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Changes in carotenoids during processing and storage of foods

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SUMMARY. Being highly unsaturated, carotenoids are susceptible to isomerization and oxidation during processing and storage of foods. Isomerization of *trans*-carotenoids to *cis*-carotenoids, promoted by contact with acids, heat treatment and exposure to light, diminishes the color and the vitamin A activity of carotenoids. The major cause of carotenoid loss, however, is enzymatic and non-enzymatic oxidation, which depends on the availability of oxygen and the carotenoid structure. It is stimulated by light, heat, some metals, enzymes and peroxides and is inhibited by antioxidants. Data on percentage losses of carotenoids during food processing and storage are somewhat conflicting, but carotenoid degradation is known to increase with the destruction of the food cellular structure, increase of surface area or porosity, length and severity of the processing conditions, storage time and temperature, transmission of light and permeability to O_2 of the packaging. Contrary to lipid oxidation, for which the mechanim is well established, the oxidation of carotenoids is not well understood. It involves initially epoxidation, formation of apocarotenoids and hydroxylation. Subsequent fragmentations presumably result in a series of compounds of low molecular masses. Completely losing its color and biological activities, the carotenoids give rise to volatile compounds which contribute to the aroma/flavor, desirable in tea and wine and undesirable in dehydrated carrot. Processing can also influence the bioavailability of carotenoids, a topic that is currently of great interest.

Key words: Carotenoids, processing, storage, isomerization, oxidation, degradation.

RESUMEN. Cambios en los carotenoides durante el procesamiento y almacenamiento de alimentos. Por ser altamente insaturados, los carotenoides son susceptibles a la isomerización y oxidación durante el procesamiento de los alimentos. La isomerización de *trans*- para *cis*-carotenoides, promovida por el contacto con ácidos, tratamiento con calor y exposición a la luz, disminuye el color y la actividad de vitamina A de los carotenoides. El principal causante de las pérdidas, sin embargo, es la oxidación por vías enzimáticas y no enzimáticas, la cual depende de la disponibilidad de oxigeno y la estructura del carotenoide. Esta es estimulada por la luz, el calor, ciertos metales, enzimas y peróxidos y es inhibida por anti-oxidantes. Si bien los datos sobre pérdidas porcentuales, durante el procesamiento y almacenamiento, son un tanto conflictivas, no hay duda de que la degradación aumenta con el grado de destrucción de las estructuras celulares, el incremento del área superficial o porosidad, tiempo y severidad de las condiciones del proceso, duración y temperatura del almacenamiento, transparencia a la luz y permeabilidad del embalaje al O_2. En contraste con la oxidación en lípidos, donde el mecanismo se encuentra bien definido, la oxidación de carotenoides no está elucidada. Esta comienza con epoxidación, formación de apocarotenoides e hidroxilación. Fragmentaciones subsecuentes presumiblemente llevan a una serie de compuestos de pequeña masa molecular. Después de perder su color y sus actividades biológicas, los carotenoides dan origen a compuestos que contribuyen al aroma/sabor, los cuales pueden ser deseables como en té y vino, pero indeseables en productos como zanahoria deshidratada. El procesamiento también puede influenciar la biodisponibilidad de los carotenoides, tema actualmente de gran interés.

Palabras clave: Carotenoides, procesamiento, almacenamiento, isomerización, oxidación, degradación.

INTRODUCTION

Processing and storage of foods have become integral parts of the modern-day food chain. Seasonal produce are processed during peak harvest, diminishing losses and making the products available all year round. Moreover, processing seasonal and perennial foods permits transportation of these foodstuffs to places far removed from the site of production.

Processing, however, can cause degradation of labile nutrients, biologically active compounds and substances important to food quality, such as colorants. Being highly unsaturated, carotenoids, for example, are prone to isomerization and oxidation, resulting in loss of color and biological activity. Thus, necessary measures will have to be taken to insure their retention during processing. Although industrial processing is more often focalized, losses on home preparation can also be, at times even more, considerable.

Literature on carotenoid retention during processing and storage of food is quite voluminous. However, published results are difficult to interpret because of the following reasons: (a) processing and storage conditions are not or are only partially described; (b) different foods are processed differently, making comparisons of processing methods difficult; (c) different conditions (e.g. time and temperature)

are used for the same method of processing; (d) the procedure followed for calculating losses is not specified; and (e) no correction is made for weight changes during processing and the usually greater efficiency with which carotenoids are extracted from processed (except for dehydrated products) compared to raw samples during analysis (1). Additionally, in most papers total carotenoid or carotene content was measured. In the present article, emphasis will be given to work involving determination of individual carotenoids. An inherent problem that cannot be overlooked is the possibility of isomerization and oxidation of carotenoids taking place during analysis and/or during storage of samples prior to analysis, these reactions being erroneously attributed to the processing or storage of food. Nevertheless, some conclusions can be drawn (1):

