

Vitamin Retention in Eight Fruits and Vegetables: A Comparison of Refrigerated and Frozen Storage

Ali Bouzari,[†] Dirk Holstege,[‡] and Diane M. Barrett^{*,†}

[†]Department of Food Science and Technology and [‡]Analytical Lab, University of California, Davis, California 95616, United States

ABSTRACT: Four vitamins were analyzed in several fruit and vegetable commodities to evaluate the differences between fresh and frozen produce. Ascorbic acid, riboflavin, α -tocopherol, and β -carotene were evaluated in corn, carrots, broccoli, spinach, peas, green beans, strawberries, and blueberries. Samples of each commodity were harvested, processed, and analyzed for nutrient content at three storage times per treatment. Ascorbic acid showed no significant difference for five of the eight commodities and was higher in frozen samples than fresh for the remaining three commodities. Apart from broccoli and peas, which were higher and lower in frozen vs fresh samples, respectively, none of the commodities showed significant differences with respect to riboflavin content. Three commodities had higher levels of α -tocopherol in the frozen samples, while the remaining commodities showed no significant difference between fresh and frozen. β -Carotene was not found in significant amounts in blueberries, strawberries, and corn. Peas, carrots, and spinach were lower in β -carotene in the frozen samples, while green beans and spinach showed no significant difference between the two storage methods. Overall, the vitamin content of the frozen commodities was comparable to and occasionally higher than that of their fresh counterparts. β -Carotene, however, was found to decrease drastically in some commodities.

KEYWORDS: vitamins, fruits, vegetables, refrigerated storage, frozen storage, nutrients, hplc

■ INTRODUCTION

Consumption of fruits and vegetables plays an important role in preventing disease and maintaining positive overall health.^{1–4} Ideally, these foods would be consumed immediately after harvest, however. Most fresh produce arrives to the consumer several days to weeks after it is harvested. During this time, cellular respiration and oxidation can cause substantial nutrient degradation.⁵ To halt spoilage and eliminate pathogens, food processing methods such as blanching and freezing have been developed.⁶ While some organoleptic degradation has been previously noted in these products, it has been found that the nutritive degradation suffered by foods during processing is less substantial than that which occurs over prolonged postharvest holding periods of fresh produce.^{6,7}

In this study we seek to evaluate the effects of freezing and frozen storage on the vitamin content of peas, green beans, broccoli, spinach, corn, carrots, strawberries, and blueberries. Most previous studies on this topic were carried out on produce purchased at market. This introduces a level of uncertainty with regard to the history of the samples, including soil and climate quality during the growing season, ripeness at harvest, handling, shipping, and storage. To minimize these sources of uncertainty, all commodities were harvested directly from their source, immediately processed, and used for both fresh and frozen storage studies.

Vitamins are typically categorized as either water- or fat-soluble. Water-soluble ascorbic acid and riboflavin and fat-soluble α -tocopherol and β -carotene were used to evaluate vitamin degradation.

Ascorbic acid is one of the most heat labile vitamins. Its relatively low stability makes it an ideal indicator of the effects of processing on degradation of nutrients. This is based on the idea that if a given process leaves ascorbic acid levels relatively

unchanged, it is likely that most other nutrients have survived the process as well.^{6,8,9} Degradation of ascorbic acid has been shown to vary dramatically among different commodities, and even various cultivars of the same commodity can exhibit different trends in ascorbic acid retention.^{6,8–10} In fresh produce, ascorbic acid begins to degrade quickly soon after the produce is harvested. Refrigeration helps to slow this degradation. Frozen storage is effective in preserving ascorbic acid, but the blanching process prior to freezing often causes significant degradation in addition to leaching into the blanch water.^{6,8,10} Steam blanching results in less leaching of water-soluble nutrients than water blanching.¹¹

Riboflavin can be degraded during thermal processing.¹² Riboflavin is light sensitive, and thus, food products must be stored carefully to avoid exposure.¹² Riboflavin levels in processed products that are blanched have been shown to decrease due to leaching into the blanch water.^{13–15} Riboflavin is readily degraded during ambient temperature storage of fresh produce, and research has shown that some minor degradation occurs at temperatures encountered during frozen storage as well.^{13,16}

Unlike the water-soluble vitamins, α -tocopherol is not prone to leaching during water-based processing steps such as blanching. It has been found in some studies that α -tocopherol content appears to increase to a certain extent during thermal processing, possibly due to increased extractability, before declining due to thermal degradation.^{6,17} Vitamin E is also susceptible to oxidative degradation,¹⁸ which can occur in both fresh and frozen storage.

Received: October 13, 2014

Accepted: December 19, 2014

Published: December 19, 2014

While fat-soluble vitamin A is not normally found in fruits and vegetables, it can be indirectly obtained through consumption of the carotenoid compound β -carotene. β -Carotene is a metabolic precursor to vitamin A, and in fact, many dietary descriptions of plant-based foods report a vitamin A correlation that is based on the concentration of β -carotene in the product. β -Carotene does not leach out of produce during washing and blanching but is very sensitive to degradation due to oxidation. This potential for oxidation is dependent on the various processing and storage conditions which include exposure to high temperatures, light, and oxygen.^{6,19} Retention of β -carotene in frozen storage seems to vary by commodity, with studies showing decreases to different degrees in β -carotene over a prolonged period of frozen storage.^{6,20} This is in contrast to fresh storage, where there is reported to be little degradation.¹³

MATERIALS AND METHODS

Raw Materials. Vegetable seeds were donated by the Seminole Vegetable Seed Co., Inc., Woodland, CA. Six replicate samples were harvested from different randomly selected points along linear rows for each commodity. Commodities were harvested according to the times and locations listed in Table 1.

