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Lycopene in Tomatoes: Chemical and Physical Properties Affected by Food Processing

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ABSTRACT: Lycopene is the pigment principally responsible for the characteristic deep-red color of ripe tomato fruits and tomato products. It has attracted attention due to its biological and physicochemical properties, especially related to its effects as a natural antioxidant. Although it has no provitamin A activity, lycopene does exhibit a physical quenching rate constant with singlet oxygen almost twice as high as that of β-carotene. This makes its presence in the diet of considerable interest. Increasing clinical evidence supports the role of lycopene as a micronutrient with important health benefits, because it appears to provide protection against a broad range of epithelial cancers. Tomatoes and related tomato products are the major source of lycopene compounds, and are also considered an important source of carotenoids in the human diet. Undesirable degradation of lycopene not only affects the sensory quality of the final products, but also the health benefit of tomato-based foods for the human body. Lycopene in fresh tomato fruits occurs essentially in the all-*trans* configuration. The main causes of tomato lycopene degradation during processing are isomerization and oxidation. Isomerization converts all-*trans* isomers to *cis*-isomers due to additional energy input and results in an unstable, energy-rich station. Determination of the degree of lycopene isomerization during processing would provide a measure of the potential health benefits of tomato-based foods. Thermal processing (bleaching, retorting, and freezing processes) generally cause some loss of lycopene in tomato-based foods. Heat induces isomerization of the all-*trans* to *cis* forms. The *cis*-isomers increase with temperature and processing time. In general, dehydrated and powdered tomatoes have poor lycopene stability unless carefully processed and promptly placed in a hermetically sealed and inert atmosphere for storage. A significant increase in the *cis*-isomers with a simultaneous decrease in the all-*trans* isomers can be observed in the dehydrated tomato samples using the different dehydration methods. Frozen foods and heat-sterilized foods exhibit excellent lycopene stability throughout their normal temperature storage shelf life.

Lycopene bioavailability (absorption) can be influenced by many factors. The bioavailability of *cis*-isomers in food is higher than that of all-*trans* isomers. Lycopene bioavailability in processed tomato products is higher than in unprocessed fresh tomatoes. The composition and structure of the food also have an impact on the bioavailability of lycopene and may affect the release of lycopene from the tomato tissue matrix. Food processing may improve lycopene bioavailability by breaking down cell walls, which weakens the bonding forces between lycopene

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and tissue matrix, thus making lycopene more accessible and enhancing the *cis*-isomerization. More information on lycopene bioavailability, however, is needed. The pharmacokinetic properties of lycopene remain particularly poorly understood. Further research on the bioavalability, pharmacology, biochemistry, and physiology must be done to reveal the mechanism of lycopene in human diet, and the *in vivo* metabolism of lycopene.

Consumer demand for healthy food products provides an opportunity to develop lycopene-rich food as new functional foods, as well as food-grade and pharmaceutical-grade lycopene as new nutraceutical products. An industrial scale, environmentally friendly lycopene extraction and purification procedure with minimal loss of bioactivities is highly desirable for the foods, feed, cosmetic, and pharmaceutical industries. High-quality lycopene products that meet food safety regulations will offer potential benefits to the food industry.

KEY WORDS: bioactivity, bioavailability, degradation, isomerization, lycopene, oxidation, processing, tomato.

I. INTRODUCTION

The red color of many kinds of fruits is due to the presence of lycopene and other carotenoids. Lycopene is a natural pigment synthesized exclusively by plants and microorganisms. One of the functions of lycopene and related carotenoid species is to absorb light during photosynthesis, thereby protecting plants against photosensitization. Lycopene is among the most widespread and important natural pigments. Inasmuch as lycopene and other carotenoids are photosynthesized by plants and microorganisms, they constitute the main source of all animal carotenoids. Sometimes the brilliant colors of lycopene are masked by the green chlorophyllic pigments (i.e., in green vegetables and leaves). In a number of cases, the chlorophyll content decreases as plants mature, leaving the lycopene and other carotenoids responsible for the bright colors of most fruits (pineapple, orange, lemon, grapefruit, strawberry, tomato, paprika, rose hip) and many flowers (Eschscholtzia, Narcissus). Carotenoids also contribute to the colors of some birds (flamingo, canary), insects, and marine animals (shrimp, lobster, and salmon).

Tomatoes are an important agricultural commodity worldwide. The tomato fruit is comprised of skin, pericarp, and locular contents. The locular cavities are filled with jelly-like parenchyma cells that surround the seeds. Tomatoes normally contains 5 to 10% dry matter, of which about 75% is soluble, and about 1 to 3% of which consists of skin and seed. Nearly half of the total dry matter is reducing sugars, and about 10% is organic acid, principally citric and malic acids. More than 80% of processed tomatoes are consumed in the form of tomato juice, paste, puree, catsup, sauce, and salsa (Gould, 1992).

Tomatoes and tomato-based foods are considered healthy foods for several reasons. They are low in fat and calories, cholesterol-free, and a good source of fiber and protein. In addition, tomatoes are rich in vitamins A and C, β-carotene, potassium, and lycopene. The characteristic deep-red color of ripe tomato fruits and tomato-based foods, which serves as a measure of total quality, is mainly due to lycopene. Tomatoes and tomato foods are the major sources of lycopene and are considered to be important contributors of carotenoids to the human diet. Other sources of lycopene include watermelon, guava, rosehip, papaya, and pink grapefruit (Gross, 1987, 1991; Mangels et al., 1993) (Table 1). Lycopene is an important natural color ingredient in food formulations. The widespread use of tomato paste as a colorant makes lycopene a commercially important natural pigment. However, Llcopene undergoes degradation via isomerization and oxidation during tomato processing, which has

TABLE 1
Lycopene Content of Fruits and Vegetables

Material	Lycopene content (mg/100 g wet basis)
Fresh tomato fruit	0.72–20
Watermelon	2.3–7.2
Guava (pink)	5.23–5.50
Grapefruit (pink)	0.35–3.36
Papaya	0.11–5.3
Rosehip puree	0.68–0.71
Carrot	0.65–0.78
Pumpkin	0.38–0.46
Sweet potato	0.02–0.11
Apple pulp	0.11–0.18
Apricot	0.01–0.05

Data from Beerh and Siddappa, 1959; Gross, 1987, 1991; Mangels et al., 1993.

a direct impact on the food sensory quality and health benefit. Degradation of lycopene not only affects the sensory quality such as color of final products, but also their health benefits to consumers. Therefore, it is important to study the effects of food processing on the lycopene stability in tomato products and bioavailability of lycopene in tomato-based foods.

II. LYCOPENE DISTRIBUTION IN TOMATO FRUITS

A. Lycopene in Tomato Fruits

Lycopene is the most abundant carotenoid in ripe tomatoes, comprising approximately 80 to 90% of those pigments present. Other carotenoids (α-carotene, β-carotene, lutein, and β-cryptoxanthin) are negligible (Curl, 1961). The amount of lycopene in fresh tomato fruits depends on variety, maturity, and the environmental conditions under which the fruit matured. Normally, tomatoes contain about 3 to 5 mg lycopene per 100g of raw material (Hart and Scott, 1995). Higher amounts are found in some tomato varieties. Recently, Tonucci et al. (1995) reported that lycopene content in whole tomato fruit was more than 9.27 mg/100 g. Some deep-red varieties contain more than 15 mg per 100 g, whereas the yellow varieties contain only about 0.5 mg per 100 g (Hart and Scott, 1995). Liu and Luh (1977) reported that the harvest maturity affected carotenoids in tomato paste. Lycopene increases as tomatoes mature. Ellis and Hammer (1943) also found that there was a greater concentration of lycopene and other carotenoids in the stem than in the blossom end of the fruit, the transverse segments having intermediate contents. Edwards and Reuters (1961) examined the lycopene contents of 11 commercial varieties of tomatoes differing appreciably in variety and maturity factors. Heinonen et al. (1989) reported that the lycopene concentration in tomatoes was higher in summer (from June to August) and lower in winter (from October to March). Tomato fruits grown in the greenhouse either in summer or winter are lower in lycopene content than fruits produced outdoors during summer, and fruits picked green and ripened in storage are substantially lower in lycopene than vine-ripened fruits (Gould, 1992). Furthermore, Lurie et al. (1996) reported that relatively high temperatures (38°C) inhibited lycopene production while low temperatures inhibited both fruit ripening and lycopene production.

Lycopene formation occurred about 2 days earlier if tomato fruits were treated with ethylene (Jeffery et al., 1984). It was reported that lycopene synthesis in the *rin* mutant was enhanced by high O_2 in the presence of 10 ppm ethylene (Frenkel and Gurrison, 1976). On the other hand, ethanol inhibited ripening and the synthesis of lycopene in tomatoes (Sahveit and Mencarelli, 1988). Additionally, Sheehy et al. (1988) found that a reduction in polygalacturonase did not affect synthesis of lycopene. Lampe and Watada (1971) and Mohr (1979) indicated that the lycopene content in tomato fruits may be enhanced by improved techniques in fertilizer, harvest time, and variety selection. Table 2 shows the lycopene content in tomato fruits of different varieties, growing locations, and maturity.

McCallum (1955) studied the distribution of lycopene and other carotenoids in the tomato and found that the outer pericarp was highest in lycopene and total carotenoids, and the locule was the highest in carotene (Table 3). According to Al-Wandawi et al. (1985), tomato skin contains 12 mg lycopene/100 g skin (wet basis) lycopene, while whole mature tomato contains only 3.4 mg lycopene/100 g (wet basis). Therefore, the concentration of lycopene in tomato skin is about three times higher than in whole mature tomatoes. D'Souza et al. (1992) also found that the skin and the pericarp of tomato fruits were rich in lycopene. Sharma and Le Maguer (1996) found that skins were a rich source of lycopene, as they contained about five times more lycopene (53.9 mg/100 g) than the whole tomato pulp (11 mg/100 g). This indicates that most of the lycopene is found attached to the insoluble fiber portion of the tomatoes.

B. Lycopene Biosynthesis in Plant Cells

At the cellular level, lycopene is localized in the chloroplasts of tomato fruits, and can be found among the thylakoid membranes in the photosynthetic pigment-protein complex (Bouvier et al., 1998; Akhtar et al., 1999). In the early stages of tomato fruit maturation, the dominant pigment in the chloroplasts is green chlorophyll. As the chlorophyll degrades, the color change from green to white. When chlorophyll in the chloroplasts is reduced, lycopene is biosynthesized with concomitant changes in the ultrastructure of the fruit, which results in the color change from white to red (Harris, 1970; Khudairi, 1972; Matienco and Yedalty, 1973). The final stage of chromoplast development is the formation of lycopene crystals that occupy a large portion of chromoplast and appear as volumnous red sheets in the chromoplasts (Laval-Martin, 1974). The largest concentrations of lycopene are found in the pericarp (Simpson et al., 1977). The biosynthesis of lycopene and other carotenoids in tomatoes has been studied extensively with the use of ^{14}C tracers (Porter and Anderson, 1967; Buggy et al., 1969). Mevalonic acid, believed to be a precursor, is converted step by step by a loss of hydrogen in each step, to produce lycopene. Dehydrogenation is most likely involved in each step. Thus, lycopene exists as small globules, that is, in the chromoplasts, which are suspended in the tomato pulp throughout the fruit. Lycopene appears as solid microcrystals and thus the light reflected from them gives the tomato its typical bright red color.