1. The tropical climate of many poor areas of the world enhances biosynthesis of carotenoids, increasing their concentrations during ripening/maturing of fruits and vegetables. On the other hand, this same ambient condition may hasten destruction of carotenoids during post-harvest handling and storage.
2. Carotenoid biosynthesis may continue in fruits, fruit vegetables and root crops, even after harvest, provided these plant materials are kept intact and not treated in any way that would inactivate the enzymes responsible for carotenogenesis. In leaves and other vegetables, post-harvest degradation of carotenoids appears to prevail, especially at high storage temperature and under conditions that favor wilting.
3. Carotenoids are naturally protected in plant tissues; cutting of fruits and vegetables into small pieces or maceration increases exposure to oxygen and brings together carotenoids and enzymes, which catalyze carotenoid oxidation.
4. The stability of carotenoids differs in different foods, even when the same processing and storage conditions are used. Carotenoids per se have different susceptibilities to degradation. Thus, optimum conditions for carotenoid retention during preparation/processing differ from one food to another.
5. The major cause of carotenoid destruction during processing and storage of foods is enzymatic or non-enzymatic oxidation. Isomerization of *trans*-carotenoids to the *cis*-isomers, particularly during heat treatment, also lessens the color and the vitamin A value of foods, but not to the same extent as oxidation. Enzymatic degradation of carotenoids may be a more serious problem than thermal decompositon in many foods.
6. Reported increases in carotenoid content during cooking or thermal processing are not likely to be true increases but are artifacts of the analytical procedure, due to loss of carotenoids in fresh samples because of enzymatic activity, greater extractability of carotenoids from processed samples, and unaccounted loss of water and leaching of soluble solids.
7. In home preparation, losses of carotenoids generally increase in the following order: microwaving < steaming < boiling < sautéing. Deep-frying, prolonged cooking, combination of several preparation and cooking methods, baking and pickling all result in substantial losses of carotenoids.
8. Whatever the processing method chosen, retention of carotenoid decreases with longer processing time, higher processing temperature and cutting or puréeing of the food. Reducing processing time and temperature, and the time lag between peeling, cutting or puréeing and processing improve retention significantly. High temperature, short-time processing is a good alternative.
9. The heat treatment in blanching may provoke some losses of carotenoids, but the inactivation of oxidative enzymes will prevent further and greater losses during holding before thermal processing, slow processing and storage.
10. Freezing (especially quick-freezing) and frozen storage generally preserve the carotenoids.
11. Peeling and juicing result in substantial losses of carotenoids, often surpassing those of heat treatment.
12. Traditional sun-drying, although the cheapest and most accessible means of food preservation in poor regions, causes considerable carotenoid destruction. Drying in a solar dryer, even of simple and inexpensive design, can appreciably reduce losses. Protecting the food from direct sunlight also has a positive effect.
13. Natural or added antioxidant and sulfiting may reduce carotenoid degradation.
14. Exclusion of oxygen (e.g. through vacuum or hot filling, oxygen-impermeable packaging, inert atmosphere), protection from light and low temperature diminish carotenoid decompositon during storage.

Alteration or losses of carotenoids during processing and storage therefore occur through physical removal, geometrical isomerization and enzymatic or non-enzymatic oxidation.

Freezing and frozen storage

Recent years have seen commercialization throughout Brazil of frozen fruit pulps, from tropical fruits hitherto available only in the producing Northeastern states. Used for the preparation of juices, these frozen pulps are generally processed by small industries. In frozen (-18°C) *Eugenia uniflora* pulp, ß-cryptoxanthin, γ-carotene and lycopene were considerably reduced (Table 1) (2). The product was not subjected to thermal treatment, the losses being apparently due to the removal of the peel during pulping. The carotenoids affected were those commonly concentrated in the peel. Carotenoids are found at higher levels in the peel than in the pulp of most carotenogenic fruits (3,4).

TABLE 1
Carotenoid composition (μg/g)* of fresh fruit and frozen *Eugenia uniflora* pulp

Carotenoid	Fresh fruit	Frozen pulp
Phytofluene	12a	11a
ß-Carotene	8a	7a
ζ-Carotene	4a	3a
ß-Cryptoxanthin	45a	12b
γ-Carotene	50a	15b
Lycopene	72a	26b
Rubixanthin	22a	22a
Total	215a	99b

*Means and standard deviations of 6 determinations. Values in the same row bearing different letters are significantly different ($p \leq 0.05$).
Reference: Cavalcante and Rodriguez-Amaya (2).

Further substantial reduction of the carotenoids of *E. uniflora* occurred during the first two months of storage at -15°C, stabilizing thereafter. Since the pulp was unblanched, enzymatic oxidation was the probable cause of these losses. The extent of loss was much greater than that usually seen in thermally processed products. Moreover, carotenoid decomposition in the latter products is usually insignificant during the first several months, increasing rapidly when it ensues.

The ß-carotene and lutein contents of unblanched and blanched (100°C, 4 min) chopped green beans and intact Padrón pepper, all frozen at -22°C, were monitored over 12 months (5). Both pigments decreased considerably during the first month in green beans packed in manually sealed and vacuum-sealed polyethylene bags. Lutein stabilized during the next 11 months; ß-carotene decreased further in the second month but stabilized thereafter. The smaller overall decrease of ß-carotene in blanched beans was attributed to deactivation of lipoxygenase. Reduction of lutein was roughly the same for blanched and unblanched beans. In contrast, the ß-carotene and lutein levels in the frozen pepper fluctuated around more or less constant values over the 12 months. Wu et al. (6) found no change in the ß-carotene content of green beans and broccoli during U.S. retail market simulation and frozen storage (blanched) at -20°C for 16 weeks.

