Stability of lycopene during food processing and storage

With an increasing understanding of the health benefit of lycopene, how to preserve lycopene during food processing and storage has caused much attention. Lycopene belongs to the carotenoid family and mostly exists in nature as the all-trans form. Heat, light, oxygen, and different food matrices are factors that have an effect on lycopene isomerization and autooxidation. Lycopene may isomerize to mono- or poly-cis forms with the presence of heat or oil or during dehydration. Reisomerization takes place during storage. After oxidation, the lycopene molecule split, which causes loss of color and offflavor. The effects of heat, oxygen, light, and the presence of oil on the stability of lycopene are uniform in much of the literature; however, controversy still exists on some details, such as the conditions causing the occurrence of isomerization, the optimal moisture, and temperature for storage.

Lycopene is a natural pigment that imparts red color to tomato, guava, rosehip, watermelon, and pink grapefruit[1]. Tomatoes (especially deep-red fresh tomato fruits) and tomato products are considered the most important source of lycopene in many human diets (see Tables 1 and 2); therefore most of the research on lycopene focus on tomato and tomato products. Lycopene is deposited in the liver, lungs, prostate gland, colon, and skin in the human body, and its concentration in body tissues tends to be higher than those of all other carotenoids[3,4] .

Lycopene has been shown in epidemiological and experimental studies to protect against prostate cancer, breast cancer, atherosclerosis, and associated coronary artery disease. It reduces low-density lipoprotein oxidation and helps reduce cholesterol levels in the blood. In addition, preliminary research suggests lycopene may reduce the risk of macular degenerative disease, serum lipid oxidation, and cancers of the lung, bladder, cervix, and skin[3].

The configuration of lycopene enables it to inactivate free radicals. As an antioxidant, lycopene has a singlet-oxygenquenching ability twice as high as that of β-carotene and 10 times higher than that of α-tocopherol (a vitamin E relative)[5]. According to Rao and Shen[6], lycopene intake of 5–20mg produced a significant increase in serum lycopene levels for both ketchup and lycopene capsules. Lipid and protein oxidations were also observed to be reduced significantly.

Lycopene participates in a host of chemical reactions hypothesized to prevent carcinogenesis and atherogenesis by protecting critical cellular biomolecules, including lipids, proteins, and DNA. Although the antioxidant properties of lycopene are thought to be primarily responsible for its beneficial properties, nonoxidative mechanisms are involved in lycopene's bioprotective activity. Evidence is accumulating to suggest that other mechanisms such as intercellular gap junction communication, hormonal and immune system modulation, and metabolic pathways may also be involved[7].

With increasing interest and awareness of the health benefits of lycopene, lycopene has been used in functional foods and nutraceuticals, and its stability during food processing and storage has drawn more and more attention.

TABLE 1 - LYCOPENE CONTENTS OF COMMON FRUITS AND VEGETABLES

Frutis/vegetables	Lycopene (μg/g of weight)
Tomatoes	8.8-42.0
Watermelon	23.0-72.0
Pink guava	51.0
Pink grapefruit	33.6
Papaya	20.0-53.0
Apricot	<0.1

TABLE 2 - LYCOPENE CONTENTS OF COMMON TOMATO-BASES FOODS

Tomato product	Lycopene (μg/g of weight)
Fresh tomatoes	8.8-42.0
Cooked tomatoes	37.0
Tomato sauce	62.0
Tomato paste	54.0-1,500.0
Tomato soup (condensed)	79.9
Tomato powder	1126.3-1,264.9
Tomato juice	50.0-116.0
Pizza sauce	127.1
Ketchup	99.0-134.4

PHYSICAL AND CHEMICAL PROPERTIES OF LYCOPENE

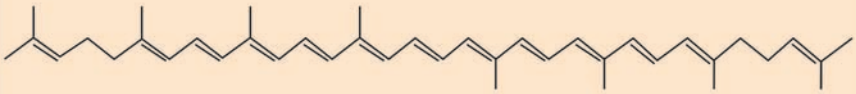
Lycopene belongs to the carotenoid family. Carotenoids are red, yellow, and orange pigments that are widely distributed in nature. Of the more than 700 naturally occurring carotenoids identified thus far, as many as 50 may be absorbed and metabolized by the human body. Only carotenoids have been identified in human serum, and lycopene is the most abundant. Chemically, carotenoids can be divided into two major classes. Carotenoid species in the first class are the highly unsaturated hydrocarbon carotenoids such as lycopene, α-carotene, β-carotene, γ-carotene, and ξ-carotene, which contain no oxygen and are usually orange and red in color. Because they are highly unsaturated, they are particularly susceptible to oxidation. Xanthophylls are the second class, which are oxygenated derivatives and contain one or more oxygenated group substituents at particular sites on the terminal rings[4,8]. Physical and chemical factors known to degrade carotenoids include elevated temperature, exposure to light, oxygen, and extremes in pH, and active surfaces[9]. Carotenoids are sensitive to isomerization in heat, light, or iodine, and to aerial oxidation[10,11]. During food thermal processing (cooking, heating, or dying), *trans–cis* isomerization of carotenoids can take place relative to the time–temperature exposure, while

during storage there is no further *trans–cis* isomerization, and only *cis–trans* reversion and autioxidation are observed initially, followed by the depletion of *cis* isomers and then by all-*trans* autooxidation only[12]. *Cis–trans* reisomerization is explicable as a return from an unstable, energy-rich state to the more favored and stable "ground state," since introduction of *cis* bond(s) twists and contracts the molecule, making it energy richer and relatively more reactive[13].