Table 1. Harvest Times and Locations for Each Commodity Studied

commodity	month and year	harvest location
spinach	December 2012	Full Belly Farm (Guinda, CA)
carrots	November 2012	UC Davis (Davis, CA)
broccoli	February 2013	UC Davis (Davis, CA)
blueberries	March 2013	California Coastal Blueberry Farms (Oxnard, CA)
peas	April 2013	Iacopi Farm (Half Moon Bay, CA)
green beans	June 2013	UC Davis (Davis, CA)
strawberries	July 2013	Driscoll's (Watsonville, CA)
corn	August 2013	UC Davis (Davis, CA)

All commodities were harvested at uniform maturity as determined by both color and approximate size, as recommended by the grower. All commodities were transported to the UC Davis (University of California, Davis) Food Science and Technology pilot processing plant in refrigerated Styrofoam coolers (Lifoam Industries, Hunt Valley, MD) and processed immediately.

Processing. Throughout the processing and storage chains, each of the six field replicates was maintained as discrete samples. All commodities were given a preliminary rinse with water prior to entering the pilot plant to avoid unnecessary contamination of the facilities. Commodities were then submerged in a flume wash (Food Science and Technology Machine Shop, Davis, CA) filled with water and rinsed thoroughly to remove any surface dirt. Some commodities received additional processing steps prior to blanching: carrots were diced into 1.5 cm cubes using an Urschel G-A dicer (Urschel Laboratories, Inc., Valparaiso, IN), strawberries had their crowns removed by hand, green beans and peas were destemmed by hand, broccoli was cut into 3–5 cm florets by hand, and individual corn kernels were removed from the cob by hand using a Zyliss corn stripper (Zyliss, Irvine, CA).

For each field replicate of each commodity, cleaned, prepared samples were randomized and separated into two parts. Half of each field replicate was then marked for fresh storage, while the other was blanched and frozen. The samples to be blanched were loaded onto the steam blanching line (Food Science and Technology Machine Shop) in stainless steel baskets for the specified amount of time and temperature (Table 2). Following blanching, the samples were transferred onto wire mesh racks and placed immediately into a –32

Table 2. Blanching Protocols for Each Commodity

commodity	blanch time (min)	blanch temp (°C)	commodity	blanch time (min)	blanch temp (°C)
blueberries	N/A	N/A	corn	3.5	93.3
strawberries	N/A	N/A	green beans	3.5	93.3
broccoli	1.5	90.5	peas	2	93.3
carrots	2	96.1	spinach	3	93.3

°C walk-in freezer (Estes Refrigeration, Inc., Richmond, CA). After 1 h, the frozen commodity was divided into three 300 g storage samples which were packaged in UltraSource 3 mil polyethylene pouches (UltraSource LLC, Kansas City, MO) and stored at –27.5 °C (18 °F) for up to 90 days. Blueberries and strawberries were not blanched prior to freezing, in accordance with industry practices.

Stability Study. The fresh half of each field replicate was divided into three 300 g storage samples which were stored in breathable Tuf-R low-density polyethylene bags (U.S. Plastic Corp., Lima, OH) and stored at 2 °C (35.6 °F) in a walk-in refrigerator (Estes Refrigeration, Inc.) for up to 10 days. The frozen half of each field replicate was divided into three 300 g storage samples which were packaged in UltraSource 3 mil polyethylene pouches (UltraSource LLC) and stored at –27.5 °C (18 °F) for up to 90 days. For each field replicate, one frozen pouch and one fresh pouch were analyzed within 24 h of harvest (day 0) and after each storage time: 3 and 10 days for fresh; 10 and 90 days for frozen. Upon completion of each storage period, samples were removed from storage and transported in refrigerated coolers to the UC Davis Analytical Laboratory facilities for analysis.

Homogenization and Sample Preparation. Fresh or frozen samples were blended in a blender (Vita-Prep 3, Vitamix, Cleveland, OH) with the addition of 6 g of deionized water for every 10 g sample.