Papaya slices without previous treatment were vacuum-packed in plastic bags and frozen in air-blast freezer operating at -40°C. The bags were left in the freezer until the center of the slices reached -24°C and then stored at -18°C for 12 months (7). The carotenoid content decreased significantly, the reduction being markedly higher in the female papaya slices than the hermaphrodite papaya slices (Table 2). The difference was attributed to greater enzymatic activity in the female papaya slices.

The influence of packaging materials with high, medium and low oxygen transmission rates on astaxanthin retention in rainbow trout fillets, containing three different levels of astaxanthin, during dark or illuminated frozen storage (-18°C) was studied (8). Samples were analyzed after 17, 29 and 36 weeks of frozen storage. Packaging material had significant effect on astaxanthin retention in the fillets while light or initial astaxanthin level did not have a significant influence.

TABLE 2
Carotenoid composition (μg/g)* of fresh and frozen papaya slices (stored for 12 months at -18°C) cultivar Sunrise

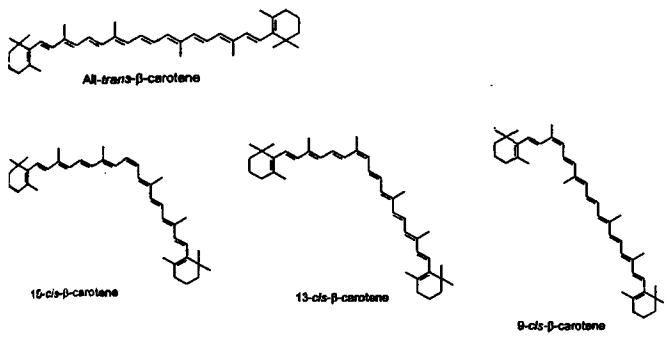
Carotenoid	Female/Hermaphrodite	
	Fresh	Frozen
Zeaxanthin	0.47/0.44	0.22/0.35
Cryptoflavin	0.42/0.16	-/0.10
ß-Cryptoxanthin	6.1/4.4	1.8/3.0
Lutein ester	0.70/0.32	0.25/0.33
Lycopene	19/20**	4.8/13
Neolycopene A	1.4/-	1.8/3.9
ß-Carotene-5,6-epoxide ester + ß-carotene	1.7/1.2	0.64/1.0
9-*Cis* or 9'-*cis*-cryptoxanthin ester	1.2/1.2	0.57/1.0
ß-Cryptoxanthin-5,6-epoxide ester	2.0/1.3	0.69/1.1
ß-Cryptoxanthin ester	3.9/2.4	1.8/2.6
ß-Cryptoxanthin ester	0.74/0.40	0.51/0.43
ß-Cryptoxanthin ester	- / -	0.19/0.13
Total	38/31	13/26

*Means of two determinations. Concentrations are reported as ß-carotene equivalents, except for zeaxanthin, ß-cryptoxanthin, lycopene and neolycopene A.
**Included neolycopene A
Reference: Cano et al. (7).

Thermal processing and storage

Occurrence of *trans* to *cis*-isomerization as a consequence of thermal processing has been shown by several authors. The major *cis* isomers of ß-carotene detected are shown in Figure 1. In a recent work, in which a polymeric C_{30} column was used for the separation of the isomers, a 10-39% increase in the percentage of total *cis*-isomers of provitamin A carotenoids in several fruits and vegetables was observed (Table 3) (9). Canning of sweet potato caused the largest increase, followed by processing of carrot, tomato juice, collard, tomato, spinach, peach and orange juice. The principal *cis*-isomers in processed red, yellow and orange fruits and vegetables were 13 *cis*-(and 13'-*cis*-), although 9-*cis*- and 15-*cis*-isomers were also detected. In processed green vegetables (in which ß-carotene was the only provitamin A carotenoid detected), 9-*cis*-ß-carotene predominated, followed by 13-*cis*-ß-carotene, an unidentified *cis*-isomer and 15-*cis*-ß-carotene.

FIGURE 1
Common geometrical isomers of ß-carotene



The isomerization pattern reported by Lessin et al. was also observed in earlier studies, the 13-*cis*- being the major *cis*-isomer in processed fruits and vegetables, except in processed green vegetables in which the 9-*cis*- prevailed (10-12).

In sweet potatoes, heat induced formation of 13-*cis*-ß-carotene in the different thermal treatments investigated, the quantity formed being related to the severity and length of processing (Table 4) (12). Only canned sweet potato contained appreciable amount of the 9-*cis*-isomer. Carotene content was reduced 20% on canning, 21% on dehydration, 23% on microwaving and 31% on baking. Apparent increases on blanching (4-12%) and puréeing (10%) were attributed to an enhanced extraction efficiency of heat-treated samples.

