

Flavor Stability of High-Oleic Peanuts Stored at Low Humidity

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ABSTRACT: Shelf-life studies were conducted on roasted high-oleic peanuts (HOP; F1250, BC93Q10) and a reference peanut with normal oleic acid content (NOP, Florunner). HOP contained at least 80% oleic acid and 3% linoleic acid, whereas normal-oleic peanuts contained 53% oleic and 27% linoleic acids. Peanuts were dry-roasted to a medium roast (Hunter lab L = 50) and stored at 40°C at 18% relative humidity. Samples were removed from storage at different intervals (0, 2, 4, 7, and 10 wk) for sensory evaluation and chemical oxidation measurements. Sensory attributes rated included roasted peanutty flavor, sweetness, crunchiness, and oxidized flavors (cardboardy and painty). The two HOP lines were not significantly different from each other in flavor quality or stability during storage but had better flavor quality and stability than NOP. The latter oxidized faster and developed painty off-flavors to a greater extent than did the HOP lines. Chemical oxidation measurements confirmed higher levels of oxidation in NOP than in the HOP lines. Peroxide values at 10-wk storage were 47 meq/kg oil for NOP and <3 meq/kg oil for the HOP lines. Both HOP lines had greater shelf lives than NOP.

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KEY WORDS: Flavor stability, high-oleic peanuts, peroxide value.

Peanut oil generally contains 55–65% monounsaturated fatty acids, 26–28% polyunsaturated fatty acids, and 17–18% saturated fatty acids (1). Owing to the high content of unsaturated fatty acids, the potential for off-flavors is significant. Oxidative rancidity of peanut oil is a major cause of spoilage of roasted peanuts and peanut-based confections during storage. Oxidation leads to the formation of tasteless and odorless hydroperoxides as primary products. Decomposition of hydroperoxides results in a wide variety of compounds, such as aldehydes and ketones, which result in off-flavors and odors. To improve stability of edible oils and oilseeds, attempts have been made to lower the degree of unsaturation by fatty acid modification. In sunflower, for example, oleic acid has been increased from about 23 to 85% (2), whereas in canola, linoleic acid has been increased to 40% with a subsequent decrease in linolenic acid to less than 3% (3). Other examples include reduction of linolenic acid in soybean to less than 2% (4), and an increase of oleic acid in peanuts (5).

Many factors influence the shelf life of roasted peanuts. These include variety (6), maturity at harvest (7), market grade and seed size (8,9), processing methods, and production conditions. Most importantly, the shelf life of peanut products highly depends on oil stability.

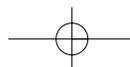
Shelf life is often measured as the number of days before the onset of oxidative rancidity, which is generally induced by exposure to heat and oxygen. Oxidative rancidity increases with higher levels of polyunsaturated fatty acids in oils, and the total amount of unsaturation is roughly inversely proportional to shelf life. The oleic/linoleic acid ratio (OL) is regarded as the major factor that influences stability of peanut oil (10,11), which, in turn, affects the overall flavor quality and stability of roasted peanuts during storage.

Chemical measures of oxidative stability have indicated that high-oleic peanut (HOP) oil was much more stable than normal-oleic peanut (NOP) oil (12). The chemical and flavor stabilities of HOP have been shown to be better than NOP (13,14). However, in this study peanuts were stored at 40% humidity and developed poor texture (decreased crunchiness) during storage. Because humidity affects the rate of oxidation in peanuts and walnuts (15), it is unclear what the relative advantages of HOP would be when stored at a lower humidity, where moisture pickup and crunchiness changes would not occur. Also, most of the work to date has focused on F1250 (SunOleic95R) or F435. New varieties of HOP have been developed with disease resistance and yield superior to that of F1250, yet no data are available comparing their relative performances. The objective of this research was to compare the flavor quality and stability of two HOP lines (F1250 and BC93Q10) and one NOP (Florunner) during storage at 40°C and low relative humidity [~18% equilibrium relative humidity, which equals a water activity (a_w) of 0.18].