The basic chemical information on lycopene is fairly complete, with a research history dating back to the beginning of the century [9]. The molecular formula of lycopene is $C_{40}H_{56}$, and is an acyclic open-chain polyene with 13 double bonds. There are 11 conjugated double bonds arranged in a linear array, making it longer than any other carotenoid. The acyclic structure of lycopene causes symmetrical planarity, and therefore lycopene has no vitamin A activity. Lycopene is more soluble in chloroform, benzene, and other organic solvents than in water. The solubility of lycopene in vegetable oil is about 0.2 g/L at room temperature[14]. In aqueous systems, lycopene tends to aggregate and to precipitate as crystals. This behavior is suspected to lower lycopene bioavailability in humans[15]. In ripe tomato fruits, lycopene exists as elongated, needlelike crystals. The molecular structure of lycopene is shown in Figure 1.

Lycopene may be expected to undergo two changes during processing and storage: isomerization from all-*trans* to mono-*cis* or poly-*cis* forms, and oxidation[16, 17]. The all-*trans* isomer of lycopene is the most predominant geometrical isomer in fruits and vegetables (about 94–96% of total lycopene in red tomato fruit) and is the most thermodynamically stable form. In nature, lycopene exists in the all-*trans* form, and seven of these bonds can isomerize from the *trans* form to the mono- or poly-*cis* form under the influence of heat, light, or certain chemical reactions. In human serum and tissue, on the other hand, *cis* isomers of lycopene contribute more than 50% of total lycopene[4, 18]. *Cis* isomers of lycopene have physical characteristics and chemical behaviors distinct from those of their all-*trans* counterpart, including decreased color intensity and lower melting points; they are more polar than their all-*trans* counterparts, less prone to crystallization, and more soluble in oil and hydrocarbon solvents[9]. Experimental results revealed that *cis* isomers of lycopene are better absorbed by human than the all-*trans* form[19].

FIGURE 1 - MOLECULAR STRUTURE OF LYCOPENE



The autooxidation of lycopene is irreversible and will lead to fragmentation of the molecule, producing acetone, methylheptenone, laevulinic aldehyde, and probably glyoxal, which cause apparent color loss, and typically hay- or glass-like odors evolve[16, 17]. A reaction pathway of lycopene during production and storage of tomato powder was proposed by Boskovic[13] as shown in Figure 2.

Lycopene is absorbed more efficiently by the human body after it has been heat-processed into juice, sauce, paste, or ketchup[20, 21]. Because that lycopene is enclosed in the fresh fruit or vegetable tissue, only a portion of the lycopene is released. Food processing may improve lycopene's bioavailability by breaking down cell walls, which weakens the bonding forces between lycopene and tissue matrix and increases the surface area available for digestion. Additionally the chemical form of lycopene may be altered from *trans* isomers to *cis* isomers by the temperature changes involved in processing and therefore enhancing absorption in the body[4]. Also, because lycopene is fat-soluble, absorption into tissues is improved when oil is added to the diet. At the same time, although lycopene is available in supplement form, it is likely there is a synergistic effect when it is obtained from the whole fruit instead, where other components of the fruit enhance lycopene's effectiveness[5].

DEGRADATION OF LYCOPENE DURING PROCESSING

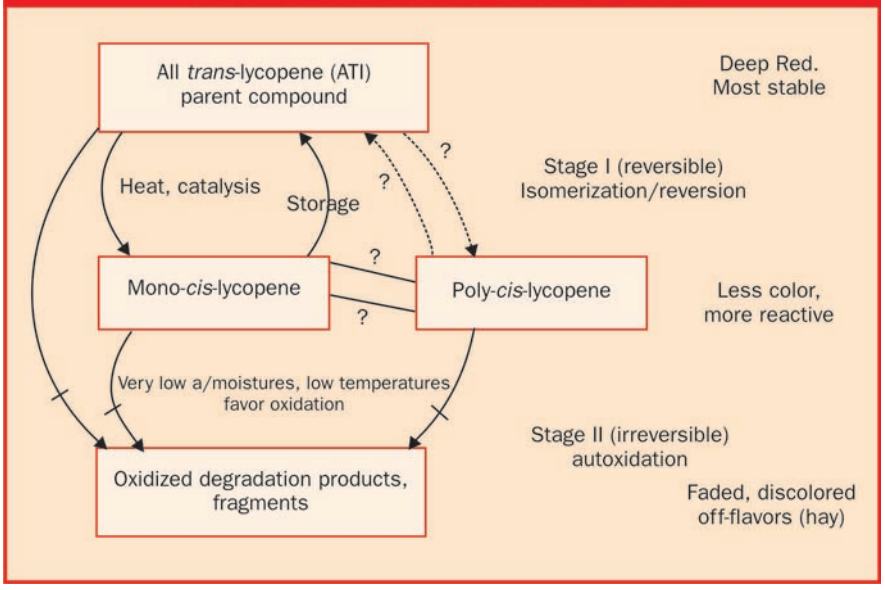
Under different food processing conditions, lycopene undergoes degradation via isomerization and oxidation, which impact its bioactivity and reduce the functionality for health benefits. The degradation reactions of lycopene are influenced by factors such as reaction medium, temperature, physical state, and environmental conditions. The most important factors during processing are heat, light, and oxygen.

HEAT

Lee and Chen[22] studied the stability of lycopene by heating standard lycopene (dissolved in high-performance liquid chromatography-grade hexane) at 50°C, 100°C, or 150°C. For 50°C treatment, there was no significant change of all-*trans*-lycopene found within the first 12 hours; however, the content began to decline thereafter. The levels of the mono-*cis* forms of lycopene were found to decrease with increasing heating time, which indicate that the degradation rates of mono-*cis*-lycopene may be greater than the formation rate. Unlike the mono-*cis* forms of lycopene, the percent change of two di-*cis* isomers showed increasing trends, which were probably because of conversion of mono-*cis*-lycopene.