TABLE 3
Quantitative distribution of provitamin A carotenoid isomers (µg/g dry wt)* in fresh and processed fruits and vegetables

Product	ß-Carotene					α-Carotene					ß-Cryptoxanthin		
	all-*trans*	9-*cis*	13-*cis*	15-*cis*	other *cis*	all-*trans*	9-*cis*	13-*cis*	13'-*cis*	other *cis*	all-*trans*	13/13'-*cis*	15-*cis*
Carrot													
fresh	534					373							
canned	420	33	90	30		291	6.1	91	56	37			
Collard													
fresh	206	33	16	8.5	11								
canned	230	128	19	9.2	24								
Orange juice													
fresh	2.2	tr	0.4	tr		1.9	tr	0.2	0.1		2.5	0.2	tr
pasteurized	1.5	tr	0.3	tr		1.3	tr	0.1	0.1		1.3	0.2	tr
Peach													
fresh	2.2	0.3	0.5	tr							0.3	0.1	0.1
canned	0.9	0.2	0.4	tr							0.2	0.1	tr
Spinach													
fresh	312	39	24	tr	22								
canned	310	97	29	15	23								
Sweet potato													
fresh	256												
canned	191	25	77	19									
Tomato													
fresh	71	4.8	5.8										
canned	49	5.5	12	4.8									
juice	40	4.5	10	4.8									

*Means of two lots, except for orange juice, which had only one lot. Tr- trace.
Reference: Lessin et al. (9).

Cis-isomers also increased during heating of carrot juice (Table 5) (13), 13-*cis*-ß-carotene being formed in largest amount, followed by 13-*cis*-lutein and 15-*cis*-α-carotene. Canning (121°C, 30 min) resulted in the greatest loss of carotenoids, followed by high-temperature short-time heating at 120°C for 30 sec, 110°C for 30 sec, acidification plus 105°C heating for 25 sec and acidification. The carrot juice color turned from orange to yellow with intensive treatment.

Carrot juice was acidified, pasteurized and then subjected to lighted and dark storage at 4, 25 and 35°C for three months (14). Reduction of lutein, α-carotene and ß-carotene concentrations increased with increasing storage temperature and was also greater under illumination than under dark storage. The formation of 13-*cis*-isomers appeared to be favored under lighted storage and the 9-*cis*-isomers in the dark.

TABLE 4

Cis-trans ß-carotene isomer concentrations (µg/g dry wt)* in raw and processed sweet potatoes

Treatment	13-*Cis*-	All-*Trans*	9-*Cis*
Raw product	22	418	-
Strips (2-min blanch 100°C)	39	460	-
Strips (10-min blanch 100°C)	70	388	-
Puree (lye peeled, Fitzmill comminutor with 0.06" screen)	25	461	-
Steam injection (81°C to gelatinize starch, hold 30 min)	34	461	-
Steam injection (100°C to inactivate amylases)	37	419	
Canned (still retort, 90 min at 116°C)	57	323	11
Dehydrated (drum dried at 160°C at 25 rpm with contact time of 1.8-2 sec)	101	249	tr
Microwaved (full power for 7 min until internal temp. of 99°C)	56	284	tr
Baked (conventional oven at 191°C 80 min until internal temp. of 99°C)	69	232	tr

*Means of two replicate samples for each treatment. Tr - trace
Reference: Chandler and Schwartz (12).

TABLE 5

Cis-trans isomer concentration (µg/ml) changes of α-carotene, ß-carotene and lutein of carrot juice under various processing treatments

Carotenoid	Control	Acidified	I	II	III	IV
α-Carotene						
all-*trans*-	28a	26a	25a	15b	13c	11d
9-*cis*-	0.2a	0.2a	0.2a	0.4b	0.5c	0.5c
13-*cis*-	0.2a	0.3a	0.2a	0.6d	0.7e	0.5c
15-*cis*-	0.0a	0.0a	0.0a	1.5b	2.1d	1.3c
ß-Carotene						
all-*trans*-	62a	61a	60a	34b	33b	28c
9-*cis*-	1.1a	1.1a	1.2b	2.5c	3.1d	4.8e
13-*cis*-	3.4a	3.5a	4.5b	8.0c	11d	7.7c
15-*cis*-	1.1a	1.2a	1.5b	2.6c	3.3e	3.0d
13,15-di-*cis*-	1.3a	1.4a,b	1.4b	1.7c	1.9d	2.8e
Lutein						
all-*trans*-	6.0a	5.2b	4.6c	4.2c	3.2d	3.0e
9-*cis*-	0.4a	0.4a	0.5b	0.4a	0.6c	0.6c
13-*cis*-	0.6a	0.7a	0.8b	0.9c	1.5d	1.5d

Values in the same row bearing different letters are significantly different ($p < 0.05$). Carrot juice acidified to pH 4.0, heated at 105°C for 30 sec (I), juice (pH 6.1) heated at 110°C for 30 sec (II), juice (pH 6.1) heated at 120°C for 30 sec (III), juice (pH 6.1) heated at 121°C for 30 min (IV) for canning.
Reference: Chen et. al. (13).

Pesek and Warthesen (15) studied carotenoid photodegradation in vegetable juice containing mainly tomato and carrot juice, which had been exposed to 230 ft-c of light at 4°C. After four days of light exposure, only 25 percent of the initial α- and ß-carotene remained, while 75 percent of lycopene was still present. Structural differences were considered responsible for the difference in the degradation rates. Carotene loss was extensive after eight days. The control samples (held in darkness) showed no or negligible destruction of carotenoids.