Riboflavin. Extraction. Homogenized sample (3.2 g, equivalent to 2 g of sample) was weighed into 50 mL plastic centrifuge tubes. To this was added 20 mL of 0.1 M HCl (Fisher Scientific Co., Pittsburgh, PA), and the tubes were capped, shaken for 5 min, and then incubated at 100 °C for 30 min. Once cool, 2.5 mL of 2.5 M sodium acetate (Fisher Scientific Co.) was added, to an approximate pH of 4.87, and then 100 mg of amyloglucosidase (Sigma-Aldrich, St. Louis, MO) was added to each sample. The samples were shaken and incubated at 37 °C for 15 h. After cooling, 2 mL of trichloroacetic acid (Fisher Scientific Co.) was added to each tube, and the samples were heated to 60 °C for 15 min. After cooling, the samples were diluted with deionized water to a final volume of 40 mL, shaken, and centrifuged for 10 min at 4000 rpm. From the supernatant, 10 mL aliquots were taken, 50 μ L of 10 ppm internal standard ($[^{13}\text{C}_4,^{15}\text{N}_2]$ riboflavin, Sigma-Aldrich) was added, and the tubes were vortexed. A 10 mL sample aliquot was loaded onto an Oasis HLB 3 mL³ (60 mg) extraction cartridge (Waters Corp., Milford, MA) which was prewashed with 1 column volume of methanol followed by 1 column volume of deionized water. The extraction column was washed with 2.5 mL of trichloroacetic acid and dried for 5 min under vacuum. The column was eluted with 1 mL of methanol (Fisher Scientific Co.) into glass test tubes. The extracts were filtered through 0.20 μ m IC Millex-LG (EMD Millipore Corp., Billerica, MA) filters into autosampler vials. A 15 μ L aliquot of sample was then injected onto the high-performance liquid chromatography (HPLC) column for liquid chromatography/mass spectrometry (LC/MS) determination.

Analysis. The samples were analyzed using HPLC in conjunction with MS. The apparatus consisted of a PerkinElmer LC-200 chromatograph (PerkinElmer, Waltham, MA) with a Sciex API 2000 mass spectrometer (AB SCIEX, Framingham, MA) in the positive ion ESI mode. The transition ions m/z 377 to m/z 243 (riboflavin) and m/z 283 to m/z 249 ($[^{13}\text{C}_4,^{15}\text{N}_2]$ riboflavin, internal standard) were used. An isocratic mobile phase of 90% methanol with 0.2% acetic acid (Fisher Scientific Co.) and 10% water with 0.2% acetic acid (v/v) at 0.4 mL/min was used on a Waters XTerra RP18 column, 3.5 μ m pore size, 4.6 \times 150 mm (Waters Corp.).

Ascorbic Acid. Extraction. Homogenized sample (6.4 g) was mixed with 13.6 mL of 2% oxalic acid (Fisher Scientific Co.) and

Table 3. Vitamin Content of Eight Commodities Stored under Either Refrigeration or Frozen Conditions for Three Storage Times^a

	storage time (days)	ascorbic acid content (mg/kg)	riboflavin content (mg/kg)	α -tocopherol content (mg/kg)	β -carotene content(mg/kg)
Peas					
fresh	0	3786 abc (240)	6.74 a (0.16)	10.95 b (1.73)	65.6 b (2.9)
fresh	3	3595 c (84)	6.73 a (0.37)	9.42 bc (1.18)	65.5 b (4.8)
fresh	10	4056 a (168)	6.91 a (0.52)	7.82 c (1.71)	55.1 c (10.9)
frozen	0	3716 bc (145)	6.57 a (0.34)	29.83 a (1.57)	89.2 a (4.5)
frozen	10	3737 bc (186)	6.61 a (0.48)	30.71 a (1.92)	89.2 a (2.2)
frozen	90	3998 ab (214)	5.19 b (0.32)	31.10 a (1.07)	28.2 d (1.4)
Spinach					
fresh	0	2969 bc (477)	24.38 a (0.80)	231.30 b (31.37)	1019.1 ab (55.8)
fresh	3	3568 ab (477)	22.98 ab (1.14)	246.85 b (14.99)	990.3 ab (136.5)
fresh	10	2956 bc (482)	22.05 abc (1.08)	246.00 b (14.75)	914.0 b (51.1)
frozen	0	2916 c (395)	20.05 c (1.29)	311.88 a (23.14)	1013.5 ab (50.7)
frozen	10	3864 a (394)	22.97 d (0.82)	304.52 a (11.47)	1113.8 b (76.7)
frozen	90	3475 abc (364)	21.53 bc (1.19)	329.30 a (12.41)	466.0 c (30.8)
Green Beans					
fresh	0	943 b (55)	6.23 a (1.02)	9.22 b (0.64)	17.7 b (1.7)
fresh	3	805 c (79)	6.09 a (0.26)	8.41 b (0.71)	17.6 b (0.7)
fresh	10	595 d (77)	6.66 a (0.55)	8.56 b (1.80)	21.3 a (1.5)
frozen	0	1056 ab (93)	6.63 a (0.41)	23.39 a (2.18)	22.9 a (0.7)
frozen	10	1085 a (115)	6.44 a (0.34)	23.56 a (1.62)	21.7 a (1.2)
frozen	90	1051 ab (102)	6.24 a (0.22)	24.79 a (2.59)	22.7 a (0.9)
Broccoli					
fresh	0	6202 b (424)	7.08 d (0.77)	139.32 c (7.63)	32.6 b (4.2)
fresh	3	6481 b (588)	7.97 cd (0.56)	141.11 c (12.24)	33.8 b (2.8)
fresh	10	7045 ab (556)	9.22 c (0.80)	174.32 b (19.60)	41.9 a (6.2)
frozen	0	7001 ab (394)	11.63 b (0.32)	208.42 a (10.28)	42.0 a (5.0)
frozen	10	6852 ab (345)	11.92 b (1.32)	176.7 b (20.62)	47.5 a (4.0)
frozen	90	7422 a (661)	14.0 8 a (0.83)	179.46 b (16.21)	45.1 a (3.9)
Carrots					
fresh	0	264 a (22)	1.74 a (0.21)	53.15 bc (4.18)	1382.8 a (229.3)
fresh	3	281 a (14)	1.84 a (0.27)	50.36 bc (4.20)	1244.8 ab (58.2)
fresh	10	227 a (22)	1.84 a (0.16)	53.00 bc (5.94)	1110.6 bc (59.4)
frozen	0	252 a (20)	1.93 a (0.22)	56.37 ab (5.70)	959.6 cd (131.7)
frozen	10	249 a (21)	1.64 a (0.31)	64.34 a (6.97)	813.8 d (94.3)
frozen	90	267 a (28)	1.45 a (0.17)	48.00 c (8.51)	398.7 e (68.8)
Corn					
fresh	0	707 a (21)	2.20 c (0.19)	6.71 a (0.73)	<1.0
fresh	3	587 b (30)	2.27 c (0.12)	4.22 bc (0.97)	<1.0
fresh	10	446 d (52)	2.82 b (0.21)	3.88 c (0.99)	<1.0
frozen	0	484 cd (49)	2.97 ab (0.26)	6.40 a (0.80)	<1.0
frozen	10	489 cd (35)	3.23 a (0.11)	5.90 a (0.71)	<1.0
frozen	90	537 bc (35)	3.09 ab (0.23)	5.40 ab (0.84)	<1.0
Blueberries					
fresh	0	489 bc (26)	2.42 b (0.12)	75.81 c (4.98)	<1.0
fresh	3	454 c (25)	2.43 b (0.12)	80.12 c (6.98)	<1.0
fresh	10	389 d (15)	2.71 ab (0.28)	93.19 b (6.73)	<1.0
frozen	0	505 b (32)	2.44 b (0.16)	84.63 bc (6.68)	<1.0
frozen	10	509 b (15)	2.74 ab (0.18)	93.14 b (6.24)	<1.0
frozen	90	567 a (16)	3.11 a (0.55)	104.86 a (3.87)	<1.0
Strawberries					
fresh	0	6193 ab (410)	2.08 a (0.13)	37.23 ab (2.17)	<1.0
fresh	3	5928 b (287)	1.77 ab (0.21)	37.74 a (1.90)	<1.0
fresh	10	6561 a (287)	1.89 ab (0.31)	34.20 ab (1.57)	<1.0
frozen	0	5840 b (476)	1.41 b (0.21)	37.42 ab (1.17)	<1.0
frozen	10	6199 ab (415)	1.82 ab (0.27)	34.94 ab (0.66)	<1.0
frozen	90	6383 ab (689)	1.47 b (0.36)	32.72 b (2.85)	<1.0