There was a significant decrease of total lycopene after heating for 9 hours. This result revealed that isomerization was the main reaction during heating in the first 9 hours, after which the degradation reaction dominated. A similar result was observed for the concentration change of all-*trans*-lycopene and its *cis* isomers during heating at 100°C: The level of all-*trans*-lycopene decreased by 78% after 120 minutes of heating. The mono-*cis* forms of lycopene showed a decreasing trend. The levels of

FIGURE 2 - REACTION PATHWAY OF LYCOPENE DURING TOMATO POWDER PRODUCTION AND STORAGE



two di-*cis* isomers were found to rise in the first 60 minutes and then decreased, implying that di-*cis*-lycopene might be converted to mono-*cis*-lycopene or undergo degradation after prolonged heating. However, a large decrease was shown for the concentration of all-*trans*-lycopene during heating at 150°C, and no lycopene was detected after 10 minutes. The levels of all the mono-*cis* forms of lycopene showed the same trend. In the first 4 minutes, the levels of di-*cis* isomers rose and then decreased afterward. The result indicated that the isomerization reaction was favored at the beginning and then the degradation dominated after prolonged heating at 150°C. Comparing the results, apparently with increasing temperature and heating time, degradation dominated over isomerization.

Shi et al.[23] dissolved extracted lycopene into canola oil and heated the sample at 25°C, 100°C, or 180°C. It was observed that increasing the temperature from 100°C to 180°C or increasing thermal treatment time increased the degradation of *trans* isomer and *cis* isomer of lycopene. Compared with the treatment at 25°C, the *cis* isomers increased with thermal treatment at 100°C, but dropped significantly with treatment at 180°C. These investigators suggested that degradation of lycopene was the main mechanism of lycopene loss when heated above 100°C and that lycopene in general undergoes isomerization with thermal processing. However, the presence of certain macromolecules in fruits, such as in tomato, may offer protection for lycopene.

It was observed that lycopene loss and the rate of thermal isomerization were less while heating tomato pulp than when heating lycopene in organic solution[16, 17]. The results from Schierle[18] showed that heating tomato-based food in oil caused increased lycopene isomerization over that with heating in water, as shown in Table 3. Furthermore, Nguyen and Schwartz[24] assessed the effect of several different heat treatments on lycopene's isomeric distribution in a variety of tomato products, as well as in organic solvent mixtures (hexane, methanol, acetone, etc.) containing all-*trans*-lycopene.

Experimental results indicated that lycopene remained relatively resistant to heat-induced geometrical conversion during typical food processing of tomatoes and related products. The presence of fat is a factor that slows the isomerization reaction and protects the *trans*- and *cis*-lycopene isomers against oxidation. These researchers also found similar results as Lee and Chen[22] that lycopene in organic solvent isomerized readily as a function of time even in the absence of light and in the presence of other antioxidants.

According to Sharma and Maguer[25], heating tomato pulp at 100°C for 120 minutes decreased lycopene content from

TABLE 3 - EFFECT OF HEATING TREATMENT ON LYCOPENE *TRANS* AND *CIS* ISOMERIZATION IN AQUEOLUS AND OILY DISPERSIONS OF TOMATO PASTE (70°C)

Heafing time (minutes)	Lycopene (%)				
	All-*trans*	5-*cis*	9-*cis*	15-*cis*	Other *cis*
In water					
0	92.6	4.5	0.9	1.6	0.5
15	92.3	4.4	0.9	1.6	0.5
30	88.1	5.1	2.1	2.3	2.5
60	87.1	5.2	2.2	2.7	3.0
120	86.2	5.5	2.7	2.6	3.1
181	83.4	6.1	3.6	3.2	3.8
In olive oil					
0	87.4	4.8	4.3	3.0	0.5
30	85.2	5.8	5.5	2.9	0.5
90	83.5	6.2	5.9	3.3	1.2
120	80.3	7.0	6.9	3.2	2.6
180	76.7	8.1	8.8	3.1	3.3

185.5 to 141.5 mg/100 g of total solids; however, the heating did not induce any observed isomerization. Research from Agarwal[26] showed that subjecting tomato juice to cooking temperatures in the presence of corn oil resulted in the formation of the *cis* isomeric forms. According to Ax et al.[27], total lycopene content of oil-in-water emulsions decreased during thermal treatment with and without exposure to oxygen. Higher temperatures are directly correlated with increasing lycopene losses, and thermal treatment leads to a significant decrease in the concentrations of all-*trans* and 13-*cis* isomer, while the concentration of the 9-*cis* isomer increased. Zanoni et al.[28] and Anese et al.[29] carried out thermal sterilization on tomato puree at temperatures around 100°C, and found no significant variations in the lycopene content. Takeoka[30] showed no consistent changes in lycopene levels as the fresh tomatoes were processed into juice; however, a statistically significant decrease in lycopene levels of about 9–28% occurred as the tomatoes were processed into paste, which requires a long heating time.

Shi et al.[31] subjected tomato puree to intensive heat treatment—90°C, 110°C, 120°C, and 150°C for 1–6 hours—to promote isomerization and degradation of lycopene. The results, shown in Figures 3 and 4, indicate that the concentration of total lycopene steadily decreases with treatment (the higher the temperature, the faster the degradation), while the *cis* isomer levels increased but only during the first hour of heating. It was suggested that oxidation of lycopene was the main mechanism of lycopene loss when heated above 100°C, and that an optimum heating condition could be found to promote *cis* isomerization in tomato-based foods. Shi et al.[31] subjected another set of tomato puree samples to moderate heat treatment at 100°C for 5, 10, 30, and 60 minutes and found the longer the cooking time, the more lycopene loss occurred.