To minimize hydrolytic rancidity in the oil, red palm fruits are sterilized immediately after harvest to inactivate lipases. Though necessary, this treatment (128°C, 66 min) provokes substantial isomerization, as shown in Table 6 for oils from *Elais guineensis* and *E. oleifera* fruits (16).

TABLE 6

Carotenoid composition (µg/g) of palm fruit oils

	From fresh fruits/From sterilized fruits			
Carotenoid	*E. guineensis* Dura Dumpy	*E. guineensis* Psífera	*E. guineensis* Tenera	*E. oleifera*
Cis-phytofluene	28/-	15/-	8.9/-	25/-
13-*Cis*-α-carotene	4.8/87	0.5/5.5	4.5/64	-/144
All-*trans*-α-carotene	296/228	18/14	164/94	425/342
13-*Cis*-ß-carotene	12/200	8.2/63	13/129	61/352
All-*trans*-ß-carotene	576/255	202/88	363/229	1026/400
9-*Cis*-ß-carotene	12/179	1.2/55	1.7/53	-/241
ζ-carotene	13/21	1.1/3.3	10/5.0	-/-
Zeaxanthin	tr/tr	6.0/tr	tr/tr	tr/tr
ß-Cryptoxanthin	tr/tr	tr/tr	tr/tr	31/14
Poly-*cis*-lycopene	41/4.7	8.8/1.2	22/-	-/-
Mono-*cis*-lycopene	7.4/38	3.5/4.8	3.1/7.1	-/tr
All-*trans*-lycopene	17/22	0.7/4.5	7.3/9.3	tr/tr
Unidentified	113/125	17/16	63/40	8.4/14
Total	1121/1160	283/255	660/631	1577/1506

All fruits were collected from the same experimental station. For each type of fruit, the oil sample was prepared from three bunches of fruits, part of which was sterilized before oil extraction.
Reference: Trujillo-Quijano et. al. (16).

The traditional method of palm oil production retained more ß-carotene (80 percent) than a mechanized process (23 percent) (17). The explanation was that the palm fruits processed in the traditional manner were not exposed to very high temperatures. When palm oil was heated to 160 to 200°C, the destruction rate of ß-carotene doubled for every 20°C rise in temperature.

Since pigment destruction was evident in commercial juices (18), pasteurization of guava juice was simulated in a pilot plant, the immersion of the bottled juice in boiling water being purposely extended to 30 min, double the usual pasteurization time needed for this type of product (19). Thermal treatment also involved blanching of the fruits for 5 min and heating of the juice up to a temperature of 87°C in a steam-jacketed kettle before hot filling. Pigment alteration was much less drastic than that noted in commercial juices at that time. *Cis*-lycopene increased five-fold on processing, but reduction of *trans*-lycopene was slight and statistically insignificant (Table 7). Both isomers decreased on storage (Table 8). The small amount of ß-carotene was retained during processing and storage.

Aside from geometrical isomerization, epoxidation and transformation of the 5,6-epoxide group to the 5,8-furanoid oxide are common alterations of carotenoids during heat treatment (Figure 2).

FIGURE 2
Formation of epoxy carotenoids from ß-carotene and transformation of violaxanthin during processing and storage of foods

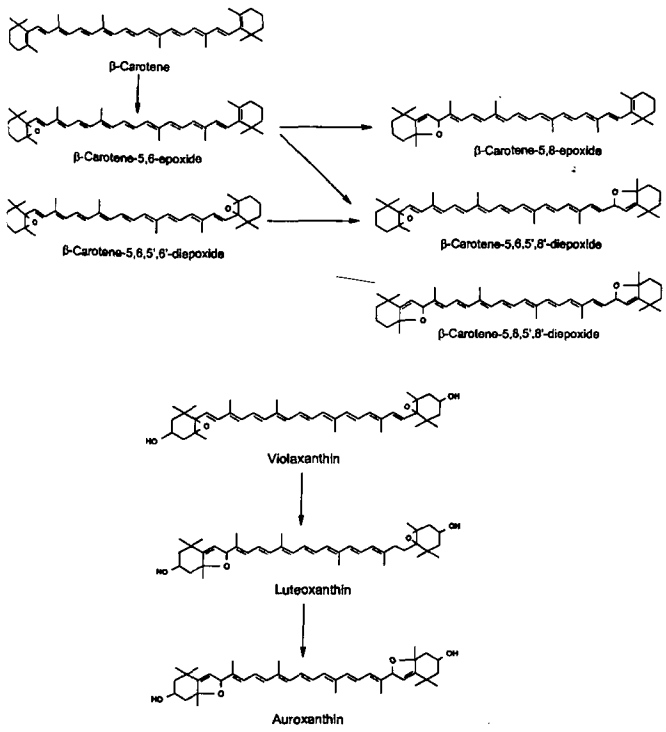


TABLE 7
Effect of processing on the carotenoids (µg/g)* of guava cultivar IAC-4 juice

Carotenoid	Fresh juice	Processed juice
ß-Carotene	2.7a	2.7a
ζ-carotene	tra	0.2b
γ-carotene	tra	0.1a
Zeinoxanthin	0.8a	0.8a
Cis-lycopene	1.2a	7.8b
Lycopene	31a	27a
Trihydroxy-ß-carotene-5,8-epoxide	2.9a	0.3b
ß-carotene-5,6,5',6'-diepoxide	tra	tra
Total	39a	39a

*Means of two determinations. Values in the same row bearing different letters are significantly different ($p < 0.05$). Tr-trace.
Reference: Padula and Rodriguez-Amaya (19).