EXPERIMENTAL PROCEDURES

Preparation and roasting of peanut samples. Shelled and sized mature peanuts (*Arachis hypogaea* L.) from the 1994 crop were obtained from the University of Florida Institute of Food and Agricultural Sciences (Gainesville, FL). They were sorted by size, and the splits and discolored peanuts were discarded. Raw peanuts were put in glass jars and the jars flushed with nitrogen before storage at 2°C





Before roasting, peanuts were allowed to equilibrate to room temperature overnight while still in glass jars. They were then placed in a single layer in aluminum baking pans and roasted with periodic stirring in a preheated electric oven for 50–55 min at 170°C. They were roasted until a Hunter Lab L value of 50–51 was reached (medium roast). Color measurements were taken on hand-blanched peanuts with a colorimeter (Colorguard model 05; Gardner, Silver Spring, MD) to verify uniformity of degree of roasting. Peanuts were then cooled by forced air at room temperature.

Storage of roasted peanuts. Roasted, unblanched peanuts were stored at $40 \pm 1^\circ\text{C}$ in open 600-mL beakers in vacuum desiccators. Relative humidity was controlled with a saturated solution of lithium chloride, which maintained a measured a_w of 0.17–0.19. Peanuts were stirred twice weekly and sampled at 0, 2, 4, 7, and 10 wk for sensory analysis and chemical oxidation measurements. All experimental procedures (including roasting) were replicated twice.

Peanut oil extraction. Lipids were extracted from replicate samples of raw and roasted peanuts with methylene chloride according to a method described previously (12). Samples of peanuts (25 g) were mixed with 75 mL methylene chloride in a Waring blender and blended for 4 min, stopping occasionally to scrape the paste from the sides of the blender jar. The mixture was filtered through Whatman No. 4 filter paper (Maidstone, England). The cake and the filter paper were reblended with another 75 mL methylene chloride for 4 min and filtered, rinsing twice with 10 mL of solvent. Fifty grams of anhydrous sodium sulfate was added to the oil/solvent mixture, which was then allowed to stand for 15 min. It was then filtered into evaporating flasks through Whatman filter paper No. 4 and rinsed with 10 mL solvent. The solvent was rotary-evaporated under vacuum at 40°C for 15 min. A vacuum pump (Model 4143; Emerson, Motor Division, St. Louis, MO) was used to ensure complete solvent removal. The lipid was transferred to glass amber vials, flushed with nitrogen, and stored at -28°C until analyzed.

Fatty acid composition. Fatty acid composition of peanut oils was determined by gas chromatography (GC) of fatty acid methyl esters (16). About 20 mg (1 drop) of lipid was added to a leak-proof, Teflon-lined 15-mL screw-cap tube and dissolved in 2 mL isoctane. A volume of 100 μL 2 N KOH in methanol (1.1 g/10 mL) was added, and the tube was vortexed for 1 min and then centrifuged for 4 min at $4000 \times g$. The lower methanol layer was discarded. To the remaining top layer, 200 μL of saturated ammonium acetate (aqueous) was added, and the mixture was vortexed and centrifuged again. The lower aqueous layer was discarded, and the organic phase was washed with 500 μL distilled deionized water, then dried with anhydrous sodium sulfate. After centrifuging the mixture, the top layer, which contained the fatty acid methyl esters, was removed into vials. These were analyzed by GC (Shimadzu GC-14A, Kyoto, Japan) with a flame-ionization detector (FID). A 50 m \times 0.25 mm i.d., 0.25 μm film, BXP-70 (SGE, Ringwood, Australia) fused-silica capillary column was used. The linear velocity of helium car-

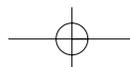
rier gas was 22 cm/s, and the split ratio was 40:1. The column temperature was held at 185°C for 20 min, then increased at a rate of 5°C/min to 250°C, then held for 15 min. Fatty acid methyl ester standards GLC 68A (20 mg/mL; Nu-Chek-Prep, Inc., Elysian, MN) were used as references. Percentage fatty acid composition was calculated by integrating the specific area under each peak with area normalization.