^aEach data point represents the mean of six field replicates and is followed by the standard deviation for those replicates in parentheses. Significantly different values between storage points for a given commodity and nutrient are followed by different online letters.

homogenized for 30 s. From this mixture, 10 mL was transferred to a 15 mL centrifuge tube and centrifuged at 10 000 rpm for 10 min at 4 °C. A 1.8 mL aliquot was taken, 400 μ L of 5% dithiothreitol (Sigma-Aldrich) was added, and the sample was filtered through a 0.2 μ m filter. The filtered sample was transferred to an autosampler vial for HPLC analysis.

Analysis. The samples were analyzed using HPLC with UV/vis diode array detection at 261 nm. The apparatus consisted of a PerkinElmer 200 quaternary HPLC system with a PerkinElmer 200 diode array detector (PerkinElmer). A Phenomenex Luna C-18 HPLC column (100 mm \times 4.6 mm, 100A) with a C-18 guard column (Phenomenex, Torrance, CA) was used. The mobile phase was 95% water and 5% methanol with 5 mM hexadecyltrimethylammonium bromide and 50 mM potassium dihydrogen phosphate (Sigma-Aldrich) at 1.2 mL/min.

α -Tocopherol and β -Carotene. Extraction. Homogenized sample (1.6 g) was weighed into a 50 mL glass centrifuge tube along with 5 mL of ethanol containing 6% (w/v) pyrogallol (Sigma-Aldrich), and the mixture was sonicated for 10 min. A 1 mL volume of 50% KOH (aqueous) (Fisher Scientific Co.) was added, the mixture was mixed by vortexing and heated at 70 °C for 10 min, and mixed and heated for an additional 10 min. The sample was cooled to room temperature, and 5 mL of 5% NaCl was added. The sample was extracted with 30 mL of extraction solvent (85:15 (v/v) hexane/ethyl acetate with 0.05% BHT, Sigma-Aldrich). A 7.5 mL aliquot was evaporated to dryness at 40 °C under nitrogen using a Zymark TurboVap LV. The extract was redissolved in 200 μ L of ethyl acetate followed by 1.8 mL of methanol, mixed, and filtered into an autosampler vial for HPLC analysis.

Analysis. The samples were analyzed using HPLC with UV/vis and fluorescence detection. The apparatus consisted of a PerkinElmer 200 quaternary HPLC system with a PerkinElmer 200 UV/vis detector (PerkinElmer) and a Shimadzu 10Axs fluorescence detector (Shimadzu Scientific Instruments, Columbia, MD). Excitation and emission wavelengths of 295 and 340 nm were used to detect α -tocopherol, and an absorbance wavelength of 450 nm was used to detect β -carotene. A Phenomenex Kinetex C-18 HPLC column (100 mm \times 4.6 mm, 100A) with a C-18 guard column (Phenomenex) and a mobile phase of 9:1 (v/v) acetonitrile/methanol (Fisher Scientific Co.) at 1 mL/min was used.