III. CHEMICAL AND PHYSICAL PROPERTIES OF LYCOPENE

Carotenoids are widely distributed in fruits and vegetables, and more than 600 carotenoids, mainly *cis-trans* isomers, have been characterized in vegetable products that humans consume. 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-caro-

TABLE 2
A Survey of Lycopene Content in Some Tomato Cultivars

Material	Lycopene (mg/100 g wet basis)	Sources
Juice from ripe tomatoes	3.71	Beerh and Siddappa, 1959
Juice from green tomatoes	0.171	
Juice from partially ripe, yellowish-red tomatoes (in India)	0.240	
VT-145-7879		Liu and Luh, 1977
Pink	12.18	
Medium red with some orange spots	20.71	
Full red ripe (in Davis, CA, U.S.A.)	30.16	
Ec61747	3.65	Madaiah et al., 1986
V687	3.61	
Ec130046	2.57	
Labonita	2.31	
Dryzbha	2.58	
Selection-4	4.45	
Ogasta	3.47	
Selection-22	3.41	
Ec154892 (in the Bangalore area of India)	1.58	
Fresh tomato (June–August)	3.8–6.6	Heinonen et al., 1989
Fresh tomato (October–March) (in Finland)	2.6–3.1	
Fresh tomato (in Malaysia)	0.723	Tee and Lim, 1991
Fresh tomato (*Solanum Lycopersicum, Mill*)		Granado et al., 1992
Common type	1.54–2.69	
Canary Islands type	1.32–1.88	
Pear type (in Spain)	54.33–70.21	
Tomato juice (in Campinas, Brasil)	1.09–5.13	Tavares and Rodriguez–Amaya, 1994
Fresh tomato (in U.S.A.)	8.25–10.29	Tonucci et al., 1995
Red varieties:		Hart and Scott, 1995
Cherry	3.780	
'Large'	2.270	
'Salad'	2.547	
Flavourtop	5.653	
Tigerella	1.582	
Ida F1 hybrid	1.711	
Shirley F1	2.347	
Craig	3.907	
Moneymaker	4.255	
Allicanti	4.037	
Beefsteak	4.833	
Yellow varieties:		
Sungold	0.528	
Gold sunrise (in U.K.)	0.021	
Ohio-8245	9.65–10.21	Sharma and Le Maguer, 1996
92-7136	7.72–7.80	
92-7025	6.23–6.59	
H-9035	10.22–10.16	
CC-164 (in Canada)	10.64–10.76	

TABLE 3
Carotenoids of Regions of Tomato at Different Ripe Stage

Region of fruit	Number of days ripened				
	4	8	12	16	20
	Total carotenoids (mg/100 g)				
Outer pericarp	4.40	7.84	8.64	8.64	8.40
Inner pericarp	2.96	4.40	4.40	4.00	4.40
Locular contents	4.80	4.16	4.00	6.56	6.32
	Carotene (mg/100 g)				
Outer pericarp	0.23	0.23	0.18	0.18	0.26
Inner pericarp	0.22	0.12	0.15	0.18	0.39
Locular contents	0.69	0.71	0.60	0.57	0.55
	Total carotenoids/carotene				
Outer pericarp	15	34	47	47	23
Inner pericarp	14	37	30	22	11
Locular contents	7	6	7	12	12

Data from McCollum, 1955.

tene, and ξ-carotene. These contain no oxygen and are usually orange and red in color. Carotenoid species in the second class are the xanthophylls (e.g., β-cryptoxanthin, lutein, and zeaxanthin), which are oxygenated derivatives and contain one or more oxygenated group substituents at particular sites on the terminal rings. The two classes of carotenoids share common structural features, such as polyisoprenoid structure and a series of centrally located conjugated double bonds. In tomato fruits, more than 21 pigments in the carotenoid class have been identified and quantified. Lycopene is the principal hydrocarbon carotenoid in tomatoes with lesser amounts of α-carotene, β-carotene, γ-carotene, ξ-carotene, phytoene, phytofluene, neurosporene, and lutein (Gould, 1992). The distribution of main the carotenoid species in tomato fruits is listed in Table 4.

A. Physical Properties

The physical properties of lycopene are outlined in Table 5. In ripe tomato fruits, lycopene takes the form of elongated, needle-like crystals that are responsible for the typical bright-red color of ripe tomato fruits. Lycopene is more soluble in chloroform, benzene, and other organic solvents than in water.

B. Chemical Structure

The chemical structures of some principal carotenoid species in tomatoes are shown in Figure 1. Lycopene, a polyene hydrocarbon, an acyclic open-chain unsaturated carotenoid having 13 double bonds, of which 11 are conjugated double bonds arranged in a linear array, has a molecular formula of $C_{40}H_{56}$. Two central methyl groups are in the 1,6 position, while the remaining methyl groups are in the 1,5 position relative to each other. A series of conjugated double bonds constitutes a chromatophore of variable length. Color and antioxidant activities of lycopene are a consequence of its unique structure, an extended system of conjugated

TABLE 4
The Contribution of Carotenoid Species in Tomato Fruits

Carotenoid species	Composition %	Conjugated double bonds	In ring	Abs. λ_{max} (nm) in hexane
Lycopene	80–90	11	—	472(457, 485, 519)
α-carotene	0.03	9	1	444(319, 348, 366)
β-carotene	3–5	9	2	450(427, 450, 477)
γ-carotene	1–1.3	7	—	450(432, 461, 490)
ξ-carotene	1–2	7	—	400(378, 400, 425)
Phytoene	5.6–10	3	—	290(275, 286, 297)
Phytofluene	2.5–3.0	5	—	350(331, 348, 366)
Neurosporene	7–9	9	—	450(415, 438, 468)
Lutein	0.011–1.1	10	—	442(424, 446, 473)

Data from Gross, 1987.

TABLE 5
Physical Properties of Lycopene

Molecular formula	$C_{40}H_{56}$
Molecular weight	536.85 Da
Melting point	172–175°C
Crystal form	Long red needles from a mixture of carbon disulfide and ethanol
Powder form	Dark reddish-brown
Solubility	Soluble in chloroform, hexane, benzene, carbon disulfide, acetone, petroleum ether
	Insoluble in water, ethanol, methanol
Sensitivity	Light, oxygen, high temperature, acids

double bonds. Lycopene owes its ruby color to its extensively conjugated polyene structure. In nature, lycopene exists in 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. Lycopene has no provitamin A activity due to the lack of a β-ionone ring structure. Conversion of lycopene to β-carotene by chloroplasts was indicated by Hill and Rogers (1969). Stereoisomeric forms of lycopene were described with special reference to the properties of light absorption in relation to their molecular structures (Zechmeister, 1962). Lycopene is also very sensitive to light, heat, oxygen and acids in degradation, and some metallic ions such as Cu^{2+}, Fe^{3+} catalyze its oxidation.

C. Biochemical Properties

Lycopene, with its acyclic structure, large array of conjugated double bonds, and extreme hydrophobicity, exhibits many unique and distinct biological properties, including as an antioxidant. Lycopene is among the most efficient singlet oxygen quenchers of the natural carotenoids (Di Mascio et al., 1989; Conn et al., 1991). There are considerable differences in the quenching rate constants (Kq) for various carotenoid species (Table 6). Comparison of the structures of lycopene, γ-carotene, β-carotene reveals that the opening of the β-ionone ring increases its quenching ability. The antioxidant activities of lycopene and other carotenoids are highlighted by their singlet oxygen quench-

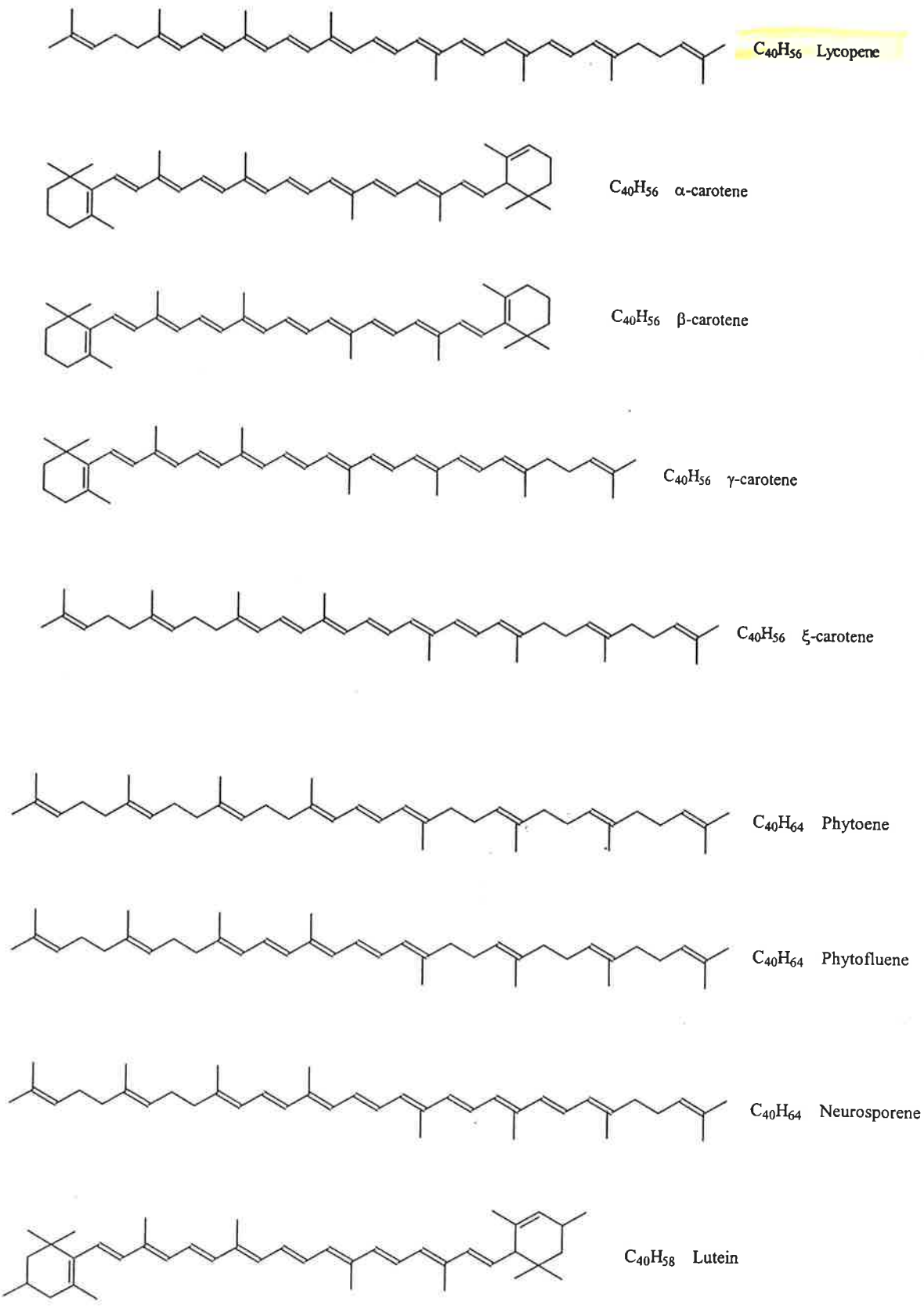


FIGURE 1. Molecular structures of carotenoid species in tomato fruits.

TABLE 6
Comparison of Antioxidant Activities of Carotenoids: Singlet Oxygen Quenching, Kq (m^{-1} s^{-1})

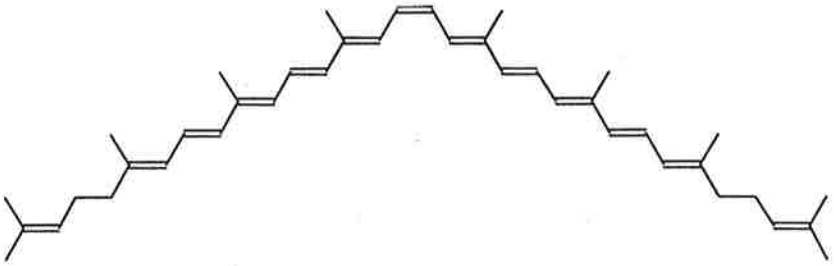
Lycopene	
Singlet oxygen quenching, $10^9 \times$ Kq (m^{-1} s^{-1})	31
Radical scavenging (Trolox equivalents)	2.9
Reaction of carotenoid radical anions with O_2, $10^8 \times k$ (m^{-1} s^{-1})	2
Other carotenoids' singlet oxygen quenching ($10^9 \times K_q$ (m^{-1} s^{-1})	
γ-carotene	25
α-carotene	19
β-carotene	14
Lutein	8
Astaxanthin	24
Bixin	14
Canthaxanthin	21
Zeaxanthin	10

Data from Di Mascio et al., 1989, 1991; Conn et al., 1991, 1992; Miller et al., 1996.

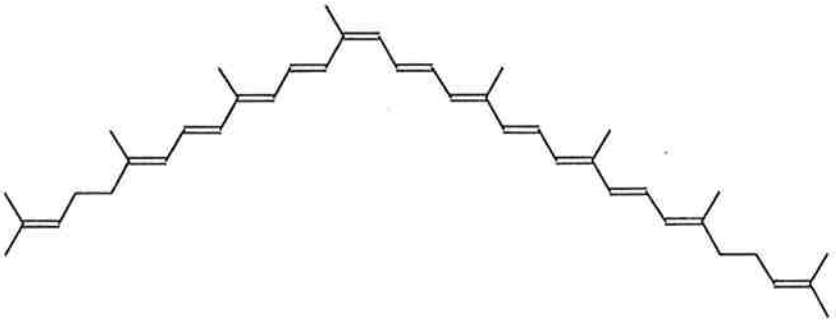
ing properties and their ability to trap peroxyl radicals (Foote and Denny, 1968; Burton and Ingold, 1984). The quenching activity of carotenoid species depends on the number of conjugated double bonds and is influenced to a lesser extent by carotenoid end groups or the nature of substituents in carotenoids containing cyclic end groups (Foote and Denny, 1968; Stahl et al., 1993).