Chemical oxidation. Oxidation of peanut oil was measured by the peroxide value (POV) method (16). The method employs iodometric titration to measure the peroxides and hydroperoxides formed during lipid oxidation. Results were expressed as meq peroxide/kg oil.

Sensory evaluation of roasted peanuts. Quantitative descriptive analysis of roasted peanuts was conducted with the simplified lexicon of peanut flavors as described previously (13). Thirteen panelists from the Food Science and Human Nutrition Department, University of Florida, participated in the study. Three sessions were held to train panelists to identify and rate intensities of the following roasted peanut attributes: roasted peanutty, raw/beany, cardboardy, painty, sweetness, dark roast, and crunchiness. Attributes were rated on a 0 to 15 point scale, with 0 being the lowest and 15 the highest intensity. During the training sessions, panelists were presented with peanuts that were roasted at three different levels (light roast, medium roast, heavy roast), oxidized peanuts (cardboardy and painty), and raw peanuts. Panelists were also presented with a reference sample (fresh medium-roasted Florunner) for which they agreed to assign the following anchor points: roasted peanutty (10–12), raw/beany (0–1), cardboardy (0–1), painty (0–1), sweetness (6–7), dark roast (2–3), and crunchiness (10–12). Samples were taken at 0, 2, 4, 7, and 10 wk. A reference sample (freshly roasted Florunner) was presented at every session. Panelists were presented with about 10 g peanuts at random in 4-oz plastic cups. Cups were coded with three-digit random numbers. Evaluations were conducted in partitioned booths under red light. Panelists were instructed to evaluate three or four nuts at once. They were provided with unsalted crackers and deionized water.

Statistics. The experiment was replicated twice at the level of peanut roasting, and replicate samples were analyzed separately. Results were analyzed by analysis of variance (ANOVA), and means were separated (when ANOVA was significant) by Fisher's Least Significant Difference by using SAS for Windows, Version 6.11 (SAS Institute, Cary, NC, 1989). For sensory analysis, a split-plot design was used with panelists as blocks, peanut genotype as subplot, and time as whole plot. For POV analyses, a completely randomized design was used. The main effects of peanut variety and time and the interaction (variety \times time) were considered significant at $P < 0.05$. The ANOVA results for variety represent a comparison of peanut varieties averaged over time. The time results for ANOVA represent a comparison of times averaged over varieties. The interaction represents different changes in measured parameter (e.g., roast peanutty score) over time for the three varieties (the peanuts behave differently during storage).





RESULTS AND DISCUSSION

Fatty acid composition of peanut oil. The O/L ratios of two HOP varieties, F1250 and BC93Q10, and NOP (Florunner) were 29, 26, and 2, respectively. There were no practical differences in the fatty acid profiles for the three varieties except for the different oleic, linoleic, and palmitic acid contents (Table 1). Oil contents of the roasted peanuts for the three varieties were similar and ranged from 54 to 55%. The fat contents and fatty acid profiles of the HOP are similar to previous reports (12,13).

POV of roasted stored peanuts. POV for HOP increased from ~0 at 0 wk to 4 meq/kg at 10 wk (Fig. 1). However, NOP oxidized much faster and reached ~41 meq/kg by 10 wk of storage. The increases in POV with time were linear over the range studied ($r^2 > 0.99$) for all varieties, in agreement with a previous study where peanuts were stored at 25°C (13,14). The slopes of the POV–time curves were 4.2, 0.25, and 0.38 for Florunner, BC93Q10, and F1250, respectively. Thus, the increases in POV were 16.8 and 11.1 times greater for NOP than for BC93Q10 and F1250, respectively. Previous work with F1250, stored at 25°C and a_w 0.4, showed that NOP oxidized at an 11.7 times greater rate than HOP (13,14). F1250 oils oxidized 9.5 times faster than NOP oils, based on Active Oxygen Method measurements and 14.5 times longer, based on Schaal oven testing (12).

HOP, coated with chocolate and stored at room temperature for 21 wk, had peroxide values that were 10.5 times higher than chocolate-coated NOP (18). A chocolate coating could potentially protect the peanuts from oxygen and moisture uptake or provide anti- or prooxidants. However, chocolate-covered HOP oxidized at rates (relative to NOP) similar to those reported for uncoated peanuts (12–14).