TABLE 8
Carotenoid (µg/g)* changes during ambient storage of processed guava cultivar IAC-4 juice

Carotenoid	Storage time (month)				
	0	1	4	7	10
ß-Carotene	2.7a	2.4a	2.5a	2.5a	2.5a
ζ-Carotene	0.2a	0.2a	0.3a	0.2a	0.3a
γ-Carotene	0.1ab	nda	0.3b	0.3b	0.2ab
Zeinoxanthin	0.8a	1.0a	0.6a	1.3a	1.2a
Cis-lycopene	7.8a	7.9a	6.6a	3.5b	2.9b
Lycopene	27a	25ab	23ab	22ab	20b
Trihydroxy-ß-carotene-5,8-epoxide	0.3a	2.9c	0.6a	1.8b	1.6b
ß-carotene-5,6,5',6'-diepoxide	tra	nda	0.2a	0.1a	nda
Zeinoxanthin-5,8-epoxide	nda	nda	tra	tra	tra
Total	39ab	40a	34abc	32bc	29c

*Means of two determinations. Values in the same row bearing different letters are significantly different. Tr - trace, nd - not detected.
Reference: Padula and Rodriguez-Amaya (19).

The carotenoid composition was practically maintained on processing mango (cultivar Tommy Atkins) slices (Table 9) (20). Thermal treatment consisted of immersion of the sealed cans in boiling water for 20 min. The only significant change was the increase in luteoxanthin, compatible with the conversion of 5,6- to 5,8-epoxide. More evident changes occurred on processing mango (cultivar Golden) purée, which involved heating of the purée in an open, steam-jacketed kettle to 80°C for 10 min and immersion of the hot-filled and sealed cans or bottles in boiling water for 10 min. ß-carotene decreased 13%. Auroxanthin, not found in the fresh fruit, appeared while violaxanthin and luteoxanthin decreased, again reflecting the transformation of 5,6- to 5,8-epoxide. During storage of mango slices in lacquered (epoxy) or plain tin-plate cans, no appreciable loss of ß-carotene was observed during 10 months (Table 9) at ambient conditions. Between the tenth and

fourteenth month, about 50% reduction of ß-carotene occurred. The degradation continued, resulting in a total loss of 84% after 24 months. Violaxanthin tended to decrease and auroxanthin to increase during storage. ß-Carotene showed a greater tendency to degrade in bottled mango purée (18% loss after 10 months) than in the canned purée. As in mango slices, however, both bottled and canned purée suffered 50% loss of ß-carotene after the tenth month, and total loss of 83% after 24 months. Violaxanthin and luteoxanthin tended to decrease while auroxanthin maintained a comparatively high level throughout storage.

TABLE 9
Changes in ß-carotene (µg/g)* on storage of mango (cultivar Tommy Atkins) slices and mango (cultivar Golden) purée

Product/Packaging	Storage time (month)						
	0	1	3	7	10	14	24
Mango slices							
- in lacquered epoxy cans	14a	14a	14a	13a	14a	7.6b	2.3c
- in plain tin-plate cans	14a	12a	12a	12a	12a	6.7b	2.3c
Mango purée							
- in lacquered epoxy cans	16ab	15b	16a	15b	15b	8.0c	2.8d
- bottled	16a	15ab	15ab	12c	13bc	7.5d	2.6e

*Means of two determinations. Values in the same row bearing different letters are significantly different ($p \leq 0.05$).
Reference: Godoy and Rodriguez-Amaya (21).

In a recent paper (21), violaxanthin was found to be actually the major carotenoid of two mango cultivars. Notoriously unstable, violaxanthin can be easily lost during analysis, probably leading researchers to underestimate its concentration in earlier papers. In commercially processed mango juice (three brands), violaxanthin was not detected while auroxanthin was found in appreciable amount and ß-carotene became the principal carotenoid.

In papaya (cultivar Solo) purée, processed in the same manner as the mango purée, no significant loss of ß-carotene, ζ-carotene and γ-carotene occurred during processing (Table 9) (22). There was a small significant decrease in ß-cryptoxanthin. *Cis*-lycopene increased seven-fold, but the slight decrease in *trans*-lycopene was statistically insignificant. Cryptoflavin, an epoxy derivative of cryptoxanthin, appeared on processing. During 14 months of ambient storage, ß-carotene, *trans*-lycopene, and *cis*-lycopene did not change significantly, although the first two carotenoids showed a slight downward trend (Table 10). ß-cryptoxanthin did not change significantly during the first 10 months, but showed a small significant decrease after the fourteenth month of storage. Auroxanthin and flavoxanthin were formed during storage.