In conclusion, temperatures higher than 100°C and longer heating time lead to a larger percentage of lycopene degradation. Additionally, there is controversy in the literature about whether the presence of oil during food preparation may increase the percentage of mono- or poly-*cis*-lycopene in food, and whether lycopene isomerization occurs in non–oil-based food. The molecular structural changes during heating are shown in Figure 5. High temperatures will break down molecules into small fractions[32].

LIGHT

Lee and Chen[22] studied lycopene by dissolving standard lycopene in hexane and illuminating illumination intensity ranged from 2,000 to 3,000 lux) the mixtures at 25°C for 6 days. The content of all-*trans*-lycopene was found to decrease with increasing illumination time; after a 144-hour exposure to light it amounted to a 94% loss (Figure 6). All the mono-*cis* isomers of lycopene showed inconsistent changes. For instance, the level of 5-*cis*-lycopene was found to increase in the beginning and then decreased after the illumination time reached 2 hours. A similar trend was observed for 9-*cis*-, 13-*cis*-, and 15-*cis*-lycopene. This result indicated that isomerization and degradation of lycopene and its *cis* isomers, during illumination, might proceed simultaneously. The increased level of

FIGURE 3 - EFFECT OF HEAT TREATMENT ON TOTAL LYCOPENE DEGRADATION

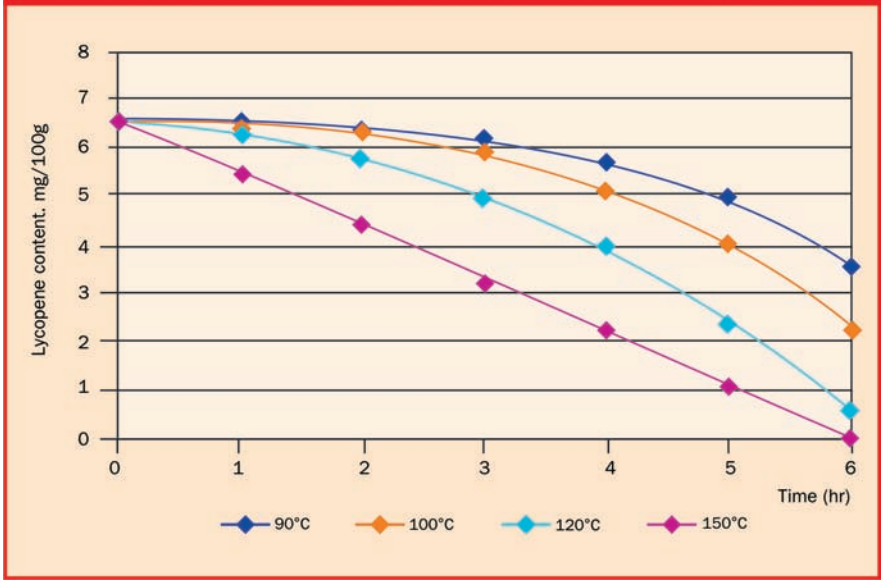


FIGURE 4 - EFFECT OF HEAT TREATMENT ON *CIS* ISOMER DEGRADATION

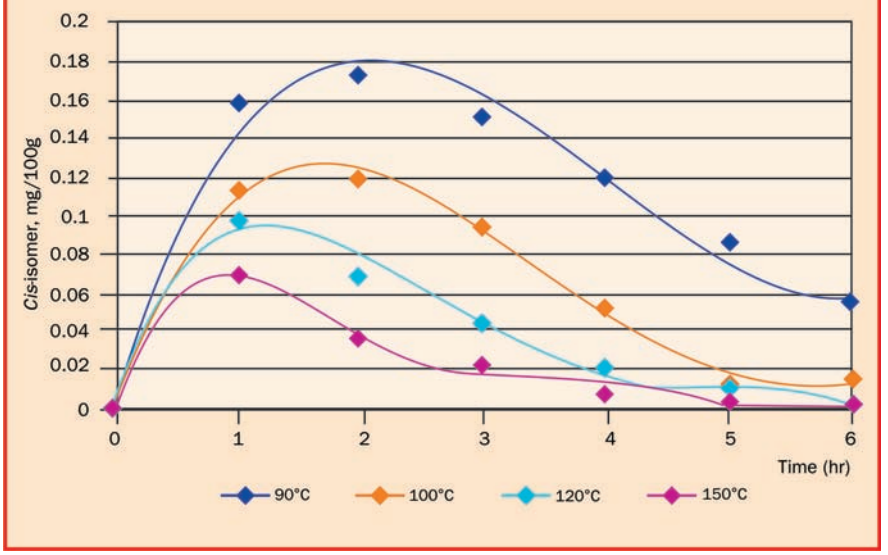
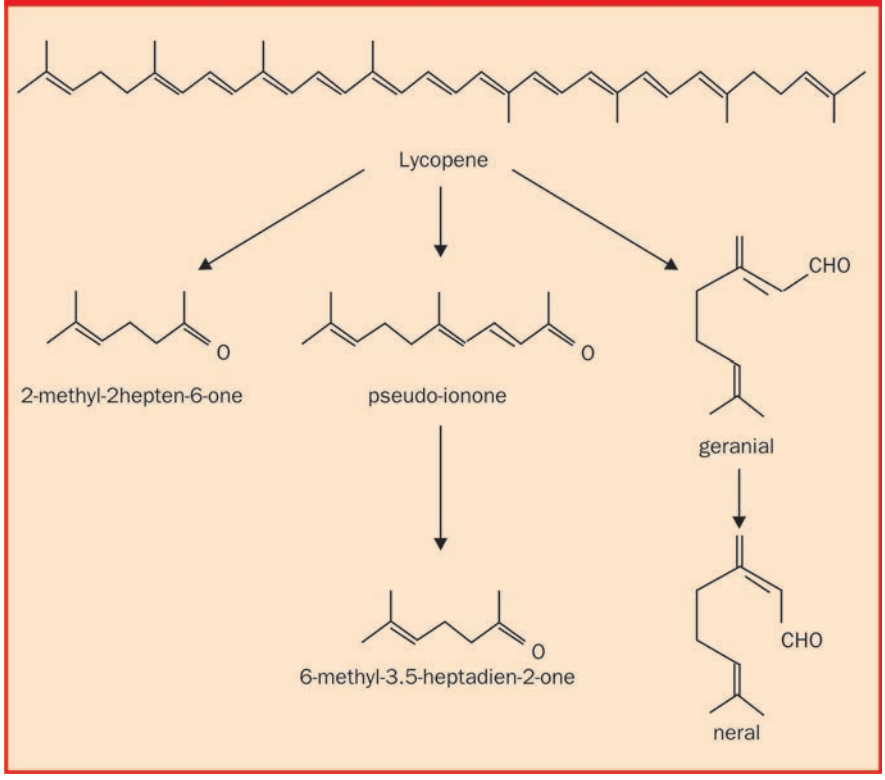