Peanuts in the current study were stored under normal atmospheric oxygen concentrations (~21% O₂ vol/vol in dry air). In another study, dry roasted peanuts stored at a_w 0.21 and 21% oxygen were reported to oxidize much faster than peanuts stored at a_w 0.21 and <2.5% oxygen, or peanuts at either oxygen concentration stored at a_w 0.53 (15). Based on these observations (15), an increase in a_w from levels that we used (~0.18) to a_w 0.53 would be expected to provide an increase in oxidative stability, but water pickup and loss of crunchiness would result in lower acceptability of the peanuts (13).

TABLE 1
Fatty Acid Weight Percentages of Normal-Oleic (Florunner) and High-Oleic (BC93Q10, F1250) Peanuts

Fatty acid	F1250	BC93Q10	Florunner
16:0 (palmitic)	7	6	10
18:0 (stearic)	3	2	3
18:1n-9 (oleic)	80	81	53
18:2n-6 (linoleic)	3	3	27
20:0 (arachidic)	1	1	1
20:1n-9 (gondoic)	2	2	1
22:0 (behenic)	2	3	3
24:0 (lignoceric)	2	2	2
18:1n-9/18:2n-6	29	26	2

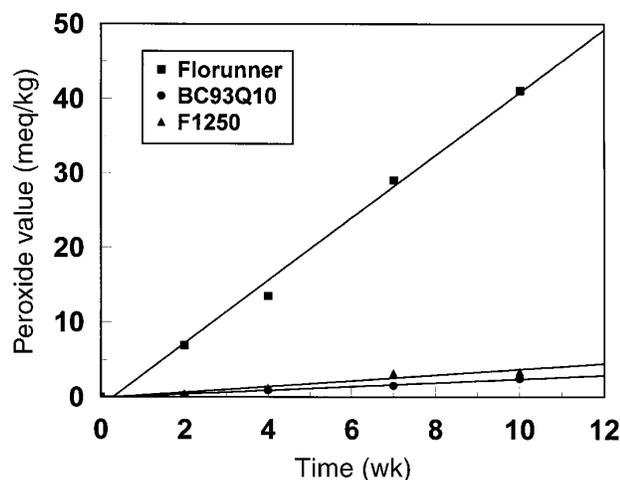


FIG. 1. Peroxide values of roasted normal-oleic (Florunner) and high-oleic peanuts (BC93Q10, F1250) during storage at 40°C and a_w 0.18.

Coating peanuts with chocolate or modifying the a_w of storage did not seem to affect the relative oxidation rates between NOP and HOP as measured by POV. In all studies published thus far, the HOP oxidation rates or levels seem to be an order of magnitude lower than for NOP (12–14,17,18).

The greater rate of oxidation of the NOP peanuts is attributable to the high level of polyunsaturated fatty acids (approximately 27% linoleic acid). Spanish peanuts were less stable to oxidation than Runner peanuts (19). Brown *et al.* (19) attributed their observations primarily to the greater linoleic acid content in Spanish peanuts. The linoleic acid content in 11 different breeding lines of HOP ranged from 2.5 to 5.1% (w/w in oil), and oleic acid ranged from 77.0 to 80.5% (17). Florunner, a widely grown NOP, has linoleic acid levels of about 27% and oleic acid of about 53% (Table 1).

Sensory evaluation of roasted peanuts. Dark roast and raw beany scores increased slightly but significantly during storage but were similar for all three varieties (Table 2). Sweetness decreased slightly during storage from a score of ~6 to ~5.2, and BC93Q10 was significantly higher than F1250 or Florunner. There was no significant effect of interaction during storage (Table 2). Crunchiness decreased slightly with storage time, from a mean score of 10.7 to 9.9, and Florunner was significantly lower than the HOP, but the differences were modest (< 0.6 units on the 15-point scale). The crunchiness of HOP and NOP in an earlier study decreased substantially with storage time, from ~10 (15-point scale) to ~6.5 by 10 wk of storage (13). However, the peanuts in that study were stored at a_w 0.40 and 25°C.