Lycopene is known to exist in a variety of geometric isomers, including all-*trans*, mono-*cis*, and poly-*cis* forms. The all-*trans* isomer of lycopene is the most predominant geometrical isomer in fresh tomatoes and is the most thermodynamically stable form. However, lycopene can undergo *trans*-to-*cis* isomerization during tomato processing and storage. In various tomato-based foods, the all-*trans* isomer is comprised of 35 to 96% of total lycopene (Schierle et al., 1996). The 5-*cis*, 9-*cis*, and 15-*cis* isomers of lycopene have been identified in various tomato-based foods and human tissues by NMR spectroscopy (Zumbrunn et al., 1985). The proportion of 5-*cis*-isomer in tomato-based foods was 4 to 27%, with considerably lower amounts of other isomers (Schierle et al., 1996). The *cis*-isomers of lycopene contribute more than 50% to total lycopene in human serum and tissue (Krinsky et al., 1990). The structures of some *cis*-isomers of lycopene are shown in Figure 2. In general, *cis*-isomers are more polar than their all-*trans* counterparts and are less prone to crystallization due to their kinked forms. The *cis*-isomers are also more soluble in oil and hydrocarbon solvents than all-*trans* isomers. The potency of bioactivity of *cis*-isomers is changed, compared with the all *trans*-isomers, because of the changes in structural shapes.

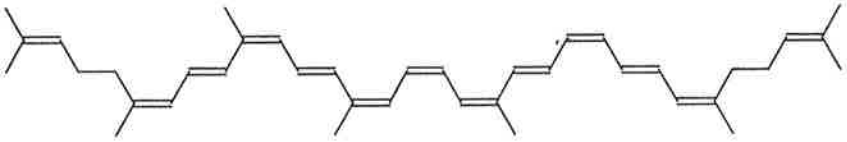
Most stability studies on lycopene in food systems concern degradation. Lycopene may be partially destroyed in processed tomato products by heating in the presence of metallic ions (Cu^{2+}, Fe^{3+}, etc.) or oxygen. Lycopene, as a conjugated polyene, may be expected to undergo at least two changes during tomato processing, isomerization and oxidation. Lycopene isomerizations have been shown to take place both in tomato products and in pure lycopene forms and can take place during processing. On the other hand, the conversion of *cis*-isomer to *trans*-form is



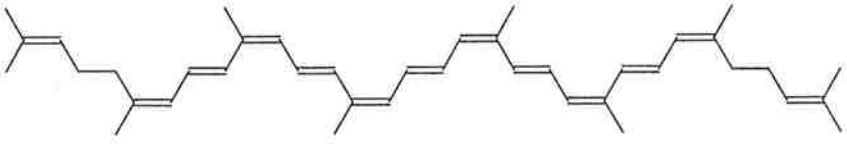
Central - mono *cis*-lycopene (15-*cis*)



next-to-central-mono *cis*-lycopene (13- *cis*)



5- *cis*-lycopene



6- *cis*-lycopene

FIGURE 2. The chemical structures of *cis*-isomers of lycopene.

another reaction that can occur during the product storage. *Cis*-isomers are in the unstable, whereas *trans*-isomers are in the stable ground state.

Lycopene as an efficient antioxidant quenches highly reactive singlet oxygen ($O_2^{\cdot-}$) and traps peroxyl radicals (ROO.). Lycopene-oxygen radical interactions can be considered as second-order rate reaction. Lycopene is less efficient and electron transfer is observed in both directions (Conn et al., 1992). The potential reduction is related to the formation of the superoxide radical anion, $O_2^{\cdot-}$ (Palozza, 1998).

$$L\text{–}C + ROO^{\cdot-} \rightarrow L\text{–}C^{\cdot} + ROOH$$
$$L\text{–}C + ROO^{\cdot-} \rightarrow L\text{–}ROO\text{–}C^{\cdot-}$$

It is also possible to form peroxyl radical capable of acting as a prooxidant and undergoes autoxidation. The proposed degradation pathway of lycopene is shown in Figure 3A,B. The oxygen functions seem to be introduced by reactions of two main types: (1) substitution of a methyl or methylene group, and (2) addition to a carbon-carbon double bond. Apparently, oxidative degradation can also occur at both ends of the normal C40-carbon skeleton. On the basis of widely accepted nomenclature rules, a degraded product that does not retain the C20 and C20' methyl groups of the original C40 structure is no longer a carotenoid. While lycopene degradation occurs, the final products obtained are the results of direct oxidative scission at the sites of double bonds in the molecules.

IV. IMPORTANCE OF LYCOPENE IN THE HUMAN DIET

A. Benefit for Human Health–Clinical Case Studies

There has been a growing interest in investigating the ability of lycopene to act as a preventative agent for cancers. Three major directions of research have emerged: (1) epidemiological studies with patients with various malignancies, (2) experiments studying the direct effect of lycopene on tumor proliferation in cell lines and in animal models, (3) studies on the putative biochemical or immunological mechanisms of lycopene action (Levy et al., 1995). Recent interest in the consumption of lycopene-rich foods as a means of reducing the risk of cancer has prompted researchers to investigate the level of lycopene in foods frequently consumed by people. Although it has no provitamin A activity, lycopene is able to function as an antioxidant and exhibits a physical quenching rate constant with singlet oxygen *in vitro*. The quenching constant of lycopene was found to be more than double that of β-carotene and 10 times more than that of α-tocopherol, which makes its presence in the diet of considerable interest (Di Mascio et al., 1989, 1991; Conn et al., 1991; Devasagayam et al., 1992; Ribaya-Mercado et al., 1995). The ability of lycopene to function as an antioxidant may contribute to a reduction in disease risk (Sies et al., 1992). Increasing clinical evidence supports the role of lycopene as an important micronutrient, because it appears to provide protection against prostate cancer, lung cancer, and a broad range of epithelial cancers (Micozzi et al., 1986; Olson, 1986; Levy et al., 1995).

The serum level of lycopene and the dietary intake of tomatoes has been inversely correlated with the incidence of cancer (Helzlsouer et al., 1989; Van Eenwyk et al., 1991). A study in Italy with 2706 cases of cancer of the oral cavity and pharynx, esophagus, stomach, colon, and rectum matched with 2879 controls showed that protection for all sites of digestive-tract cancers was associated with an increased intake in tomato-based food (Franceschi et al., 1994). The correlation between consumption of tomatoes and the diminished cancer risk was related to an increased supply of lycopene.

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$$L\text{–}C + ROO^{\cdot -} \rightarrow L\text{–}ROO\text{–}C^{\cdot -}$$

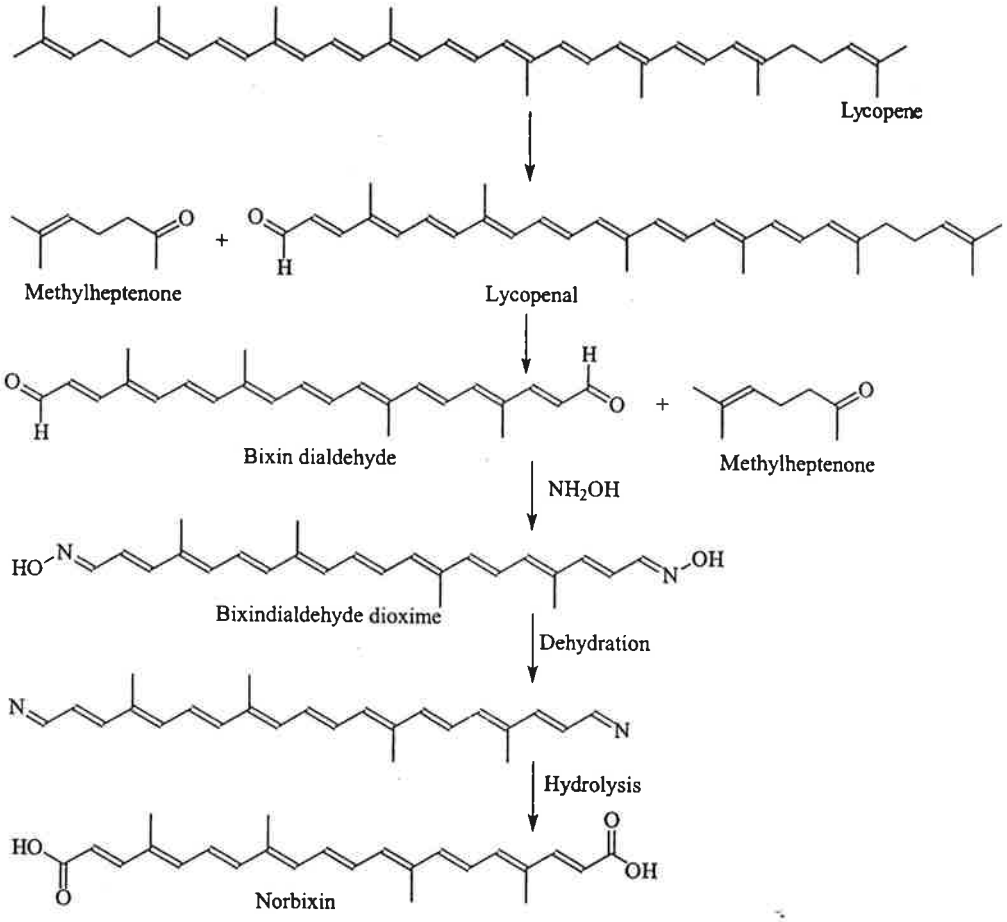
It is also possible to form peroxyl radical capable of acting as a prooxidant and undergoes autoxidation. The proposed degradation pathway of lycopene is shown in Figure 3A,B. The oxygen functions seem to be introduced by reactions of two main types: (1) substitution of a methyl or methylene group, and (2) addition to a carbon-carbon double bond. Apparently, oxidative degradation can also occur at both ends of the normal C40-carbon skeleton. On the basis of widely accepted nomenclature rules, a degraded product that does not retain the C20 and C20' methyl groups of the original C40 structure is no longer a carotenoid. While lycopene degradation occurs, the final products obtained are the results of direct oxidative scission at the sites of double bonds in the molecules.

IV. IMPORTANCE OF LYCOPENE IN THE HUMAN DIET

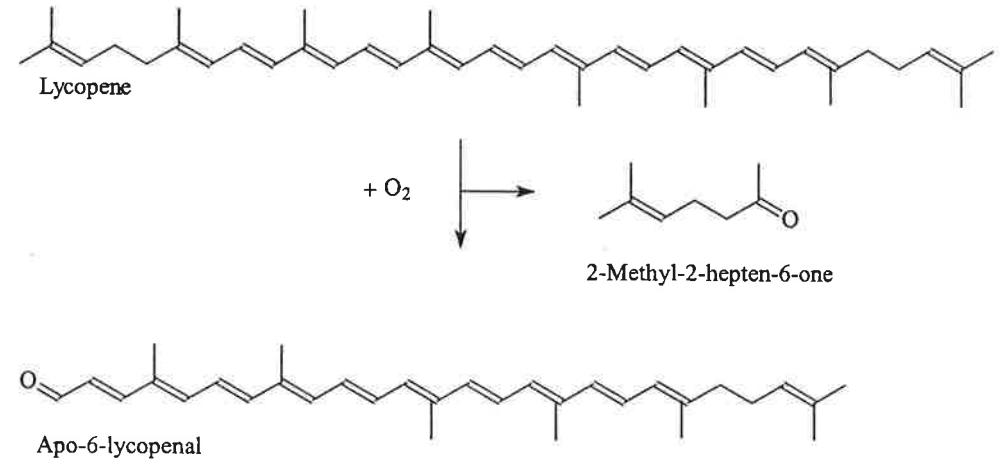
A. Benefit for Human Health–Clinical Case Studies

There has been a growing interest in investigating the ability of lycopene to act as a preventative agent for cancers. Three major directions of research have emerged: (1) epidemiological studies with patients with various malignancies, (2) experiments studying the direct effect of lycopene on tumor proliferation in cell lines and in animal models, (3) studies on the putative biochemical or immunological mechanisms of lycopene action (Levy et al., 1995). Recent interest in the consumption of lycopene-rich foods as a means of reducing the risk of cancer has prompted researchers to investigate the level of lycopene in foods frequently consumed by people. Although it has no provitamin A activity, lycopene is able to function as an antioxidant and exhibits a physical quenching rate constant with singlet oxygen *in vitro*. The quenching constant of lycopene was found to be more than double that of β-carotene and 10 times more than that of α-tocopherol, which makes its presence in the diet of considerable interest (Di Mascio et al., 1989, 1991; Conn et al., 1991; Devasagayam et al., 1992; Ribaya-Mercado et al., 1995). The ability of lycopene to function as an antioxidant may contribute to a reduction in disease risk (Sies et al., 1992). Increasing clinical evidence supports the role of lycopene as an important micronutrient, because it appears to provide protection against prostate cancer, lung cancer, and a broad range of epithelial cancers (Micozzi et al., 1986; Olson, 1986; Levy et al., 1995).