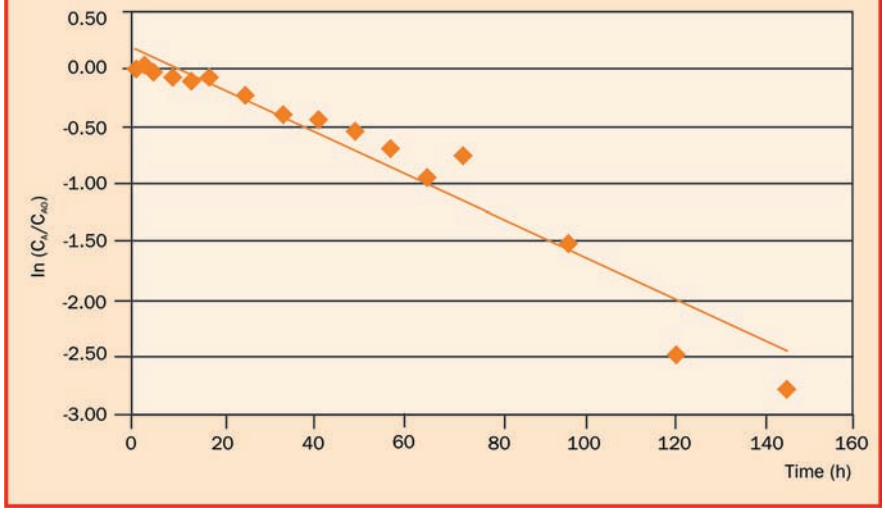
FIGURE 5 - MOLECULAR STRUCTURAL CHANGES AND OXIDATED PRODUCTS OF LYCOPENE DURING HEATING



mono-*cis*-lycopene is probably because of the conversion of all-*trans*-lycopene, after which a decrease could occur for mono-*cis*-lycopene because it might be further converted to another *cis* form of lycopene through intermediate all-*trans*-lycopene or undergo degradation. Compared with concentration, the percent changes of all-*trans*-lycopene and its *cis* isomers showed a different trend when the total amount of lycopene was taken into account.

Prior to illumination, the total amount of lycopene was found to contain 96.4% all-*trans*-lycopene, 0.99% 5-*cis*-lycopene, 0.71% 9-*cis*-lycopene, 0.60% 13-*cis*-lycopene, and 0.27% 15-*cis*-lycopene. After storage in light for 144 hours, a lycopene loss of 13.1% occurred for all-*trans*-lycopene, while an increase of 1.47%, 0.92%, 5.28%, and 0.44% was found for 5-*cis*-, 9-*cis*-, 13-*cis*-, and 15-*cis*-lycopene, respectively. Di-*cis*-lycopene also rose by 3.04%. The small percent loss of all-*trans*-lycopene during storage in light revealed that all-*trans*-lycopene might be isomerized to form mono-*cis*- or di-*cis*-lycopene. This result may account for the percent increase of all the mono-*cis* and di-*cis* forms of lycopene during illumination.

FIGURE 6 - FIRST-ORDER PLOT FOR THE DEGRADATION OF AMOUNT OF LYCOPENE DURING ILLUMINATION AT 25°C FOR 144 HOURS



Shi et al.[23] irradiated lycopene in canola oil at 2,010 (outdoor), 900, 650, and 140 (indoor) μmol/m^2 s for 1–6 days and found that the loss in total lycopene, *trans* isomers, and *cis* isomers increased significantly as the intensity of the light irradiation increased. In their experiment, they found the light irradiation treatment caused more losses in total lycopene than heating treatments at 25°C, 100°C, and 180°C, while in both treatments the rate of *trans* isomer loss was greater than the *cis* isomer formation.

Again, since the research of Lee and Chen[22] and Shi et al.[23] was conducted using standard lycopene in organic solvent, it could be expected that a protective effect may occur when lycopene exists in vegetable or fruit matrices. The study of Sharma and Maguer[25] used fiber-rich fraction samples of tomato pulp under three different conditions: vacuum and dark, dark and air, and air and light, with storage at -20°C, 5°C, and 25°C for 60 days. The lycopene loss was highest in the presence of air and light at 25°C, and lowest under vacuum and dark.

According to Landers and Olson[33], exposure of extracted lycopene to light should be avoided, and only gold, yellow, or red lights should be used.