TABLE 10
Effect of processing on the carotenoid composition (µg/g)* of papaya (cultivar Solo) purée

Carotenoid	Fresh	Processed
ß-Carotene	2.6a	2.3a
ζ-Carotene	1.5a	1.3a
γ-Carotene	0.2a	0.2a
ß-Cryptoxanthin	7.4a	5.5b
Trans-lycopene	28a	23a
Cis-lycopene	0.2a	1.5b
Cryptoflavin	nd	0.2
Total	40a	34a

*Means of two determinations. Values in the same row bearing different letters are statistically different ($p < 0.05$). Nd - not detected.
Reference: Godoy and Rodriguez-Amaya (22).

In industrial dehydration (hot-air drying at 65°C) and lyophilization (freezing at -30°C and lyophilization at -10°C) of spinach previously immersed in salt and bicarbonate solutions, only a 12 percent loss of ß-carotene occurred and lutein, violaxanthin and zeaxanthin did not change significantly in both drying methods (23). These losses are small, considering the drastic processing treatment involved in dehydration and the greater exposure to oxygen. Sixty-seven % of all-*trans*-ß-carotene was retained after freeze-drying Italian spinach and 57 to 62 percent after solar-drying Italian spinach, spring cabbage and cowpea leaves (24).

TABLE 11
Changes in carotenoid composition (µg/g)* of bottled papaya purée during ambient storage

Carotenoid	Storage time (month)					
	0	1	3	6	10	14
ß-Carotene	2.3a	2.7a	1.9a	2.1a	1.9a	1.8a
ζ-Carotene	1.3a	0.9a	1.2a	0.9a	1.1a	1.3a
γ-Carotene	0.1a	0.2a	0.2a	0.2a	0.1a	0.3a
ß-Cryptoxanthin	5.5a	5.1a	4.8a	4.9a	5.1a	4.0b
Trans-lycopene	23a	22a	22a	22a	20a	21a
Cis-lycopene	1.5a	1.9a	1.6a	1.4a	2.1a	1.9a
Cryptoflavin	0.2a	0.6a	0.3a	0.3a	0.2a	0.3a
Flavoxanthin	nd	0.3a	0.2a	0.2a	0.3a	0.6b
Auroxanthin	nd	nd	1.0a	0.7b	1.1a	0.9a
Total	34a	34a	33a	32a	35a	32a

*Means of two determinations (three bottles were mixed for each determination). Values in the same row bearing different letters are significantly different ($p < 0.05$).
Reference: Godoy and Rodriguez-Amaya (22).

Among the various forms of processed foods, dried or dehydrated products are considered more likely to undergo

carotenoid degradation during storage because of the increase in surface area and porosity, the latter being associated with lyophilized (freeze-dried) foods.

Changes in carotenoid composition during blanching and storage of frozen and freeze-dried winter squash were investigated by Kon and Shimba (25). There was no loss of carotenoids during blanching. Lutein decreased slightly but ß-carotene was stable during freezing. Under frozen storage, lutein was stable while ß-carotene decreased 32% after three months. No loss of carotenoids was observed on freeze-drying. During storage of freeze-dried squash at 30°C, loss of ß-carotene reached 15, 20 and 53% after one, two and three months, respectively. However, after 3 months of storage at 3°C, reduction of ß-carotene was only 10%.

Processing of paprika

The influence of industrial processing of paprika on carotenoid composition was investigated by Minguez-Mosquera et al. in a series of studies. The drying and milling stages did not affect all of the pigments equally (26). The yellow pigments, particularly ß-carotene, were the most unstable; the red pigments (capsanthin and capsorubin) were highly stable. In drying the pepper variety Bola at 35°C, a period of continued carotenoid biosynthesis occurred (27), which was strongly favored by light. At the final stages of drying, light had a strong degradative effect. It was suggested that in order to obtain dry peppers for paprika with a 20 to 40 percent increase in carotenoid concentration, the drying process should consist of a first phase of illumination and a second phase of darkness. Two industrial drying processes were compared: slow drying with wood combustion and fast drying using hot air (28). The concentration of some pigments increased in Bola peppers dried with wood combustion, which was interpreted as a reflection of biosynthesis. During fast drying, degradative losses were evident.

Carotenoids in two varieties of peppers, Bola and Agridulce, behaved differently during drying (29). Capsanthin and capsorubin increased in the Bola variety and decreased in the Agridulce variety. In contrast, ß-cryptoxanthin and zeaxanthin went down in the Bola variety but increased slightly in the Agridulce pepper. The ß-carotene level was reduced in both varieties. All the carotenoids quantified decreased during milling. The Agridulce variety, which had higher carotenoid content, was found to be more suitable for paprika production, giving a final product with a more intense color and higher provitamin A content.

During slow industrial drying (30 to 35°C) of the Agridulce variety, three phases were discerned (30). In the first phase, there was a decrease of the carotenoid concentrations of the fruits. The second phase indicated an increase in carotenoid levels, although the previous losses were not compensated. In the third phase, degration prevailed. This pattern was observed under illumination and in darkness.

Fermentation

While other carotenoids underwent transformations, ß-carotene and lutein in olives resisted fermentation and the curing process (210 or 89 days) (31,32). The xanthophylls with 5,6-epoxide groups (violaxanthin and neoxanthin) were converted into their corresponding 5,8-furanoid derivatives (auroxanthin and neochrome), such transformations fitting first-order kinetics with respect to pigment concentration. In mustard, ß-carotene and lutein were reportedly reduced to one-third of their original contents after 50 days of curing (33).