Roast peanutty sensory scores decreased with storage time for all peanut varieties (Table 2, Fig. 2A). The main variety effect was significant ($P < 0.05$), and HOP varieties were rated significantly higher in roast peanutty flavor than NOP (Table 2), but the HOP lines were not significantly different from one another.

The loss of roast peanutty flavor during storage is called flavor fade. The roast peanutty flavor intensities of the HOP



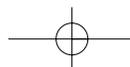


TABLE 2
Statistical Probability Values (*P* values) of Main Effects of Peanut Variety (Florunner, BC93Q10, F1250) and Time and Their Interaction^{a,b}

Attribute	Significance of effects		
	Variety	Time	Variety × time
Peroxide value	.0001	.0001	.0001
Roast peanutty flavor	.0001	.0001	.244
Painty flavor	.0001	.0001	.0001
Cardboardy flavor	.0021	.0001	.1075
Sweetness	.0019	.0001	.1813
Crunchiness	.0013	.0001	.4432
Dark roast	.0814	.0011	.6614
Raw beany	.4279	.0002	.4576

^aFor attributes of roasted peanuts stored at 40°C and *a_w* 0.18.

^bEffects are considered significant at *P* < .05.

were initially similar to NOP but were consistently higher for the HOP during storage, owing to lower slopes of the roast peanutty–time curves (Fig. 2A). The loss of roast peanutty flavor in HOP occurred at lower measured oxidation levels (POV) than for NOP (Fig. 2B). It has been suggested that flavor fade is a result of the masking of peanutty flavors (mainly pyrazines) by off-flavor compounds derived from lipid oxidation (20). If this were true, one would expect that plots of the roast peanutty flavor scores with POV (or oxidation volatiles)

would be similar for HOP and NOP. However, results from our laboratory and others (13,21) suggest that loss of roast peanutty flavor may be due to loss of pyrazines and not to masking of pyrazines by flavors from lipid oxidation products.

A decrease in pyrazines (compounds regarded as key compounds in roast peanutty flavor) during storage of roasted peanuts has been reported in some (13,21) but not all studies (20). Pyrazines were stable with time in a model system of peanut paste stored at 65°C. Headspace trapping was conducted at 145°C (20). Peanuts were stored whole at 37 (21) or 25°C (13) in studies where pyrazines were found to decrease during storage, raising the possibility that the differences are a result of the model systems used. In addition, quantitation of pyrazines was conducted by FID–GC in those studies that showed a loss in pyrazines with time (13,21) and by selective ion monitoring GC–mass spectroscopy in the study that reported a decrease (20).

The off-flavor attributes, cardboardy and painty, increased in intensity with storage time. There was no effect of variety or interaction on cardboardy flavor, but cardboardy flavor increased with time (*P* < .05) for all peanut varieties (Table 2, individual data not shown). For painty flavor scores, there was a significant effect of variety, time, and interaction (Fig. 3A, Table 2). NOP had a significantly higher rate of increase

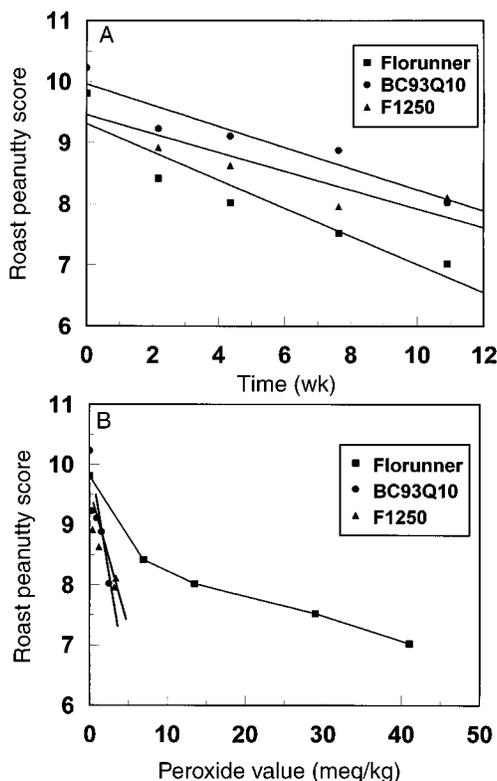


FIG. 2. (A) Peanutty sensory scores during storage of roasted normal-oleic (Florunner) and high-oleic peanuts (BC93Q10, F1250) at 40°C and *a_w* 0.18. (B) Relationship between peanutty sensory scores and peroxide values of roasted normal-oleic (Florunner) and high-oleic peanuts (BC93Q10, F1250) stored at 40°C and *a_w* 0.18.