OXYGEN

The study of Wong et al.[34]found that air-packed tomatojuice powder retained the lowest lycopene evels compared with CO2-, N2-, or vacuum-packed samples. Also, as discussed earlier, vacuum and dark storage combination also gave the lowest lycopene loss in tomato pulp according to Sharma and Maguer[25].

Henry et al.[35] studied the effect of

oxygen on the degradation of carotenoids in an aqueous model system. The standard lycopene was adsorbed onto a C_{18} solid phase and exposed to a continuous flow of water saturated with oxygen at 30°C. The results showed that 90% of lycopene was lost after 1 and 2 hours, while other carotenoids did not achieve an equivalent loss until 7 hours of exposure.

Ax et al.[27] dissolved lycopene in the oil phase of oil-in water emulsions, and the emulsions were filled into a glass flask with a sintered-glass frit, allowing continuous flushing with either synthetic air or nitrogen gas, thus providing oxygen saturation or oxygen-free conditions. At 25°C, about 25% of lycopene was degraded within 30 hours in the oxygen-removed emulsions, whereas a lycopene loss of about 80% was found for oxygen saturation. In the presence of oxygen, lycopene destabilization was about three times higher than in the absence of oxygen under inert conditions.

Nitrogen or argon headspace can be employed to keep exposure to atmospheric oxygen to a minimum. However, according to Ribeiro et al.[36], removing oxygen in water by flushing the system with nitrogen produced no improvement of stability. Instead, the lycopene degradation was accelerated. On the other hand, complete exclusion of oxygen using the enzyme glucose oxidase led to far better stability.

DEHYDRATION

In the dehydration procedure, degradation of lycopene is complex and depends on many factors such as oxygen exposure, moisture, temperature, presence of pro- and antioxidants, and lipids[28, 30].

Effect of dehydration techniques on lycopene degradation. Shi[37] researched lycopene degradation in tomatoes using different dehydration methods: vacuum-drying (55°C, 4–8 hours), conventional air-drying (95°C, 6–10 hours), and osmotic-vacuum-drying (first dehydrated with an osmotic treatment at 25°C for 4 hours, followed by vacuum-drying at 55°C for 4–8 hours). They found that the general tendency of lycopene retention in samples slightly decreased during the dehydration processes. During osmotic treatment, lycopene content remained essential constant. After osmotic-vacuum-drying, total lycopene retention in tomatoes was greater than that using vacuum-drying. Conventional air-drying decreased lycopene retention greatly in tomato samples, which was attributed to the influence of heat and oxygen. Possible reasons for good retention of lycopene during osmotic dehydration may be that the sugar solution keeps oxygen from the tomatoes, therefore reducing the oxidation of lycopene. Zanoni et al.[38] performed a study on the loss of lycopene during air-drying. Tomato halves were dried in a cabinet air-dryer, at 80°C and 110°C, with an airflow rate of 1.5 m/second. During drying at 80°C, no significant lycopene loss occurred, whereas a significant, though small, loss (12% maximum) occurred at 110°C. Also, Sharma and Maguer[25] found that freeze-drying and ovendrying (25–75°C) of tomato pulp solids did not cause any loss in lycopene content.

These investigations demonstrated that lycopene is substantially stable to industrial dehydration; however, it was also noticed that air is a critical factor in terms of oxidative damage, when the product is exposed to high temperature and high oxygen levels.

Effect of dehydration techniques on lycopene isomerization. According to the study of Wong et al.[34], the all-*trans*-lycopene levels of vacuum-dried tomato-juice powder samples packed under CO2, N2, or vacuum showed an initial loss, but in the 6- and 12-month examinations showed apparent recoveries to a value approaching that of the

all-*trans*-lycopene content of the tomato concentrate from which the experimental powders were made. This observation parallels that of publications by Zechmeister et al.[10] on the tendency of lycopene compounds to isomerize from one form to another with accompanying color changes. It was previously suggested that the first stage of lycopene degradation during drying and storage of tomato powders is the reversible isomerization of all-*trans*-lycopene to less colored, more oxidizable *cis* isomers[13]. Anguelova and Warthesen[39] found that *cis*-lycopene isomers, while present at low levels in raw tomatoes, may have increased during spray-drying of the powders. According to Nguyen and Schwartz[24], dehydration of tomatoes at mild temperatures does not usually cause significant losses in total lycopene content, but the conversion of *trans* to *cis* isomers always occurs in the dehydrated products. A study by Shi et al.[37] showed (Table 4) that *cis* isomers were not detected in the fresh tomato samples, but a significant increase in the *cis* isomers with simultaneous decrease in the all-*trans* isomers was observed in the dehydrated tomato samples through the osmotic-vacuum-drying, vacuum-drying, and air-drying dehydration methods. It was observed that fewer *cis* isomers were present in osmotically dehydrated tomatoes as compared with those directly air-dried and vacuum-dried, which may due to the fact that osmotic solution remaining on the surface layer of the tomato prevents oxygen from penetrating and oxidizing lycopene. The highest amount of *cis* isomers was found in conventional air-dried samples. Obviously, oxygen also played an important role in lycopene isomerization. However, a study on the stability of spray-dried tomato powder conducted by Miers et al.[40] found the existence of some factor that prevented the reversion of the isomers to the all-*trans*-lycopene. They suggested that the factor might have been related to the presence of sulfite in the spray-dried powder or related to the spray-drying process.

Lycopene degradation and color changes of tomato-based foods. Lycopene is located in chromoplasts dispersed throughout the tomato fruits. Lycopene appears as solid microcrystals so that the light reflected from them gives the tomato its typical bright red color. When lycopene is dissolved in lipids or other solvents, its color is yellow or dark orange, not red.