The serum level of lycopene and the dietary intake of tomatoes has been inversely correlated with the incidence of cancer (Helzlsouer et al., 1989; Van Eenwyk et al., 1991). A study in Italy with 2706 cases of cancer of the oral cavity and pharynx, esophagus, stomach, colon, and rectum matched with 2879 controls showed that protection for all sites of digestive-tract cancers was associated with an increased intake in tomato-based food (Franceschi et al., 1994). The correlation between consumption of tomatoes and the diminished cancer risk was related to an increased supply of lycopene.



A



B

FIGURE 3. Schematic of proposed reaction pathways of lycopene degradation. (A) Proposed pathways of lycopene degradation. (Modified from Karrer and Jucker, 1950.) (B) Proposed pathway of the formation of apo-6-lycopenal and 2-methyl-2-hepten-6-one from lycopene during photosensitization. (Modified from Ukai *et al.*, 1994.)

The intake of lycopene has been found to be associated with a reduced risk of cancers of other sites, such as the digestive tract, pancreas, and bladder (Gerster, 1997). A study released by the University of Milan suggested that people who ate at least one serving of a tomato-based product per day had a 50% less chance of developing digestive tract cancer than those who did not eat tomatoes (Franceschi et al., 1994). A study conducted at the Harvard University found that older Americans who regularly eat tomatoes were less likely to die from all forms of cancer (Colditz et al., 1985). A scientific report from Harvard School of Public Health suggested that men who ate 10 or more servings per week of tomato products, including tomatoes, tomato sauce, and pizza sauce, were up to 34% less likely to develop prostate cancer (Giovannucci et al., 1995). This study monitored dietary habits and the incidence rate of prostate cancer in 48,000 men for 4 years and assessed over 46 different fruits and vegetables and related products on the basis of their consumption frequency. Tomato sauce was most strongly associated with a lower risk of prostate cancer. The protective effects were even stronger when the analysis focused on the risk of more advanced or aggressive prostate cancer.

Lycopene has been reported to increase the survival rate of mice exposed to X-ray radiation (Forssberg et al., 1959). Ribaya-Mercado et al. (1995) reported the protective effects of lycopene toward oxidative stress-mediated damage of the human skin after irradiation with UV light. Peng et al. (1998) examined the levels of different carotenoids, including lycopene, and vitamins A and E in plasma and cervical tissues obtained from 87 women subjects (27 cancerous, 33 precancerous, and 27 noncancerous). Women with cancer had lower plasma levels of lycopene, other carotenoids, vitamin A and E compared with pre- and noncancerous women. The results indicate that women who have high levels of lycopene are less likely to suffer from cervical cancer than those having lower lycopene levels in their body. In the study of Goodman et al. (1998) involving 147 confirmed cervical cancer patients and 191 noncancerous subjects, only lycopene was found to be significantly lower in cancerous patients. Kanetsky et al. (1998) studied non-Hispanic, black women, involving 32 women with cervical cancer and 113 noncancerous women and measured the micronutrient levels in the blood. It was found that women with higher levels of blood lycopene had consumed higher levels of lycopene and vitamin A and had one-third less chance of developing cervical cancer.

Riso et al. (1997) concluded that the consumption of tomato-based foods may reduce the susceptibility of lymphocyte DNA to oxidative damage. Lycopene has a preventive effect on atherosclerosis by protecting plasma lipids from oxidation. Lower blood lycopene levels were also associated with increased risk of coronary heart disease according to studies with Lithuanian and Swedish people (Kristenson et al., 1997). Kohlmeir et al. (1997) measured the relationship between antioxidant levels and acute heart disease in a case study of people from 10 different European countries. It was found that the consumption of lycopene in fruits and vegetables may reduce the likelihood of developing heart disease. Lycopene prevents oxidation of low-density lipoprotein (LDL) cholesterol and reduces the risk of developing atherosclerosis and coronary heart disease (Agarwal and Rao, 1998). Rao and Agarwal (1998) suggested daily consumption of tomato products providing at least 40 mg of lycopene was enough to substantially reduce LDL oxidation. This lycopene level can be achieved by drinking just two glasses of tomato juice a day.

Inhibition of cancer cell growth by lycopene has been demonstrated extensively in tissue culture experiments. Wang et al. (1989) studied an *in vivo* model of glioma cells transplanted in rats and showed that lycopene was as effective as β-carotene in inhibiting the growth of the glioma cells. Tissue

samples taken from the Breast Cancer Serum Bank in Columbia, Missouri, were analyzed to evaluate the relationship between carotenoid level (including lycopene), selenium, and retinol and breast cancer (Dorgan et al., 1998). Only lycopene was found to reduce the risk for developing breast cancer. Other carotenoids did not reduce the risk of breast cancer. In cell culture studies, lycopene's activities in inhibiting breast cancer tumors were compared with those of α- and β-carotene using several human cancer cells (Levy et al., 1995). It was found that the cell cultures that were enhanced with lycopene had inhibited growth of breast cancer cells (MCF-7), and that α- and β-carotene were far less effective growth inhibitors than lycopene.

From mechanistic studies, two possible functions of lycopene have been proposed. Lycopene is recognized to be the most efficient singlet oxygen quencher among biological carotenoids (Di Mascio et al., 1989, 1991). Antioxidant functions are associated with lowering DNA damage, malignant transformation, and reducing biological oxidative damage of proteins, lipids, and other cell components *in vitro*. Lycopene has also been found to increase gap-junctional communication between cells and to induce the synthesis of connexin-43 (Zhang et al., 1992). Loss of gap-junctional communication may be important for malignant transformation, and its restoration may reverse the malignant process. Further studies are required to gain a better understanding of the role of lycopene in human health.

B. Lycopene Bioavailability (Absorption) in Foods

In addition to knowing the amount of lycopene present in a food, it is important to know the bioavailability with respect to the absorption in the human body. Bioavailability is defined as the fraction of an ingested nutrient that is available to the body through absorption for utilization in normal physiological functions and for metabolic processes (Macrae et al., 1993; Jackson, 1997). The U.S. FDA definition of bioavailability of a drug is "the rate and extent to which the active substances or therapeutic moiety is absorbed from a drug product and becomes available at the site for action" (Benet and Shiner, 1985). The concept of bioavailability of a nutrient has a close relationship with the estimate of bioavailability of pharmaceutical compounds. The absorption of lycopene in the human diet is reported to be highly variable and can be affected by a number of dietary factors and food properties. These factors include molecular linkage, amount of lycopene consumed in a meal, food matrix in which the lycopene is incorporated, co-ingestion of high amounts of dietary fiber, co-ingestion of fat as a delivery medium, effects of absorption and bioconversion, interaction of lycopene with other carotenoids and nutrient components, dietary protein content, xanthophyll and chlorophyll contents, the particle size of the material, and genetic factors (Deshmukh and Ganguly, 1964; Kemmerer et al., 1974; Jayaarahan et al., 1980; Rock and Swendseid, 1992; Bowen et al., 1993; Erdman et al., 1993; Olson, 1994; De Pee et al., 1996; Parker, 1996; Castenmiller and West, 1998; Dimitrov et al., 1988). Other characteristics that can influence lycopene absorption are lycopene location in the food matrix (lycopene-protein complexes of cell chloroplasts vs. the crystalline form in chromoplasts) and the presence of factors that interfere with proper micelle formation (Rock and Swendseid, 1992; Erdman et al., 1993).

1. Effect of Trans *and* Cis*-Isomer Forms*

Lycopene is the most predominant carotenoid in human plasma and has a half-life of about 2 to 3 days in the human body (Stahl and Sies, 1996). In human plasma, lycopene is an isomeric mixture containing 50% of the total lycopene as *cis*-isomers.

There are some indications of *in vivo trans* to *cis* isomerization reactions (Sakamoto et al., 1994). Very little is known about the *in vivo* metabolism of lycopene. Boileau et al. (1999) demonstrated that *cis*-isomers of lycopene are more bioavailable than *trans*-form probably because *cis*-isomers are more soluble in bile acid micelles and may be preferentially incorporated into chylomicrons. It was suggested that *cis*-isomers of lycopene may be better absorbed than their all-*trans* parent structure (Britton, 1995; Stahl and Sies, 1996). This may be the result of greater solubility of *cis*-isomers in mixed micelles, possibly preferential incorporation into chylomicrons, and a lower tendency of *cis*-isomers to aggregate. Lycopene from heat-processed tomato juice (*cis*-isomers) is absorbed more easily than lycopene from unprocessed juice (*trans*-isomers). With the different geometrical isomers of lycopene, the *cis*-isomers (5-*cis*, 9-*cis*, 13-*cis*, 15-*cis*) are better absorbed than the all-*trans* form by the human body (Stahl and Sies, 1992). *Cis*-isomers are less likely to crystallize, are more efficiently solubilized in lipophilic solutions, and are more readily transported within cells or in the tissue matrix. Although processed tomato products (juice, paste, soup, ketchup, or dehydrated tomato slices) originally contained a low percentage of *cis*-isomers, the concentration of *cis*-isomers, can be increased by processing. Lycopene exists in both human and animal tissues as 50% *cis*-isomers because this mixture is the most stable and represents an equilibrium between *trans*- and *cis*-isomers (Boileau et al., 1999). Heat treatment promotes isomerization of lycopene in foods, from *trans* to *cis* isomeric forms. The degree of isomerization is directly correlated with the intensity and duration of heat processing (Schierle et al., 1996; Shi et al., 1999).

2. Effect of Food Matrix

The composition and structure of food have an impact on the bioavailability (absorption) of lycopene, which may affect the release of lycopene from the tomato tissue matrix. Cooking or fine grinding of foods could increase the bioavailibility of lycopene by disrupting or softening plant cell walls and disrupting lycopene-protein complexes (Hussein and El-Tohamy, 1990). Giovannucci et al. (1995) compared the differences in lycopene bioavailability from fresh tomatoes with processed tomato products, and found the lycopene serum concentration was greater when consuming heat-processed tomato-based foods than unprocessed tomatoes. It was also found that 20 to 30% of total lycopene consisted of *cis*-isomers when tomatoes were heated at 100°C for 1 h (Stahl and Sies, 1992). Gartner et al. (1997) found that lycopene bioavailability from paste and processed tomato juice was significantly higher than from unprocessed fresh tomatoes. This fact could be attributed to a lower availability of lycopene from the raw material where it is probably bound in the matrix. Thermal processing such as cooking and mechanical texture disruption such as chopping are convenient ways to enhance bioavailability by breaking down sturdy cell wall structures, disrupting chromoplast membranes, and reducing cellular integrity, thus making lycopene more accessible. The food matrix (i.e., the lipid and other constituents of chromoplasts as well as the fiber contained within the tomato fruits) may contribute greatly to the stability of the all-*trans* form of lycopene in the fruits. This is supported by the observation that when whole tomatoes are heat processed, and isomerization is noted. For example, tomato sauce and tomato paste contain about 90% *trans*-isomers (Clinton et al., 1996; Nguyen and Schwartz, 1998). The food matrix that surrounds lycopene when it is present within the tomato seems to prevent this isomeric equilibrium from occurring.

3. Effect of Oil Medium

Lycopene bioavailability from tomato-based food is significantly higher than from fresh tomatoes when co-ingested with oil.

Ingestion of tomato juice cooked in an oil medium resulted in a two- to threefold increase in lycopene serum concentrations 1 day after ingestion, but an equivalent consumption of unprocessed tomato juice caused no rise in plasma concentration (Stahl and Sies, 1992). This indicated that thermal treatment and an oil medium are required to extract lycopene into the lipophilic phase. It was assumed that heating tomato juice in the presence of corn oil for 1 h converts lycopene from *trans* to *cis* form, thereby increasing its absorption by the body (Stahl and Sies, 1996).

4. Effect of Dietary Fibers

Various types of dietary fiber were found to reduce the bioavailability of carotenoids in foods (Erdman et al., 1986). Matrix effects were proposed as an explanation for the lack of improvement in vitamin A status in Indonesian women fed green leaf vegetables compared with a manufactured wafer containing a similar amount of carotene in oil solution (De Pee et al., 1995). Rock and Swendseid (1992) tested the inhibitory effect of pectin, a typical dietary fiber, and their results showed that this type of dietary fiber affected the absorption of dietary carotenoids in humans. High-methoxyl pectin is especially associated with the hypocholesterolemic effect of dietary fibers and low absorption of lycopene because of promoting high-viscosity conditions

5. Carotenoid Interaction

In principle, interactions between carotenoids might occur at various stages of the absorption process, especially in high-dose conditions. Absorption of lycopene seemed to be more efficient at lower dosages, and lycopene ingested with β-carotene was absorbed more than when ingested alone (Johnson, 1997). Lycopene can undergo an *in vivo* isomerization mechanism. Van Vliet et al. (1996) carried out the dioxygenase assay with β-carotene as substrate both alone and together with increasing amounts of lutein or lycopene and found that lutein lowered retinal formation from β-carotene, while lycopene had no effect. Prince et al. (1991) reported a strong decrease in serum lycopene levels after high-dose β-carotene supplementation, whereas another high-dose supplementation study found a decrease in LDL lycopene content (Gaziano et al., 1995). Evidence for carotenoid interactions during absorption has been reported in ferrets, in which either canthaxanthin or lycopene reduced the 0 to 24 h plasma β-carotene response when compared with the administration of β-carotene alone (White et al., 1993; Kostic et al., 1995). The importance and mechanism of carotenoid interactions need to be better characterized.