Statistical Analysis. Statistical analysis was performed using JMP statistical software version 9.0.0 (SAS Institute Inc., Cary, NJ). A blocked analysis of variance (ANOVA) was run with storage time point and processing treatment as the treatments. Tukey comparisons were used to determine the significance of differences between both fresh and frozen treatments and storage time points for each commodity and nutrient.

RESULTS AND DISCUSSION

The concentrations of four different compounds were evaluated in eight different commodities stored under either refrigeration (fresh) or frozen conditions over three time points (Table 3).

Ascorbic Acid. Ascorbic acid was degraded less in frozen-stored samples than in fresh-stored samples (Figure 1). None of the eight commodities showed losses during frozen storage. In strawberries, carrots, spinach, peas, and broccoli, the ascorbic acid content of fresh-stored products was not significantly different from that of frozen-stored products. In corn, green beans, and blueberries, significantly higher levels of ascorbic acid were found in frozen-stored samples when compared to fresh-stored samples, which could possibly be attributed to arrested enzymatic activity and slowed oxidative degradation of ascorbic acid in the frozen samples.⁶ Extensive degradation of ascorbic acid in fresh-stored produce has been previously reported in vegetables, as compared to their frozen counterparts.^{21–23}

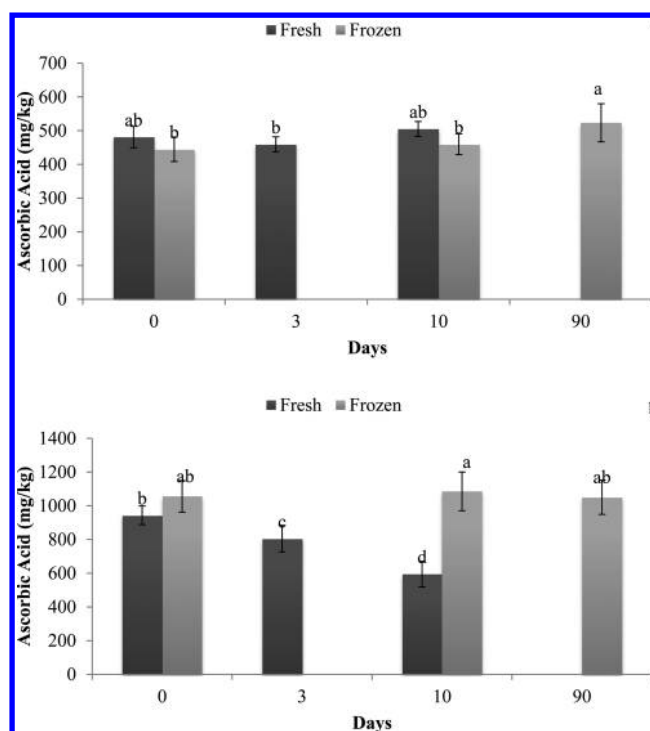


Figure 1. Ascorbic acid content of (a) strawberries and (b) green beans during fresh and frozen storage. Values reported on a dry weight basis. Values that share the same letter (a, b, c, d) are not significantly different ($p \leq 0.05$).

Riboflavin. Riboflavin was well conserved in most frozen samples. Carrots, corn, broccoli, blueberries, and green beans all followed the same trend, with fresh samples containing the same riboflavin content as frozen samples (Figure 2a). Of the eight commodities studied, only peas lost riboflavin during frozen storage (Figure 2b). The loss of riboflavin in peas is most likely due to oxidative degradation of the nutrient. Similar results were found by Gleim et al.,²⁴ who noted large decreases in riboflavin in asparagus and spinach.

Broccoli (Figure 2c) actually had higher riboflavin content in frozen-stored vs fresh-stored samples. This contrasts with the majority of the literature, such as Makhlof et al.,²⁵ who found that, while riboflavin content was higher in frozen vegetables than canned, it was not higher in frozen vegetables than fresh. Similarly, while Van Duyne et al.²⁶ found riboflavin to be well retained in frozen peas, beans, and spinach, it was not found to be present in any higher amounts in frozen produce as compared to fresh produce.

α -Tocopherol. Of all of the nutrients determined in this study, the α -tocopherol content in fruits and vegetables benefited the most from blanching, freezing, and frozen storage, as compared to fresh storage. When stored fresh, peas, carrots, and corn showed significant decreases in α -tocopherol content (Figure 3). Fresh green beans had much lower levels of α -tocopherol than frozen, but the levels of α -tocopherol did not decrease over the course of fresh storage. In the remaining commodities blueberries, broccoli, green beans, spinach, and strawberries, no significant difference between fresh- and frozen-stored samples was observed (Figure 3). Frozen peas and green beans exhibited more than 2-fold higher levels of α -tocopherol, while blueberries, spinach, and corn also had significantly higher levels (12–39%) in frozen-stored samples, as compared to fresh-stored samples (Figure 3).