Influencing factors and mechanism of carotenoid degradation

The factors that influence carotenoid degradation were discussed in detail in a previous paper (34). In model systems, carotenoid decomposition was shown to depend on carotenoid structure, nature of the system, available oxygen, exposure to light, water content or activity, temperature, atmosphere, presence of antioxidants, prooxidants, free radical initiators and inhibitors, sulfites. As shown in the previous sections, the situation is more complex in foods, considering the complicated interplay of the factors mentioned above, along with the varied nature and composition of foods, processing treatment, packaging and storage conditions, activity of lipoxygenase and other enzymes, and coupled oxidation with lipids. Nevertheless, application of available information makes this degradative process controllable.

In contrast to the wealth of information on lipid oxidation, present-day knowledge of carotenoid degradation is fragmentary. It is often accompanied by isomerization; both *cis*- and *trans*-isomers are subject to oxidation (Figure 3). It is generally accepted that the initial stage of oxidation involves epoxidation (Figure 3) and formation of apocarotenals (Figure 4). Recent work (35,36) show that hydroxylation is also involved. Presumably, subsequent fragmentations result in compounds of low molecular masses, which contribute to the desirable flavor of wine and tea but can be responsible for the off-flavor of dehydrated carrot. Full structural elucidation of the intermediate and final products of this process, as well as delineation of the mechanisms for their formation, are urgently needed.

Influence of processing on bioavailability

For a long time the main concern about processing in relation to carotenoids has been preventing losses. In recent years, attention has shifted to the effect of processing on the bioavailability of carotenoids.

Carotenoids in nature may occur as crystals, dissolved in oil droplets or complexed with protein, and protected by the cellular structure. This natural protection appears to limit its bioavailability. Processing denatures proteins and breaks down the cell walls, making the release of carotenoids from the food matrix easier.

FIGURE 3
Possible scheme for carotenoid degradation

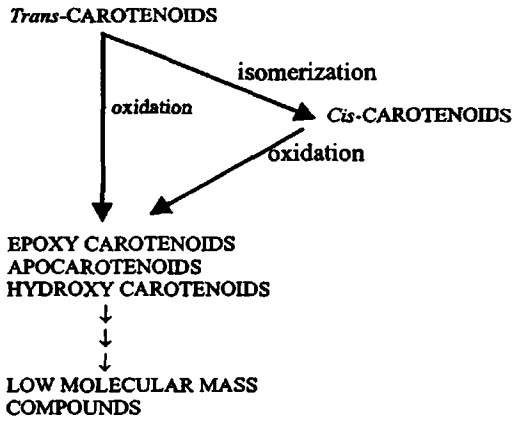
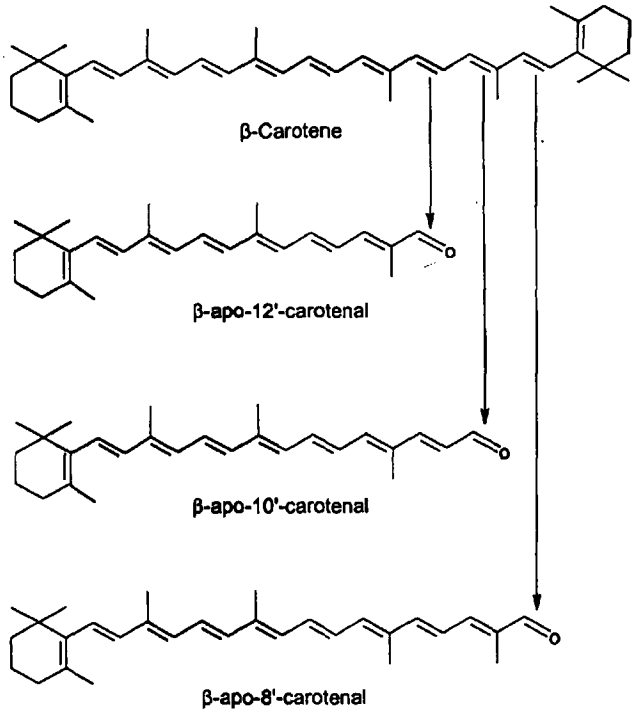


FIGURE 4
Formation of apocarotenals from ß-carotene



The carotenoid concentrations in the chylomicrons of five subjects given a single dose of fresh tomato or tomato paste were determined (36). The chylomicron carotenoid level is considered to be a more appropriate tool for studying absorption kinetics than plasma concentrations. Ingestion of tomato paste resulted in 2.5-fold higher total and all-*trans*-lycopene peak concentrations and 3.5-fold higher total area under the curve than ingestion of fresh tomato. Thus, the bioavailability of lycopene in humans appears greater from tomato paste than from fresh tomatoes.

In an earlier study based on plasma concentration, the uptake of lycopene was found to be greater from heat-processed (cooked in an oil medium) than from unprocessed tomato juice (37). Ingestion of cooked tomato juice resulted in a two- or three-fold increase in lycopene serum concentrations one day after ingestion. An equivalent consumption of unprocessed tomato juice caused no rise in plasma concentrations.

This topic is being investigated by several research groups. It is hoped that processing under appropriate conditions can serve as a means of enhancing bioavailability, at the same time retaining the carotenoid content of foods.

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