6. Enhancement of Lycopene Bioavailability

Lycopene plasma levels increased significantly in human serum when processed juice was consumed, compared with unprocessed tomato juice. Boiling for 1 h in the presence of 1% corn oil increased the bioavailability of lycopene from tomato juice significantly (Stahl and Sies, 1992). The bound chemical form of lycopene in tomatoes is converted by the temperatures during processing, which makes it more easily absorbable by the body. These results suggest that food processing may improve the availability of lycopene in tomato-based foods for absorption. Gartner et al. (1997) pointed out that heat treatment can improve the bioavailability of lycopene without significantly changing the *cis*-isomer composition of the heat-treated foods. The lycopene bioavailability from tomato-based foods may be enhanced in two ways: extraction of lyco-

pene from the food matrix into the lipophilic phase (Brown et al., 1989; Zhou et al., 1996), and thermal processing and mechanical disruption of tomato tissue cells. Heat treatment leads to an increased bioavailability of vegetable carotenoids after cooking. Stahl and Sies (1992) reported that heat treatment of tomato juice at 100°C for 1 h resulted in 20 to 30% *cis*-isomers in the serum of humans who drank the juice. They also concluded that the *cis*-isomers were absorbed slightly better or were metabolized to a lesser extent than all-*trans* lycopene. It has now been generally accepted that lycopene in a lipid medium is more bioavailable than in fresh tomatoes. Cooking and reduction of particle size by grinding or homogenization can also reduce the matrix effect. However, because thorough destruction of the matrix, for example, by extensive cooking, could also destroy lycopene, optimum processing technology parameters should be found to maximze destruction of the matrix and minimize the destruction of lycopene. Taking into account the disintegration of tomato tissue and induction of *trans*-to-*cis* isomerization during processing, possible mechanisms include the release of lycopene by thermal processing that induces the disruption of the tomato tissue structure and cell walls, change of the bonding forces between lycopene and tissue matrix, dissociation or weakening of protein-carotenoid complexes, the dissolution or dispersion of crystalline carotenoid complexes, and heat-improved extraction of lycopene into the oily phase of the mixture, using oil as vehicle. The effect of food processing on lycopene bioavailability is shown in Table 7.

Current information on lycopene bioavailability is limited. The pharmacokinetic properties of lycopene remain especially poorly understood. The lack of the knowledge of how lycopene functions in the human body and inadequate indicators have made it difficult to establish a clear and sound bioavailibility pattern of lycopene in foods. At the present time, there are few validated methods for the quantitative assessment of bioavailability of lycopene and other carotenoids from food sources. The use of plasma density fractions enriched in chylomicrons may be useful in determining the relative efficiency of the absorption of carotenoids, particularly if low doses can be accommodated and proportionality between the dose and response is demonstrated (Parker, 1996). Further research on the bioavalability, pharmacology, biochemistry, and physiology need to be done to reveal the mechanism of

TABLE 7
Comparation of Lycopene Absorption after Ingestion of Fresh Tomatoes and Tomato Paste (μmol.h/l)

	Fresh tomatoes		Tomato paste		
	AUC (0–12 h)	C_{max}	AUC (0–12 h)	C_{max}	Gartner et al., 1997
Total lycopene	28.4 ± 1.7	11.0 ± 3.6	109.3 ± 26.6	27.9 ± 9.3	
All-*trans*-isomers	22.6 ± 11.1	7.5 ± 2.0	79.5 ± 18.8	20.1 ± 6.1	
Cis-isomers	7.3 ± 4.9	3.4 ± 2.8	29.9 ± 8.5	7.8 ± 3.4	
	AUC (0–104 h)		AUC (0–104 h)		Porrini et al., 1998
Total lycopene	38.6		31.6		
All-trans-isomers	24.8		22.5		
Cis-isomers	13.7		9.1		

Note: AUC, area under curve response, C_{max}, peak concentrations in chylomicrons after ingestion.

lycopene in the human diet, and the *in vivo* metabolism of lycopene.

V. ANALYSIS OF LYCOPENE FROM TOMATO SAMPLES

The determination of the lycopene content in tomatoes and tomato-based foods can be carried out by physical and chemical methods. Physical methods are based on the relation of color parameters with lycopene concentration of the samples. In chemical analysis, lycopene is extracted from the tomato tissue and quantified.

A. Nondestructive Measurement: Color Index Method

Color evaluations of processed tomatoes traditionally has been presented as Hunter L*, a*, b* values. Yeatman (1969) indicated that the value b*L*/a* provided a high linear correlation with visual color scores of processed tomato products. Deep-red tomato fruits are processed into some products with a high degree of color, which contain high concentrations of lycopene. Because color is an important quality factor, color measurement has been a convenient means to describe the quality of tomato products. The deterioration in color quality may be due to loss of natural pigment or the introduction of off-shades as a result of nonenzymic browning, which affects the final color of tomato products. The effect of these changes is a lessening of visible color intensity. There are relatively few studies that examine the effects of processing conditions on the qualitative and quantitative distribution of lycopene that may be used as major quality indexes in tomato processing.

Nondestructive, external measurement of tomato fruit color provides a less tedious method for assessing ripening than the chemical analysis of pigments. Measurement of color is closely related to visual perception in tomatoes (Shewfelt et al., 1988). Edwards et al. (1983) correlated the lycopene content of pericarp disks with the ratio of reflectance at 550 and 650 nm for pericarp puree. The nondestructive measurement of chromaticity values with a colorimeter would be useful if it could accurately estimate lycopene concentration of tomato samples after harvest and processing. It can provide a quick, precise, nondestructive, on-line technique to determine the lycopene content in tomato products for tomato processing industry applications. D'Souza et al. (1992) developed regression equations to describe the relationship between chromaticity values determined nondestructively and lycopene concentration in tomato skin disks and pericarp plugs. Although their model did not predict lycopene concentrations accurately enough to substitute entirely for chemical extraction analysis, it may be useful for estimating lycopene concentration, especially on-line quality monitoring during the tomato processing.

B. Extraction of Lycopene for Chemical Analysis

Because lycopene is liposoluble, it is usually extracted with organic solvents such as chloroform, hexane, acetone, benzene, petroleum ether, or carbon disulfide, prior to chemical analysis for quantitative determination. In cases where solvent extraction may be slow and incomplete, the efficient mechanical grinding of the tomato material can be used to facilitate complete extraction. Dehydrated material may be extracted with water-immiscible solvents. Moistening of dehydrated material prior to solvent extraction is often necessary to get complete extraction. However, the extraction processing is more commonly carried out with moist samples or fresh material. Extraction methods for lycopene in general tend to be time-

consuming procedures and prone to error due to oxidation and losses in extraction. The conjugated double bonds of lycopene cause them to be unstable components, especially sensitive to light, heat, oxygen, and acids. Extractions done in the laboratory should be carried out in dim lighting, and in an inert atmosphere. Heating of the lycopene solution should be kept to a minimum. To avoid oxidation and isomerization of lycopene during the extraction process, antioxidants such as quinol and neutralizing agents such as calcium carbonate, pyridine, or dimethylaniline may be added. The extracted sample should be stored in the dark under nitrogen in the freezer (-20°C).

After extraction, a saponification step is the most effective method of removing unwanted lipids, chlorophylls, and other impurities. This procedure does not affect lycopene because it is generally alkali stable. Further purification of the fractions is carried out, and eventually a crystallizable lycopene product can be obtained by fractional crystallization from petroleum ether or acetone at low temperature. Some rapid, efficient extraction methods for lycopene analysis and identification have been developed involving microwave solvent extraction, and in pressurized accelerated solvent extraction technologies in which the lycopene recoveries from tomatoes ranged from 98 to 99.6% (Sadler et al., 1990; Benthin et al., 1999).

C. Spectrophotometer Method

Traditionally, lycopene concentration in tomatoes have been determined accurately in the laboratory by spectrophotometric measurements. Edwards and Lee (1986) studied two solvents (acetone and methanol) as well as several extraction methods and obtained great differences in the measured carotene concentration. Now most experiments use hexane and acetone for the extraction of lycopene from tomato tissue and measure the OD at 460 to 470 nm (Lovric et al., 1970; Mencarelli and Saltveit, 1988; Tan and Soderstorm, 1988). A pure lycopene sample is necessary for the preparation of calibration curves.

D. HPLC Method

Chromatographic separation of lycopene is the best choice for analysis and identification of lycopene, including *trans-cis* stereoisomeric sets. These methods include column chromatography, thin-layer chromatography, paper chromatography, gas chromatography, and high-performance-liquid chromatography (HPLC), using several types of adsorbents and mobile phases. The widely used chromatographic procedure for the determination of lycopene and other carotenoids such as the AOAC method (AOAC, 1995) fails to separate the *cis*-isomers from all-*trans* isomers. Both normal phase and reversed phase HPLC methods have been used to separate and quantitate provitamin A carotenoids in fruits and vegetables (Chandler and Schwartz, 1987, 1988; Quackenbush, 1987; Saleh and Tan, 1988; Godoy and Rodriguez-Amaya, 1989). Reversed phase HPLC methods utilizing C_{18} stationary phases allow for the partial separation and detection of *cis* and *trans* isomers of provitamin A carotenoids. Recently, some rapid, highly efficient HPLC methods have been developed and studied extensively to isolate lycopene and its isomers from tomatoes and tomato-based foods with minimum oxidation and isomerization (Schwartz and Patroni-Killam, 1985; Bureau and Bushway, 1986; Daood et al., 1987; Zonta et al., 1987; Craft et al., 1990; Sadler et al., 1990, Stahl and Sies, 1992; Emenhiser et al., 1995; Clinton et al., 1996; Schierle et al., 1996; Gartner et al., 1997; Nguyen and Schwartz, 1998; Shi et al., 1999). A polymeric C_{30} stationary phase has been developed that can efficiently separate the geometric isomers (Sander et al.,

TABLE 8
Quantitative HPLC Determination of Lycopene in Fresh Tomatoes and Tomato Products

Extraction	HPLC Column	Mobile phase/detector	Ref.
150 g tomato paste with 750 ml ethanol (95%), filter cake was refluxed with petroleum ether for 5 min at 48°C	250 × 46 mm Microsorb ODS column, with a 15 × 32 mm guard column cartridge	Acetonitrile/methylene chloride/ chloroform (70:20:10), flow rate 2 ml/min, UV at 450 nm	Tan, 1988
4 g tomato puree with 100 ml hexane/ethanol/acetone (50:25:25)	Analytichem C_{18} (5 μ) column (250 × 4.6 mm) with a Supelguard LC-18 guard column	Methanol/tetrahydrofuran/water (67:27:6), flow rate 2 ml/min UV at 475 nm	Sadler et al., 1990
5–30 g tomato puree with 100 ml of tetrahydrofuran, stabilized with butylated hydroxytoluene (0.01%), saponified with saturated methanolic potassium hydroxide	5-μm column Spheri-5-RP-18 or Spheri-5-ODS column, (220 × 4.6 mm), with a guard column of Aquapore ODS type RP-18 (145 × 3.2 mm, 7 μm)	Acetonitrile/dichloromethane/methanol (70:20:10), flow rate 1.8 ml/min UV at 450 nm	Granado et al., 1992
50 g tomato puree in 500 ml tetrahydrofuran	A stainless (250 × 4.6 mm i.d.) Microsorb C_{18} (5-μm spherical particles) column, with a Brownlee guard cartridge (30 × 4.6 mm i.d.)	Acetonitrile/methanol/dichloromethane/ hexane (45:10:22.5:22.5), flow rate 0.7 ml/min, UV at 470, 455 nm	Khachik et al., 1992
5 ml tomato juice in 200 ml hexane-dichloromethane solution (5:1)	5-μm RP 18 endcapped column (4 × 250 mm)	Methanol/acetonitrile/dichloromethane/ water (7:7:2:0.16), flow rate 1 ml/min UV at 460 nm	Stahl and Sies, 1992
10 g tomato puree + 300 ml petroleum ether (PE)	μ Bondapak C_{18} column (10 μm, 150 × 19 mm, i.d.) and Zorbax ODS (5–6 μm, 250 × 4.6 mm, i.d.) column, with a C_{18} guard column (10 μm, 50 × 4.9 mm i.d.)	Acetonitrile/dichloromethane/methanol (45:10:45), flow rate 2 ml/min, UV at 470 nm	Hakala and Heinonen, 1994
Tomato puree in 500 ml tetrahydrofuran solvent (10% of tomato puree)	A stainless steel Microsorb-MV C_{18} column (250 × 4.6 mm i.d.), with Brownlee C_{18} guard column	Acetonitrile/methanol/methylene chloride/hexane (40:20:20:20), flow rate 0.7 ml/min, UV at 450 nm	Tonucci et al., 1995