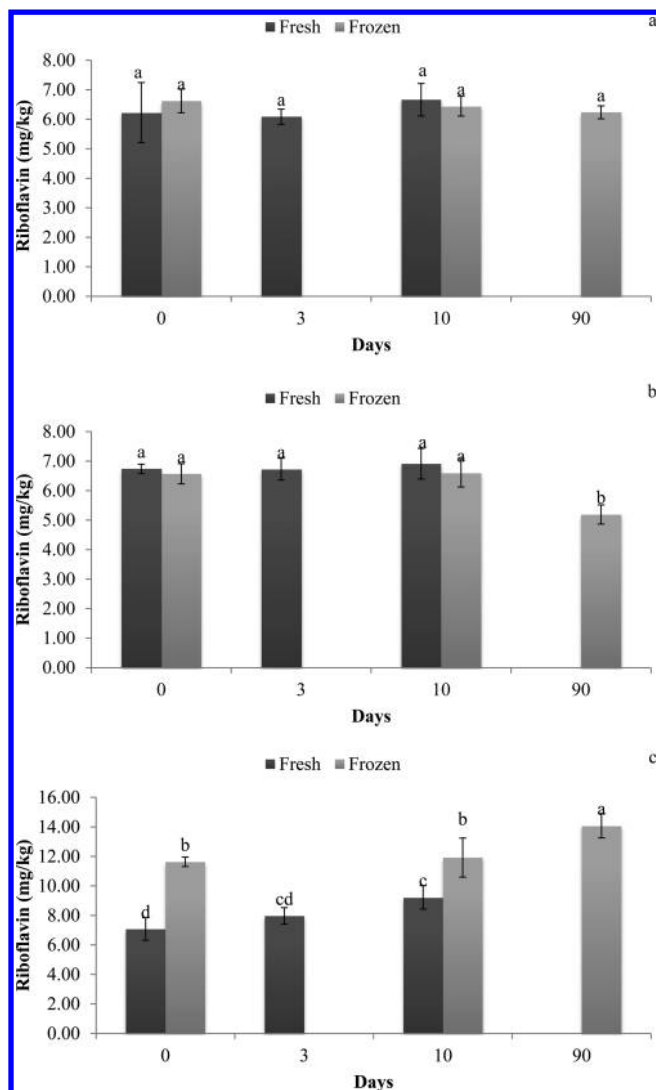


Figure 2. Riboflavin content of (a) green beans, (b) peas, and (c) broccoli during fresh and frozen storage. Values reported on a dry weight basis. Values that share the same letter (a, b, c, d) are not significantly different ($p \leq 0.05$).

The observed higher levels of α -tocopherol in some commodities, which is evident immediately after blanching and freezing on day 0, may be due to its increased availability after steam blanching.²⁶ α -Tocopherol levels in fresh broccoli were found to be more than 2-fold higher after heat treatments such as steaming or boiling by previous authors.²⁶ The heat treatment administered during blanching could have a similar effect on the commodities in this study. Previous authors have not studied the effects of freezing on peas in any detail, but lipid oxidation in peas caused by enzymatic or nonenzymatic pathways has been reported to consume α -tocopherol, a potent antioxidant.²⁷ Both of these oxidative pathways could have been responsible for preferentially lowering the levels of α -tocopherol in fresh samples. It is also unlikely that any leaching of fat-soluble α -tocopherol would occur during blanching in an aqueous environment.

β -Carotene. β -Carotene was not found in any significant amount in blueberries, strawberries, and corn, even in fresh samples (<1.0 mg/kg). Over the course of frozen storage, peas, spinach, and carrots showed losses of more than 50% of the initial β -carotene content (Figure 4). Over the course of fresh

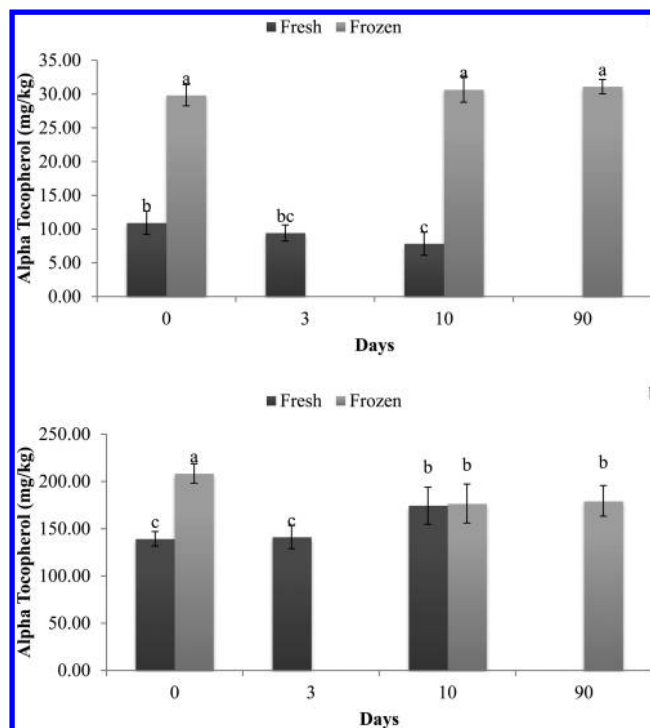


Figure 3. α -Tocopherol content of (a) peas and (b) broccoli during fresh and frozen storage. Values reported on a dry weight basis. Values that share the same letter (a, b, c) are not significantly different ($p \leq 0.05$).