Tomatoes with osmotic treatment had more red color than those treated by air-drying and vacuum-drying, which indicated there was more lycopene in the samples. It was also possible that all-*trans*-lycopene had isomerized to *cis*-lycopene, which is less red than all-*trans*-lycopene.

DEGRADATION OF LYCOPENE DURING STORAGE

Lycopene is considered relatively stable during food processing; however, storage of tomato products may contribute to lycopene loss. During storage, light and oxygen have similar effects on lycopene as during processing. Temperature plays an important role in lycopene loss during storage. Water activity is another very important factor in the storage of the food products. While *trans* to *cis* isomerization typically occurs during processing, the storage of processed foods favors reversion from *cis* to *trans*, because of the relatively unstable state of *cis* isomers compared with the *trans* isomer[41].

OXYGEN AND LIGHT

The study of Sharma and Maguer[25] found that after 4 months' storage at room temperature, in the dark, lycopene loss reached 97% and 79% in freeze-dried and oven-dried (25–75°C) tomato pulp, respectively. The freeze-dried samples were more voluminous and fluffy in texture compared with the thin crust of sheets of oven-dried samples, which led to the suggestion that exposure of freeze-dried fibers to air and light caused lycopene loss at a faster rate. Lovric and Giovanelli[12] observed the effect of oxygen during the storage of lycopene powder by comparing samples stored in N_2 and air (Table 5), and the results showed that oxygen is a critical factor for lycopene retention during storage.

Lavelli and Giovanelli[42] subjected tomato products (pulp in cans, puree in glass bottles, and paste in aluminium tubes) to accelerated aging (30°C, 40°C, and 50°C for 3 months). They found that lycopene remained stable in all samples (Table 6). Anguelova and Warthesen[39] subjected tomato powder to three treatments: light exposure at room temperature, 6°C, and 45°C in the dark. Differences among the storage treatments are not obvious from the data, but the amount of *cis* isomers as a percentage of the total lycopene increased to the 14–18% range, regardless of the storage conditions (Table 7). That the 6°C treatments did not yield a lesser

TABLE 4 - TOTAL LYCOPENE AND *CIS* ISOMER CONTENT IN DEHYDRATED TOMATO SAMPLES

Sample	Total lycopene (μg/g dry basis)	Lycopene loss (%)	All-*trans* isomers (%)	*Cis* isomers (%)
Fresh tomato	75.5[a]	0	100	0
Osmotic treatment	75.5[a]	0	100	0
Osmo-vacuum-dried	73.7[b]	2.4	93.5	6.5
Vacuum-dried	73.1[c]	3.2	89.9	10.1
Air-dried	72.6d	3.9	84.4	16.6

Data are presented as means of triplicate determinations.
Means in a column not sharing a common leter [a-d] are significantly different (P<.01).

amount of 5,5'-di-*cis*-lycopene than the other two treatments was explained by the proposal that the degradation of *cis* isomer was due to autooxidation, since *cis* isomers were more susceptible to autooxidation than the all-*trans* isomer.

MOISTURE FOR DEHYDRATED FOOD PRODUCTS

Prevention of deteriorative changes has been one of the major problems in the research on dehydrated foods. Water activity has a strong effect on stability of dehydrated food products[44,45]. The study of Ramakrishnan and Francis[46] indicated that the water content of the system exerted a protective influence on some carotenoid pigments above and below monolayer values. The extent of protection varied with water content, the nature of the system, and also the type of carotenoid pigments. They suggested that the polarity of carotenoid molecules might play a role in modifying the moisture's effect for protection. Lovric et al.[12] discussed the effect of very low moisture content on the oxidative stability of dried tomatoes and concluded that the protective activity of water can be ascribed to a number of factors: First, water can inactivate pro-oxidative metal ions, which are present in traces. Second, the hydrogen bonding between hydroperoxide molecules and water results in delayed chain propagation reactions in lipid autooxidation. Finally, water can compete with oxygen for the active absorption sites. However, literature data were controversial on the moisture level that would be favored for stability of products.

Data from Zanoni et al.[28] and Abushita et al.[43] showed that very low moisture content or very low water activity seems to favor oxidative degradation in tomato products. According to the study of Zanoni et al.[28], adequate shelf life was obtained at relatively high moisture content (30–40%) and at high water activity (0.8–0.86). A low moisture content (12%) of dried tomato halves seems to promote oxidative damage. It was explained that when the moisture content falls below the monolayer moisture content of the product, an increase in oxidation may occur.

Giovanelli and Paradiso[47] air-dried commercial tomato pulp to two final moisture levels: dried pulp (DP) (moisture ~9%, water activity ~0.35) and intermediate-moisture pulp (IMP) (moisture ~23%, water activity ~0.7) and stored them in airtight clear glass bottles in the dark without effective air exclusion for 5 months at 4°C, 20°C, and 37°C.