Tomato sample containing 2.5 mL of distilled water and ethanol (containing 2% butylated hydroxytoluene) was extracted by addition of 5 ml of 10% NaOH in methanol (30 min at 60°C)	Polymeric C_{30} reversed phase columns (250 × 4.6 mm)	Methyl-*t*-butyl ether/methanol (38:62), flow rate 1 ml/min, UV at 460 nm	Clinton et al., 1996
30 g puree, 30 ml deionized water, 1 g calcium carbonate, 1 g Celite, 25 mL methanol, homogenized and filtered, then extraction in 25 ml methanol, filter cake in 50 ml of acetone/hexane (50:50), repeated	A polymeric 5 µm C_{30} stationary phase (250 × 4.6 mm i.d.) column, with a self-packed 3 µm C_{30} guard column	Methanol/methy *tert*-butyl ether (89:11), flow rate 1 ml/min UV at 410 nm	Lessin et al., 1997
1–2 g tomato concentrate in 30 ml acetone	Three 250 × 4.6 mm column packed with Nucleosil 300-5	Hexane/0.15% *n*-ethyldiisopropylamine, flow rate 1 ml/min, UV at 471 nm	Schierle et al., 1997
10 g puree mixed with 50 ml methanol, 1 g $CaCO_3$, and 3.0 g Celite, then extracted with acetone/hexane solution (1:1), saponified with 30% KOH for 60 min	Analytical 3-µm polymeric C_{30} column (250 × 4.6 mm i.d.)	Methyl-*t*-butyl ether/methanol (40:60), flow rate 1 ml/min, UV at 200–800 nm	Nguyen and Schwartz, 1998
2 g tomato sample is extracted with tetrahydrofuran solution, using butylated hydroxytoluene as antioxidant	5 µm Vydac 201 TP 54 C_{18} column (250 × 4.6 mm, i.d.), fitted with C_{18} guard column	Methanol/tetrahydrofuran (95:5), flow rate 1 ml/min, UV at 445 nm	Porrini et al., 1998
Tomato product with hexane/methylene chloride solution (5:1), containing 0.015% butylated hydroxytoluene as antioxidant	Vydac 201HS54 reversed phase C_{18} column	Acetonitrile/methanol/methylene chloride/water (7:7:2:0.16), flow rate 1 mL/min, UV at 470 nm	Rao and Agarwal, 1998
10 g tomato puree in 100 ml hexane/acetone/ethanol solution (2:1:1)	3-µm polymeric C_{30} column (C_{30} isocratic separation 250 × 4.6 mm, i. d.)	Methanol/methl-butyl ether (62:38), flow rate 1 ml/min, UV at 460 nm	Shi et al., 1999

1994; Emenhiser et al., 1995, 1996; Lessin et al., 1997). The main steps of lycopene analysis by HPLC are listed in Table 8.

VI. LYCOPENE STABILITY DURING TOMATO PROCESSING

More than 80% of tomatoes produced are consumed in the form of processed products such as tomato juice, paste, puree, catsup, sauce, and salsa. For processing, tomatoes are washed, sorted, and sliced. Sliced tomatoes undergo a hot- or cold-break method for juice preparation. Juice from tomatoes is usually obtained using screw or paddle extractors. In the manufacturing of other tomato products such as pulp, puree, paste, and ketchup, tomato juice is concentrated with steam coils or vacuum evaporators. For canned tomatoes, sliced or whole tomatoes are retorted. For dried tomato slices and powder, tomatoes undergo a dehydration process. Either thermal or mechanical treatments are often involved in these processes, which may affect tomato product quality. Deep-red tomato fruits that contain high concentrations of lycopene would be processed into products with a dark-red color. However, the lycopene content in concentrated tomato products is generally lower than expected, because of losses during tomato processing (Tavares and Rodriguez-Amaya, 1994). The main causes of lycopene degradation in tomato processing are isomerization and oxidation. It is widely presumed that lycopene in general undergoes isomerization on thermal processing. It was believed that the changes of lycopene content and the distribution of *trans-cis* isomers result in the change of biological property (Zechmeister et al., 1943; Zechmeister, 1944, 1949, 1962). Determination of the degree of lycopene isomerization would provide better insight into the potential health benefits of the processed tomato products. The degradation of lycopene and the color loss of processed tomato products are affected by a number of factors. The loss of color in tomato juice is accelerated by high temperatures and long treatment (processing and storage), due to the degradation of lycopene. Wiese and Dalmasso (1994) reported an increase in the hue angle of tomato juice after processing and storage, indicating a loss of red color. The color retention in tomato products is better at lower temperatures (Sherkat and Luh, 1976; Villari et al., 1994).

In processed tomato products, oxidation is a complex process and depends on many factors, such as processing conditions, moisture, temperature, and the presence of pro- or autoxidants and lipids. For example, the use of fine screens in juice extraction enhances the oxidation of lycopene due to the large surface exposed to air and metal. The use of coarser screens increases the retention of color of tomato products (Kattan et al., 1956). The amount of sugar, acids, and amino acids also affects the color of processed tomato products by causing the formation of brown pigments (Gould, 1992). The lycopene content of some commercial samples are listed in Table 9. The deterioration in color that occurs during the processing of various tomato products results from exposure to air at high temperatures during processing causing the naturally occurring all-*trans* lycopene to be isomerized and oxidized. Coupled with exposure to oxygen and light, heat treatments that disintegrate tomato tissue can result in the destruction of lycopene. These changes are due mainly to heat stress imposed by the relatively harsh thermal processes required to achieve the shelf-life stability of processed tomato products. Studies on the effect of processing conditions on qualitative and quantitative changes of lycopene degradation are necessary to determine the engineering parameters of lycopene during tomato processing.

A. Effect of Temperature on Lycopene Degradation

As shown in Table 10, heating tomato juice for 7 min at 90°C and 100°C resulted

TABLE 9
A Survey of Lycopene Content in Some Commercial Samples

Industrial sample	Lycopene (mg/100 g wet basis)	Sources
Tomato juice (in Israel)	5.8–9.0	Lindner et al., 1984
Tomato ketchup (in Finland)	9.9	Heinonen et al., 1989
Tomato puree	19.37–8.93	Tavares and Rodriguez-Amaya, 1994
Tomato paste	18.27–6.07	
Tomato ketchup	10.29–41.4	
Tomato juice (in Campinas, Brasil)	61.6	
Tomato soup	8.0–13.84	Tonucci et al., 1995
Tomato juice	9.70–11.84	
Tomato paste	51.12–59.78	
Tomato puree	16.67	
Tomato sauce (in U.S.A.)	6.51–19.45	
Tomato pulp	12.09–12.83	Sharma and Le Maguer, 1996
Pulp thick fraction	41.91–42.82	
Pulp thin fraction (in Canada)	3.98–4.08	

TABLE 10
Lycopene Loss Rate in Tomato Juice during Heating

Heating temperature (°C)	Lycopene loss (%)		
	Heating time 1 min	Heating time 3 min	Heating time 7 min
90	0.6	0.9	1.1
100	0.9	1.4	1.7
110	2.2	3.2	4.4
115	2.7	4.5	7.0
118	3.7	6.0	9.1
121	4.6	7.3	10.6
124	5.5	8.5	12.5
127	6.5	9.9	14.6
130	7.4	11.5	17.1

Data from Miki and Akatsu, 1970.

in a 1.1 and 1.7% decrease in lycopene content, respectively. At higher temperatures the lycopene content decreased even more, and losses of 17.1% were observed at 130°C (Miki and Akatsu, 1970). Temperature affects the nature and extent of lycopene breakdown. In solution, 26.1% of the lycopene was lost when heated for 3 h at 65°C, and 35% was lost when heated for 3 h at 100°C (Table 11). Copper stearate catalyzes the oxidation of lycopene. At 65 and 100°C, the loss of lycopene increased to 60 and 90% (almost complete decolorization), respectively, in the presence of small amounts of copper. Cole and Kapur (1957a) reported that the oxidative degradation of lycopene at 50°C leads to fragmentation of the molecule, giving acetone, methylheptenone, laevulinic aldehyde, and probably glyoxal as products.

It has also been reported that serious losses of lycopene can occur when the holding times at high temperature are long. The

TABLE 11
Oxidation of Lycopene Loss in Hexane and Light Petroleum Solution

Temperature (°C)	Time (h)	Lycopene loss in solution (10 mg/l) (%)	Copper-catalyzed loss (29 mg/l) (%)
65	0	0	0
	1	15.0	25
	2	20.0	45
	3	26.1	60
100	0	0	0
	1	20.0	40
	2	28.5	75
	3	35.0	90

Data from Cole and Kapur, 1957a.

high temperature and large amount of air dissolved in the tomato juice during the breaking and straining operations can quickly destroy substantial amounts of lycopene. During evaporation (especially using a vacuum), smaller losses were noticed because the deaeration that occurred as soon as the juice entered the evaporating system hindered oxidative destruction of lycopene. The results suggest that length of heating is a critical factor controlling the degradation of lycopene. It appears that the deaeration and "high temperature–short duration" heat treatment of tomato juice can have beneficial effects on the retention of tomato juice quality.

B. Effect of Oxygen on Lycopene Degradation

Monselise and Berk (1954) first reported the oxidative destruction of lycopene during the processing of tomato puree. The most important contributing factor was the availability of oxygen. More than 30% of the lycopene was degraded when heated at 100°C in the presence of oxygen, while only 5% was lost in the presence of CO_2 (Table 12).

C. Effect of Light Density on Lycopene Degradation

Increasing illumination and temperature increased the loss of lycopene. The magnitude of lycopene destruction by increased lighting is less severe than that by increased temperature (Table 13).

D. Effect of Dehydration Techniques on Lycopene Degradation

The loss of lycopene during the dehydration of tomatoes is an important commercial concern. Total lycopene content in fresh and dehydrated tomatoes is shown in Table 14. The dehydration of tomato slices is typically carried out at high temperatures over an extended period under vacuum. The general tendency of lycopene retention in samples decreased slightly during the dehydration processes. During osmotic dehydration, lycopene content remains essentially constant. After osmotic-vacuum drying, total lycopene retention in tomatoes was greater than in those dehydrated by vacuum drying. The probable explanation is that the sugar solution in osmotic dehydration keeps oxy-

TABLE 12
Effect of Oxygen on Rate of Loss of Lycopene on Heating Tomato Pulp at 100°C

Condition	Time of heating (h)	Loss (%)
Dark and CO_2	0	0
	0.5	4.6
	1	4.9
	2	5.0
	3	5.1
Dark and O_2	0	0
	1	14.0
	2	23.7
	3	30.1
Daylight and CO_2	0	0
	1	5.4
	2	8.6
	3	11.3
Daylight and O_2	0	0
	1	15.1
	2	25.9
	3	33.1

Data from Cole and Kapur, 1957b.

TABLE 13
Combined Effect of Illumination and Temperature on Loss of Lycopene in Tomato Pulp in Air for 3 h

Condition	Lycopene loss (%)
100-ft candles, 60°C	18.9
150-ft candles, 60°C	23.3
50-ft candles, 100°C	31.3
100-ft candles, 100°C	34.9
150-ft candles, 100°C	38.6
50-ft candles, 110°C	50.0
100-ft candles, 110°C	53.9
150-ft candles, 110°C	58.3

Data from Cole and Kapur, 1957b.

gen from tomatoes and reduces the oxidation of lycopene in the tomato tissue matrix at low operating temperatures. Conventional air drying decreases lycopene retention in tomato samples due to the influence of heat and oxygen. Heat treatment disintegrated tomato tissue and increased exposure to oxygen and light, which resulted in the destruction of lycopene (Shi and Le Maguer, 1999 a, b)

E. Lycopene Loss during Tomato Peeling Treatments

Peeling is an important operation in tomato processing. Before tomatoes pass over mechanical peel eliminators to remove skin, they usually undergo a chemical or physical treatment. Chemical treatments include lye peeling in a hot solution of NaOH or $CaCl_2$.

TABLE 14
Total Lycopene and *Cis*-Isomer Content in the Dehydrated Tomato Samples

Sample	Total lycopene (μg/g dry basis)	Lycopene loss (%)	All-*trans* isomers (%)	*Cis*-isomers (%)
Fresh tomato	755 [a]	0	100	0
Osmotic treatment	755 [a]	0	100	0
Osmo-Vac dried	737 [b]	2.4	93.5	6.5
Vac-dried	731 [c]	3.2	89.9	10.1
Air-dried	726 [d]	3.9	84.4	16.6

Note: Data presented as means of triplicate determinations.
Means in a column not sharing common superscript (a–d) are significantly different ($p < 0.01$).

Data from Shi and Le Mague., 1999b.

