature during the postharvest storage was highlighted. Storage temperatures above 20°C increased the FFA content, and the peroxide value altered the quality characteristics of the pistachio nuts and had also a high impact on the TGs distributions after 10 days of storage. To prevent lipid oxidation and to best preserve the quality parameters of the pistachio nuts, storage temperatures lower than 20°C should be recommended to producers and importers.

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