All-*trans*-lycopene degradation was negligible in DP stored at 20°C and 37°C, while some decrease was observed in DP stored at 4°C (about 18% loss after 5 months). All-*trans*-lycopene degradation was more significant in IMP and was inversely related to storage temperature, showing about 28%, 38%, and 75% loss after 5 months of storage at 37°C, 20°C, and 4°C, respectively. The result implied that IMP was more sensitive than DP toward lycopene degradation reactions. Also, it was concluded that the moisture level

TABLE 5 - TOTAL LYCOPENE RETENTION IN TOMATO POWDER STORED IN DIFERRENT ATMOSPHERES AND TEMPERATURES FOR DIFERENT INTERVALS

Storage period (days)	Storage conditions	Total lycopene retention (%)
Fresh tomato powder		100.0
30	N_2, 2°C	85.5
	N_2, 20°C	90.0
	Air, 2°C	37.0
	Air, 20°C	46.3
80	N_2, 2°C	66.3
	N_2, 20°C	78.5
	Air, 2°C	11.3
	Air, 20°C	28.7
160	N_2, 2°C	54.2
	N_2, 20°C	76.5
	Air, 2°C	9.35
	Air, 20°C	25.5
210	N_2, 2°C	53.3
	N_2, 20°C	69.8
	Air, 2°C	8.55
	Air, 20°C	23.0
385	N_2, 2°C	53.0
	N_2, 20°C	65.8
	Air, 2°C	8.2
	Air, 20°C	21.8

TABLE 6 - PERCENT VARIATION OF LYCOPENE IN TOMATO PRODUCTS

	Temperature (°C)	Lycopene (%)
Pulp	25	100
Overheated pulp	40	99
Paste	30	99
Paste	40	89

TABLE 7 - CONTENTS OF PRESUMPTIVE 5,5' -DI-*CIS*-LYCOPENE IN TOMATO POWERDS (PERCENTAGE OF TOTAL LYCOPENE IN THE SAMPLE) AFTER A GIVEN STORAGE PERIOD UNDER FLUORESCENT LIGHT (38,500 LUX)

	Tomato powder T1			Tomato powder T2		
Weeks	Light exposure	6°C	45°C	Light exposure	6°C	45°C
0	4.3	4.3	4.3	6.2	6.2	6.2
1	5.6	4.8	6.0	6.7	6.1	5.9
2	5.8	5.4	5.3	5.2	7.6	6.3
3	7.0	5.5	5.4	5.5	6.4	7.0
4	8.6	9.4	9.1	7.7	6.8	7.8
5	8.1	11.0	12.8	11.0	11.7	12.1
6	14.2	18.4	14.6	14.1	18.2	14.1

in DP (approximately 9%) provides some of the protective effect, whereas at higher moisture levels (such as the approximately 23% found in IMP) the solvent effect of water prevails, and reactions are favored by enhanced mobility of reaction substrates and co-substrates. Since the experiments were on different kind of tomato products, the different product matrix could be a reason for the difference.

TEMPERATURE FOR DEHYDRATED FOOD PRODUCTS

Literature data about the effects of storage temperature on the stability of lycopene in dehydrated tomato products did not give concurring conclusions either. The study of Giovanelli and Paradiso[47] found that lycopene had maximum loss in DP and IMP stored at 4°C. Anguelova and Warthesen[39] found that lycopene and color retention were higher in tomato powder stored at 6°C compared with 45°C. Lovric observed that color, total lycopene, and all-*trans*-lycopene in foam-mat-dried tomato powder were better retained at 20°C compared with -10°C, 2°C, and 37°C (in both cases products were stored in air and in the dark). It was explained that all-*trans*-lycopene is partly converted to *cis* isomers during drying and that reisomerization from *cis* isomers to the all-*trans* form is favored at 20°C (with respect to -10°C and 2°C). Since *cis* isomers are more readily oxidized than all-*trans* isomers, lycopene oxidation during storage occurred faster when a high *cis* isomer ratio was present. Review of published data about lycopene stability in dehydrated tomato products leads to the conclusion that low storage temperatures as well as very low water activity and moisture levels have a pro-oxidative effect. Moreover, oxygen solubility increases at lower temperatures, and this could be of some importance in a particulate matter such as tomato pulp pieces[13].

Tissue from the fruit center of each of nine individual watermelons was stored at -20°C or -80°C as either small chunks or puree and periodically sampled over a year's time. Initial freeze-thaw experiments indicated that a small percentage of lycopene, approximately 4–6%, degraded during an initial freeze-thaw. Analyses of the samples showed a loss of approximately 30–40% lycopene over a year's storage at -20°C and a loss of approximately 5–10% over the same period at -80°C. Lycopene was slightly more stable in pureed compared with diced watermelon tissue at -20°C, but not at -80°C.48 A similar result in frozen tomato pulp was observed by Sharma and Maguer[25] in that lycopene loss in tomato pulp when stored in the frozen state under vacuum and dark was 16.2% after 60 days. They suggested the possibility of an autocatalytic reaction.

The obviously controversial results about the optimal storage moisture and temperature indicate a need for further research.

SUMMARY

Lycopene remains relatively stable during typical food processing procedures, except at extreme conditions (for example, very high temperature or very long time heating). *Trans* and *cis* isomerization may happen during processing, especially in the presence of fat, but then reisomerization always followed during storage time. Light and oxygen are two other important factors during food processing and storage, and should be avoided during long time storage. Autooxidation may cause final fragmentation of the lycopene molecule, which induces an off-flavor to the products.

Dehydrated tomato products are sensitive to color fading and loss of acceptability mainly due to lycopene isomerization and oxidation. Two major storage conditions—moisture content and temperature—and their effects are not completely understood. Therefore, a deeper investigation of lycopene isomerization and autooxidation mechanism and kinetics is needed to define optimal storage conditions for various tomato products.

Some controversial experimental results may be due to the different protective effects from different food matrices.

It was found that the carotenoid pigments (β-carotene, apo-8'-carotenal, and canthaxanthin) in starch were relatively more stable to autooxidative changes than in cellulose systems[46]. The research of Ribeiro et al.[36] also showed that lycopene stability strongly depends on the food system. When lycopene emulsions were diluted in foods, lycopene was found to be very stable in orange juice, considerable lycopene loss was found in skimmed milk, and lycopene degraded very rapidly in water. Therefore, future research should pay more attention on the protective effect of different food matrices on stability of lycopene.

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