Physical treatments include steam peeling by high-pressure or superheated steam. Some new peeling methods have been developed, such as cryogenic scalding with liquid nitrogen, liquid air or Freon 12, or infrared peeling with infrared radiation as a heat source. During lye peeling, the hot solution dissolves the epicuticular waxes, penetrates the epidermis, digests middle lamella, cell walls, and causes separation of the skin (Gould, 1992). The concentration of lye solution and temperatures used in the food industry range from 8 to 25% and from 60 to 100°C, respectively, depending on the commodity, cultivar, and fruit maturity (Floros and Chinnan, 1989). With the steam scald peeling process, tomatoes are exposed to live steam long enough to loosen the peel but not so long as to cause flesh softening or cooking. In recent years, the application of high-pressure steam for short time in combination with mechanical peel eliminators has become accepted in most tomato processing operations (Corey, 1986). Both chemical and steam peeling procedures cause relatively high losses of the edible parts of the outer pericarp layer of the tomato fruits. Schulte (1965) found that peeling tomatoes with the infrared method produced a peel loss of 5.3%, while the steam method had a peel loss of 7.5%. Reis and Stout (1962) reported about a third of the tomato volume delivered to processing plants can be lost as waste. The wastes during tomato processing are mainly seeds, pericarp tissue, and skin residues. The epidermal area of tomatoes (skin and outer pericarp tissue) contains more than 80 to 90% of the total lycopene in the tomatoes. It is clear that a large quantity of lycopene is normally discarded as tomato processing waste. This processing waste can be an important source of lycopene for the food industry.

F. Lycopene Isomerization in Food Processing

The reduction of lycopene content and *trans-cis* isomerization result in a reduction in biological property (Zechmeister et al., 1965). Lycopene isomer distribution in some commercial tomato products is listed in Table 15. However, actual determination of the degree of isomerization resulting from processing has been limited. The color changes, usually used as a quality index, cannot be explained by lycopene isomerization to *cis*-isomers. It is generally accepted that the all-*trans* form of lycopene has the highest sta-

TABLE 15
Lycopene Isomers in Various Commercial Tomato Products

Sample	Total lycopene (mg/100 g wet basis)	All-*trans* (%)	5-*cis* (%)	9-*cis* (%)	13-*cis* (%)	Other *cis* (%)
Tomato paste ('Tomatenmark', Panocchia, Italy)	52	96	4	<1	<1	<1
Tomato paste ('Maracoli', Kraft, Germany)	3.7	91	5	1	2	<1
Tomato ketchup ('Hot Ketchup', Del Monte, Italy)	9.5	88	7	2	3	1
Tomato ketchup ('Hot Ketchup', Heinz, USA)	3.0	77	11	5	7	1
Instant meal ('Eier-Ravioli', Hero, Switzerland)	0.6	76	8	5	6	5
Sauce ('Hamburger Relish', Heinz, The Netherlands)	3.0	93	5	<1	3	<1
Sauce ('Sauce Bolognaise', Barilla, Italy)	9.2	67	14	6	5	8
Canned tomatoes ('Chris', Roger Sud, Italy)	7.1	84	5	3	5	3

Data from Schierle et al., 1996.

bility and the *cis*-isomers have the lowest stability. Bioactivity potency depends on the extent of isomerization and oxidation as well as the stability when tomato-based products are subjected to processing and storage (Zechmeister, 1962; Khachik et al., 1992; Stahl and Sies, 1992; Emenhiser et al., 1995; Wilberg and Rodriguez-Amaya, 1995). Thus, isomerization would lead to degradation of lycopene. Although the processing of tomatoes by cooking, freezing, or canning does not usually cause significant changes in total lycopene content, it is widely assumed that lycopene undergoes isomerization after thermal processing. Heat, light, acids, and other factors have been reported to cause isomerization of lycopene (Boskovic, 1979; Schierle et al., 1996; Nguyen and Schwartz, 1998; Shi et al., 1999). A true assessment of the nutritional quality and healthy benefit of processed tomato-based food depends not only on the total lycopene content, but also on the distribution of lycopene isomers. Characterization and quantification of lycopene isomers would provide better insight into the potential nutritional quality and healthy benefit of the processed tomato products, and more accurately predict the lycopene bioactivity than just a total lycopene content with no knowledge of its isomeric composition. Controlling lycopene isomerization behavior during production and storage of tomato products can be of benefit in improved product color and quality.

1. Effect of Thermal Processing on Lycopene Isomerization

Lycopene isomers in various thermally processed tomato products are listed in Table 16. Lycopene isomerization and the amount of *cis*-isomers increased as a function of processing time during heating of tomatoes. Heat treatment clearly increased the percentage of the *cis*-isomers. It is obvious from these results that food processing can enhance *cis*-isomerization in tomato-based

TABLE 16
Lycopene Isomers in Various Thermally Processed Tomato Products

Sample	Total lycopene (mg/100 g, dry basis)	*Cis*-isomers (%)
Peeled tomato	149.89	5.37
Tomato juice (hot-break)	161.23	5.98
Tomato juice (retorted)	180.10	3.56
Tomato (whole, retorted)	183.49	3.67
Tomato paste (concentrated)	174.79	5.07
Tomato paste (retorted)	189.26	4.07
Tomato soup (retorted)	136.76	4.34
Tomato sauce (retorted)	73.33	5.13

Data from Nguyen and Schwartz, 1998.

foods. Heating tomato-based foods in oil had a bigger effect on lycopene isomerization than heating in water. Therefore, this indicates, that not only the duration and temperature of heat treatment, but also the food matrix components such as oil or fat influence the lycopene isomerization (Table 17).

2. Effect of Dehydration Technolog on Lycopene Isomerization

Studies on the effect of dehydratio methods on lycopene degradation show significant increase in *cis*-isomers and a s multaneous decrease in the all-*trans* isome

TABLE 17
Effect of Heating Treatment on Lycopene Isomerization in Aqueous and Oily Dispersions of Tomato Paste (70°C)

Heating time (min)	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
180	83.4	6.1	3.6	3.2	3.8
In olive oil					
0	87.4	4.8	4.4	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

Data from Schierle et al., 1996.

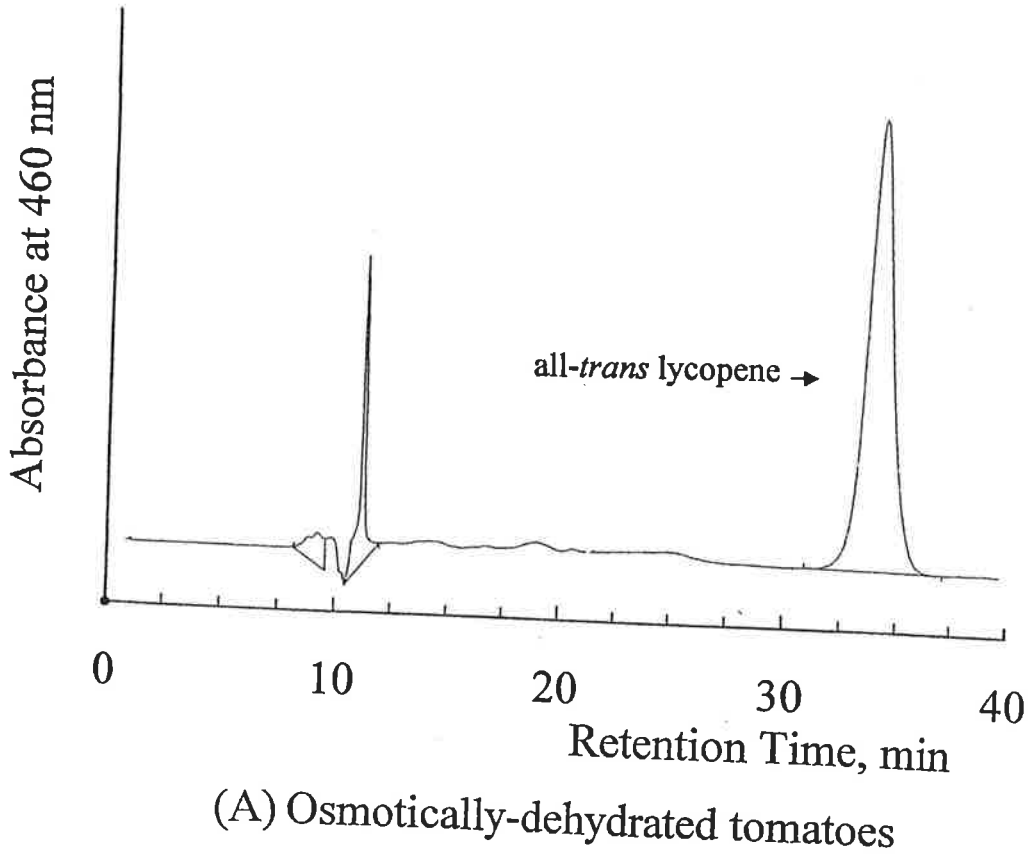
(Table 14). *Cis*-isomers were not detected in the fresh tomato samples. Chandler and Schwartz (1987, 1988) and Rodriguez-Amaya and Tavares (1992) also reported no *cis*-isomers in the fresh tomato samples after HPLC analysis. The *cis*-isomers appeared in processed tomato samples (Figure 4).

It was observed that fewer *cis*-isomers were present in osmotically dehydrated tomatoes when compared with those directly air dried and vacuum dried. The highest amount of *cis*-isomers were found in air-dried tomato samples (Shi et al., 1999). Miers et al. (1958) mentioned that the amount of *cis*-isomers exceeds those present in the initial tomato material and in osmotically treated tomato samples when dehydrated by conventional methods. The *cis*-isomers were formed in processed tomato samples and increased with temperature and time during dehydration. Each sample dehydrated by different methods had a negative factor favoring isomerization and/or oxidation of the lycopene (e.g., oxygen permeability, light exposure, and the presence of some metals in the processing system). A large loss of lycopene during processing would indicate a longer and more drastic procedure, particularly in the thermal dehydration steps. Dehydration of tomatoes at a mild temperature does not usually cause significant losses in total lycopene content (Nguyen and Schwartz, 1998), but the conversion of *trans*- to *cis*-isomers always occurred in the dehydrated products. In the osmotic treatment, the predominating mechanism may be isomerization of lycopene. Because the total lycopene content remained almost constant, only the distribution of all-*trans*- and *cis*-isomers was changed. In air drying, isomerization and oxidation were two strong factors that simultaneously affected the total lycopene content, distribution of *trans*- and *cis*-isomers, and biological potency. The changes in lycopene content and the distribution of *trans-cis* isomerization will result in a reduction in biological potency when tomato-based products are subjected to processing (Zechmeister 1962; Khachik et al., 1992; Emenhiser et al., 1995; Wilberg and Rodriguez-Amaya, 1995; Stahl and Sies, 1996). Dehydration and increase of surface area, for example, in powdered or lyophilized tomato products, generally leads to very poor stability. Osmotic solution (with sugar) remaining on the surface layer of tomato prevents oxygen from penetrating and oxidizing lycopene. Osmotic treatment could reduce lycopene losses compared with other dehydration methods. These results will be useful in developing new dehydration techniques and improve product quality (Shi et al., 1999).

G. Lycopene Degradation and Color Changes of Tomato-Based Foods

Color parameters measure and the relation with food quality have been studied extensively (Francis et al., 1975; Little, 1975; Clydesdale, 1997). A number of publications have reported the tendency of lycopene compounds to isomerize from one form to another with accompanying color changes (Wong and Bohart, 1957). It seems possible that the naturally occurring all-*trans* lycopene isomerizes to the less red *cis*-isomers with a corresponding change in absorption spectra during processing of tomato products (Miers et al., 1958). Results of color parameters L*, a*, and b* together with the ratio a*/b* and the overall color difference (DE) of the dehydrated tomato products are presented in Table 18. 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.