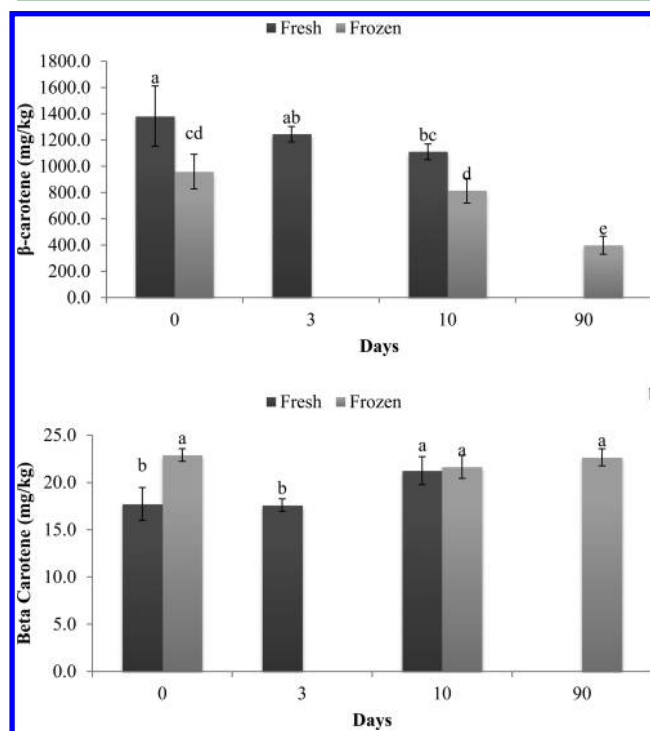


Figure 4. β -Carotene content of (a) carrots and (b) green beans during fresh and frozen storage. Values reported on a dry weight basis. Values that share the same letter (a, b, c, d, e) are not significantly different ($p \leq 0.05$).

storage, peas, green beans, and carrots lost at least 15% of the initial β -carotene content. Losses in β -carotene occurred both immediately after processing and over the course of frozen

storage. Losses during blanching are most likely not related to leaching because β -carotene is water insoluble,⁶ but may be attributed to oxidation of β -carotene.²⁰ In all of the commodities that showed decreased levels of β -carotene, the 90 day frozen samples were by far the lowest levels detected. These decreases were most likely due to oxidation during frozen storage, which was found to occur in previous studies by Desobry et al.,²⁹ but these findings are contrary to some other previous findings.^{20,26} One possible explanation for such a drastic decrease in β -carotene in carrots is that extensive cell damage and larger surface area after dicing encouraged oxidation of the tissue.²⁸ Green beans and broccoli showed no significant differences in β -carotene as a result of processing and storage (Figure 4).

Conclusions. For most nutrients in this study, frozen versions of a given commodity present viable substitutes for fresh in terms of nutritional value. While the results were highly dependent on commodity and nutrient, there were certain trends within the specific nutrients. In frozen samples of the commodities analyzed, riboflavin, α -tocopherol, and ascorbic acid were not only preserved in quantities equivalent to those of fresh samples, but in many cases were found in quantities much higher than those of the fresh samples. The most prevalent negative trend in the nutrient content of frozen fruits and vegetables is in β -carotene, which was drastically degraded over frozen storage in many of the commodities studied.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

REFERENCES

- (1) Cho, E. Y.; Seddon, J. M.; Rosner, B.; Willett, W. C.; Hankinson, S. E. Prospective study of intake of fruits, vegetables, vitamins, and carotenoids and risk of age-related maculopathy. *Arch. Ophthalmol.* **2004**, *122*, 883–892.
- (2) World Cancer Research Fund (WCRF) and American Institute for Cancer Research (AICR). *Food, Nutrition, Physical Activity, and the Prevention of Cancer: A Global Perspective*; AICR: Washington, DC, 2007.
- (3) Carter, P.; Gray, L. J.; Troughton, J.; Khunti, K.; Davies, M. J. Fruit and vegetable intake and incidence of type 2 diabetes mellitus: systematic review and meta-analysis. *Br. Med. J.* **2010**, *341*, c4229.
- (4) Appel, L. J.; Moore, T. J.; Obarzanek, E.; Vollmer, W. M.; Svetkey, L. P.; Sacks, F. M.; Bray, G. A.; Vogt, T. M.; Cutler, J. A.; Windhauser, M. M.; Lin, P. H.; Karanja, N. (DASH Collaborative Research Group). A clinical trial of the effects of dietary patterns on blood pressure. *N. Engl. J. Med.* **1997**, *336*, 1117–24.
- (5) Barrett, D. M. Maximizing the nutritional value of fruits & vegetables. *Food Technol.* **2007**, *61*, 40–44.
- (6) Rickman, J. C.; Bruhn, C. M.; Barrett, D. M. Nutritional comparison of fresh, frozen, and canned fruits and vegetables—II. Vitamin A and carotenoids, vitamin E, minerals and fiber. *J. Sci. Food Agric.* **2007**, *87*, 1185–1196.
- (7) Koh, E.; Wimalasiri, K. M. S.; Chassy, A. W.; Mitchell, A. E. Content of ascorbic acid, quercetin, kaempferol and total phenolics in commercial broccoli. *J. Food Compos. Anal.* **2009**, *22*, 637–643.
- (8) Favell, D. J. A comparison of the vitamin c content of fresh and frozen vegetables. *Food Chem.* **1998**, *62*, 59–64.
- (9) Hartmann, A.; Patz, C. D.; Andlauer, W.; Dietrich, H.; Ludwig, M. Influence of processing on quality parameters of strawberries. *J. Agric. Food Chem.* **2008**, *56*, 9484–9489.
- (10) Volden, J.; Bengtsson, G. B.; Wicklund, T. Glucosinolates, L-ascorbic acid, total phenols, anthocyanins, antioxidant capacities and colour in cauliflower (*Brassica oleracea* L. ssp. *botrytis*); effects of long-term freezer storage. *Food Chem.* **2009**, *112*, 967–976.