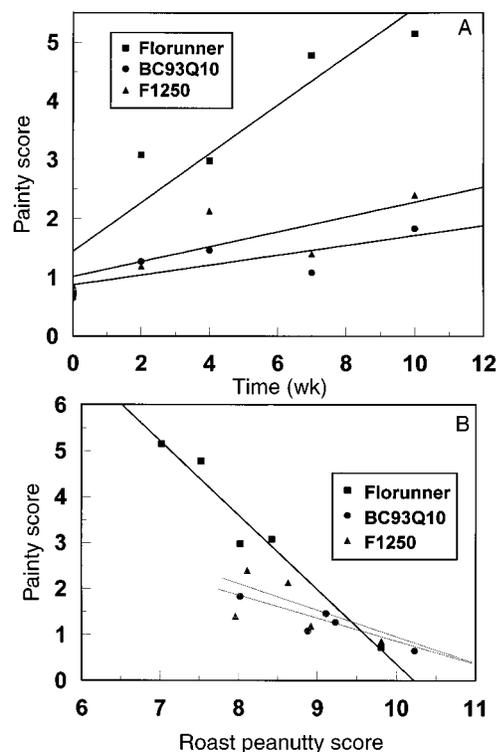
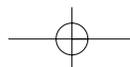


FIG. 3. (A) Painty sensory scores during storage of roasted normal-oleic (Florunner) and high oleic-peanuts (BC93Q10, F1250) at 40°C and *a_w* 0.18. (B) Relationship between roast peanutty sensory scores and painty sensory scores of roasted normal-oleic (Florunner) and high-oleic peanuts (BC93Q10, F1250) stored at 40°C and *a_w* 0.18.





in painty flavor scores than HOP. The slopes of the painty flavor—time plots were 0.41 for NOP and 0.126 and 0.084 for F1250 and BC93Q10, respectively. Thus, the increase in painty flavor scores was between 3.3 and 4.9 times greater for NOP than for HOP varieties. The relationships between painty sensory scores and peanutty roast scores are shown in Figure 3B. For a given loss in roast peanutty flavor, there was a greater increase in painty flavor in NOP than HOP. However, the painty scores for HOP never exceeded ~2.5. It is possible that the higher painty scores are a result of the 18:2n-6 content in NOP, resulting in greater production of hexanal in NOP (13).

There may be no differences in the sensory attributes of stored roasted HOP and NOP when POV are low (<9 meq/kg), even in the presence of POV differences between NOP and HOP (17). In this study, the POV of NOP reached 9 while for HOP they were <0.5, yet there were no differences in roast peanutty or painty sensory scores between HOP and NOP. The loss in peanutty sensory flavor was significant (from ~10 to ~6 on a 15-point scale), and painty sensory scores increased from ~0.5 to ~2.5 (15-point scale) in HOP, even though their POV were below 0.5 meq/kg. These data show that there can be significant flavor fade in peanuts in the absence of appreciable oxidation.

HOP initially had scores for roast peanutty flavors that were equivalent to NOP. Similar observations were made for four HOP lines (F1250, F1315, F1316, F1334) and Florunner (22). The two HOP lines (F1250 and BC93Q10) used in our study were not different in their flavor attributes or stability during storage. Both had better flavor quality and stability than NOP during storage at 40°C and a_w 0.18.

HOP have been shown to oxidize at rates about 10 times lower than NOP in a variety of model systems. HOP have lower rates of painty off-flavor development and lower losses of roasted peanutty flavors during storage.

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