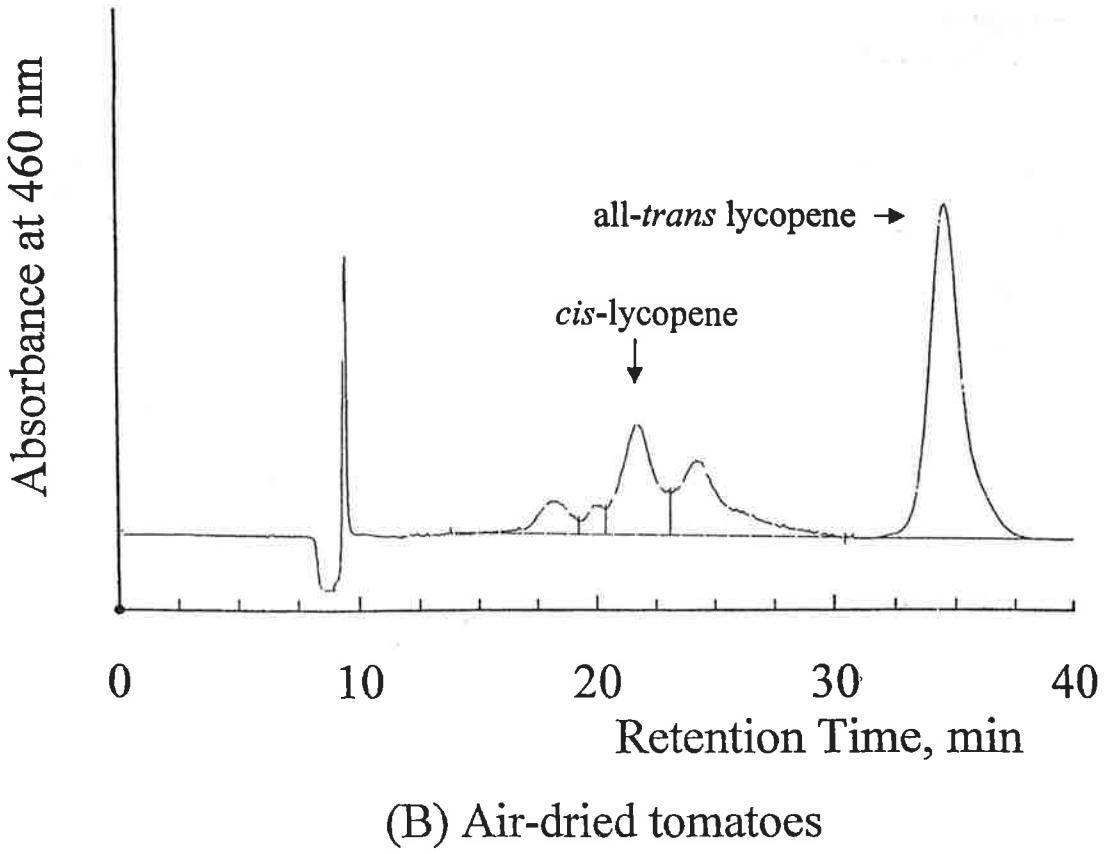
Wiese and Dalmasso (1994) reported an increase in the hue angle of tomato juice after processing and storage, indicating a loss of red color. Color retention in tomato products is better at lower temperatures (Sherkat and Luh, 1976; Villari et al., 1994). A slightly better color can be observed in the



A

FIGURE 4. HPLC chromatograms of *trans*- and *cis*-isomers of lycopene in osmotically dehydrated tomatoes and in air-dried tomatoes (B) (Shi and Le Maguer, 1999b).

samples dehydrated at low temperatures. The color differences between the samples were not readily discernible by visual evaluation. There was no significant difference between the Hunter color value a* of the different dehydrated tomatoes. This was attributed to the formation of lycopene crystals in the tomato tissue matrix after heating in the dehydration processes. After heating, the spectrum did not change significantly. The color measurement did not show the relative composition of all-*trans* and *cis*-isomers. An increase in *cis*-isomers would indicate a change of lycopene bioactivity potency, but would not show up as a significant difference in color. Lycopene content and the ratio of *trans*- to *cis*-isomers may have caused t a*/b* value to stay at a higher level (Wo and Bohart, 1957). The color quality, a*/ values, remained essentially unchanged du ing the osmotic treatment, but there we lower values of a*/b* in the convention air-dried sample. Product color showed pr gressive deterioration of overall color qua ity (DE) in conventional air drying. Th average color reflectance reading for osmot cally dehydrated fruits had color characte istics close to those of the fresh materia The L* and a* values decreased for the oth dehydration treatments. The trends in lyc pene degradation and color parameters fo the different dehydrated tomato product



(B) Air-dried tomatoes

FIGURE 4B

were not directly correlated (Figures 5 and 6). Tomatoes with the osmotic treatment had more red color than those treated by air drying and vacuum drying, which indicated there was more *trans*-isomer lycopene in the samples.

H. Lycopene Stability during Storage of Tomato-Based Food

The fate of lycopene in processed tomato products is influenced by storage factors. The percent retention of lycopene decreased at high temperatures and in the presence of oxygen after longer periods in storage (Table 19). A study on vacuum-dried tomato powder showed that in-package dessication and packaging in an inert atmosphere (e.g., nitrogen) favored color retention, which the presence of air caused a loss of lycopene and color fading by oxidation (Kaufman et al., 1957). Analyses of the storage-study samples for lycopene (Wong and Bohart, 1957) showed that air-packed samples retained the lowest lycopene levels, and all air-packed samples showed a progressive loss of lycopene throughout the storage period. The most important factor contributing to degradation is availability of oxygen during storage. With careful selection of storage conditions to protect the products from such facts as air by storing in an inert atmosphere or under vacuum, it is possible to retain initial color levels during storage.

TABLE 18
Color Values of Dehydrated Tomato Samples

Samples and dehydration condition	Color parameters					
	L*	a*	b*	a*/b*	ΔE	L*b*/a*
Fresh material	38.4[a]	37.7[a]	16.1[a]	2.3[a]	56.2[a]	16.4[a]
IM tomatoes						
Osmotic dehydration at 25°C	38.4[a]	37.7[a]	16.1[a]	2.3[a]	56.2[a]	16.4[a]
Osmo–Vac drying at 55°C	36.7[a]	35.2[a]	16.9[a]	2.1[a]	53.6[a]	17.2[a]
Vacuum drying at 55°C	34.2[a]	34.3[a]	17.4[a]	1.9[a]	51.5[b]	17.4[b]
Air drying at 95°C	29.9[b]	33.2[b]	19.9[b]	1.7[b]	48.9[c]	18.1[c]
Dehydrated tomatoes						
Osmo–Vac drying at 55°C	31.4[c]	36.4[c]	18.3[b]	1.7[b]	48.1[b]	18.3[c]
Vacuum drying at 55°C	28.3[d]	25.6[d]	18.2[b]	1.4[b]	42.3[c]	20.1[d]
Conventional air drying at 90°C	25.6[e]	23.2[e]	18.9[b]	1.2[b]	39.4[d]	20.9[e]

Note: Data presented as means of triplicate determinations.
Means in a column not sharing common superscript (a–e) are significantly different ($p < 0.01$).

Data from Shi et al., 1999b.

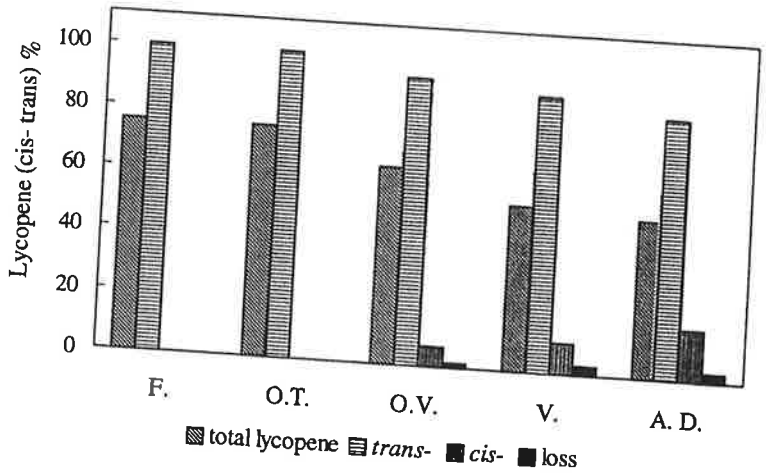


FIGURE 5. Comparison of lycopene degradation in the different dehydration processes (F, fresh tomato, O.T., osmotic treatment, O.V., osmo-vacuum-drying, V, vacuum-drying, A.D., air drying) (Shi et al., 1999).

I. Antioxidant Application

The mechanism of lycopene destruction depends on many parameters during food processing and storage. The main cause of damage to lycopene during food processing and storage is oxidation. Careful application of suitable antioxidants (e.g., ethoxyquin, ascorbic acid, sodium acid pyrophosphate) at appropriate levels could have beneficial results (Granado et al., 1992; Clinton et al., 1996; Porrini et al., 1998). Low storage tem-

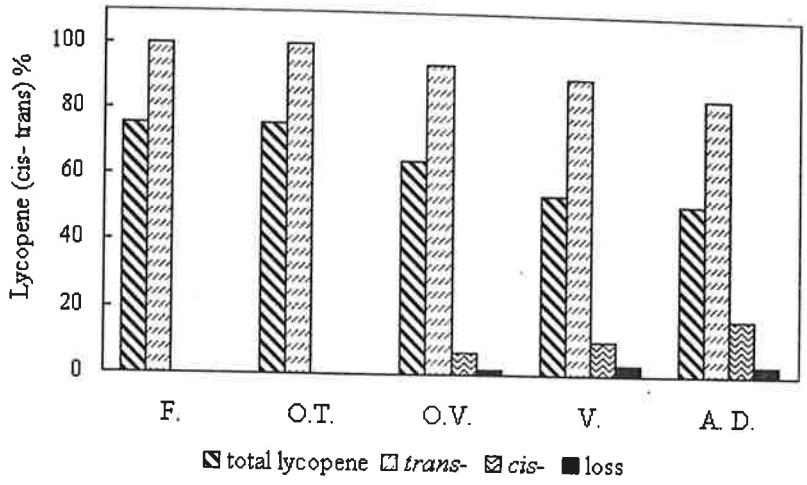


FIGURE 6. Comparison of color changes in the different dehysdration proceeses (F, fresh tomato, O.T., osmotic treatment, O.V., osmo-vacuum drying, V, vacuum drying, A.D., air drying) (Shi et al., 1999).

TABLE 19
Total Lycopene Retention in Tomato Powder Stored in Different Atmospheres, Temperatures for Different Time Lengths

Storage period (days)	Storage conditions	Total lycopene retention (%)
Fresh tomato powder		100
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

Data from Lovric et al., 1970.

perature, low oxygen content, low light, low water activity, and low moisture content in storage will also have a limiting effect on the oxidation of lycopene.

VIII. FUTURE DEVELOPMENT

Lycopene is particularly important because it has a dual influence on production

and quality as a natural color and nutrient for the food and pharmaceutical industries. Color has a strong influence on the buying behavior of consumers. Color also serves as a measure of total quality for tomato and tomato products. Consumers, researchers, and the food industry have also dramatically increased their interest and awareness of the health benefits of lycopene from tomatoes. Lycopene can be considered as "the vitamin of the twenty-first century" because of its significant physiological effect on the human diet. Lycopene can play an important role in human health and provide protection against a broad range of epithelial cancers.

It is very important to better understand the development of the tomato fruit on the plant, that is, both fruit number, size development, and the effect on lycopene content. With this knowledge, we will be able to enhance tomato yield and we will better understand what affects the quality of the fruit. It may be that the fruit development processes leading up to fruit maturation may also have an effect on fruit components such as lycopene. Lampe and Watada (1971) and Mohr (1979) indicated that lycopene content was high in tomato fruits that have a high pigment concentration index. At present, lycopene content is not a critical factor in tomato production research. More efforts are required to produce lycopene-rich tomato varieties and improve lycopene content through proper management and cultural practices. The lycopene content in tomato fruits may be enhanced by improved techniques in fertilizer, harvest time, and variety selection. This focus on lycopene may also lead to higher-quality tomatoes produced in greenhouses during winter.

The availability of lycopene in foods is influenced not only by its isomeric form, but also by the food matrix, the presence of sufficient bulk lipid for solubilization of released lycopene, and the presence of interfering factors in the lumen such as pectin and other dietary fibers. These factors should be evaluated in an attempt to maximize lycopene absorption from the diet. The degr tion of lycopene is extremely importan tomato-based food industries. Lycop needs to be protected from excessive l and extreme pH conditions, exposure to li oxygen, and lipid-degrading enzymes in der to prevent its oxidation and isomeri tion. Processing technology should be o mized to prevent lycopene oxidation isomerization.

Lycopene and other carotenoids h been accepted as natural colorants for fo use for a long period of time without to cological evidence in the same manner vegetable and fruit products. Lack of sou information regarding toxicology and bi availibility data would limit the develo ment of food safety regulations. Furth studies will be necessary to provide a to icological evaluation of lycopene and info mation on how lycopene interacts with oth nutrients.

Consumer demand for healthful foc products provides an opportunity to develc a market for food and pharmaceutical-grac lycopene products. Industrial production lycopene from tomatoes is in high deman by phamarceutical companies and for func tional food development. Little informatio on lycopene commercial production is avail able. At present, a large quantity of skin an outer pericarp tissue are normally discarde as tomato processing waste in the peelin procedure of the tomato processing. Som new technologies such as membrane separation technology, supercritical fluid CO_2 extraction technology, and solvent extractio technology are being applied to scale up the lycopene production (Zelkha et al., 1998). An environmentally friendly extraction and purification procedure on an industrial scale with minimal loss of bioactivity is highly desirable for the food, feed, cosmetic, and pharmaceutical industries. High-quality lycopene products that meet food safety regulations will offer potential benefits to the food industry. A successful commercialization of high-value lycopene production may