- (11) Turkmen, N.; Sari, F.; Velioglu, Y. S. The effect of cooking methods on total phenolics and antioxidant activity of selected green vegetables. *Food Chem.* **2005**, *93*, 713–718.

- (12) Melse-Boonstra, A.; Verhoef, P.; Konings, E. J. M.; van Dusseldorp, M.; Matser, A.; Hollman, P. C. H.; Meyboom, S.; Kok, F. J.; West, C. E. Influence of processing on total, monoglutamate and polyglutamate folate contents of leeks, cauliflower, and green beans. *J. Agric. Food Chem.* **2002**, *50*, 3473–3478.

- (13) Salunkhe, D. K.; Bolin, H. R.; Reddy, N. R. *Freezing, Storage, Processing, and Nutritional Quality of Fruits and Vegetables*; CRC Press: Boca Raton, FL, 1991; Vol. 2, pp 41–47.

- (14) Klein, B. P. Stability of nutrients in fresh and processed vegetables. Pillsbury product communication, 1997.

- (15) Davey, M. W.; Van Montagu, M.; Inze, D.; Sanmartin, M.; Kanellis, A.; Smirnoff, N.; Benzie, I. J. J.; Strain, J. J.; Favell, D.; Fletcher, J. Plant L-ascorbic acid: chemistry, function, metabolism, bioavailability and effects of processing. *J. Sci. Food Agric.* **2000**, *80*, 825–860.

- (16) Elkins, E. R. Nutrient content of raw and canned green beans, peaches, and sweet potatoes. *Food Technol.* **1979**, *33*, 66–70.

- (17) Chun, J.; Lee, J.; Ye, L.; Exler, J.; Eitenmiller, R. R. Tocopherol and tocotrienol contents of raw and processed fruits and vegetables in the United States diet. *J. Food Compos. Anal.* **2006**, *19*, 196–204.

- (18) Psomiadou, E.; Tsimidou, M. Stability of virgin olive oil. 2. Photo-oxidation studies. *J. Agric. Food Chem.* **2002**, *50*, 722–727.

- (19) Rupérez, F. J.; Martín, D.; Herrera, E.; Barbas, C. Chromatographic analysis of α -tocopherol and related compounds in various matrices. *J. Chromatogr., A* **2001**, *935*, 45–69.

- (20) Scott, C. E.; Eldridge, A. L. Comparison of carotenoid content in fresh, frozen and canned corn. *J. Food Compos. Anal.* **2005**, *18*, 551–559.

- (21) Howard, L. A.; Wong, A. D.; Perry, A. K.; Klein, B. P. β -Carotene and ascorbic acid retention in fresh and processed vegetables. *J. Food Sci.* **1999**, *64*, 929–936.

- (22) Jenkins, R. R.; Tressler, D. K.; Fitzgerald, G. A. Vitamin c content of vegetables VIII. Frozen peas 1. *J. Food Sci.* **1938**, *3*, 133–140.

- (23) Hunter, K. J.; Fletcher, J. M. The antioxidant activity and composition of fresh, frozen, jarred and canned vegetables. *Innovative Food Sci. Emerging Technol.* **2002**, *3*, 399–406.

- (24) Gleim, E. G.; Tressler, D. K.; Fenton, F. Ascorbic acid, thiamin, riboflavin, and carotene contents of asparagus and spinach in the fresh, stored, and frozen states, both before and after cooking. *J. Food Sci.* **1944**, *9*, 471–490.

- (25) Makhlof, J.; Zee, J.; Tremblay, N.; Belanger, A.; Michaud, M. H.; Gosselin, A. Some nutritional characteristics of beans, sweet corn, and peas (raw, canned, and frozen) produced in the province of Quebec. *Food Res. Int.* **1995**, *28*, 253–259.

- (26) Van Duyne, F. O.; Wolfe, J. C.; Owen, R. F. Retention of riboflavin in vegetables preserved by freezing. 1. *J. Food Sci.* **1950**, *15*, 53–61.

- (27) Bernhardt, S.; Schlich, E. Impact of different cooking methods on food quality: retention of lipophilic vitamins in fresh and frozen vegetables. *J. Food Eng.* **2006**, *77*, 327–333.

- (28) Dornenburg, H.; Davies, C. The relationship between lipid oxidation and antioxidant content in postharvest vegetables. *Food Rev. Int.* **1999**, *15*, 435–453.

- (29) Desobry, S. A.; Netto, F. M.; Labuza, T. P. Preservation of beta-carotene from carrots. *Crit. Rev. Food Sci. Nutr.* **1998**, *38*, 381–396.