

QUALITY AND NUTRITIONAL COMPOSITION OF TOMATO FRUIT AS INFLUENCED BY CERTAIN BIOCHEMICAL AND PHYSIOLOGICAL CHANGES

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ABSTRACT

The chemical constituents are concerned in the quality of tomato fruit in respect to color, texture, flavor, nutritive value, and wholesomeness. In general, high sugar contents, redness of color, and firm texture are associated with prominence of rich flavor. Biochemical changes as influenced by growth, maturation, and environment of tomato fruit are discussed.

INTRODUCTION

The tomato (*Lycopersicon esculentum* Mill.) fruit is one of the most popular, as well as important, commodities in the world. Over 20 million metric tons of tomatoes are produced each year on a world basis. The United States, Italy, Spain, and the U.A.R. are the leading producers of this crop. In the United States alone, it ranks second only to potatoes in production among vegetable crops (Fig. 1) and contributes approximately 400 million dollars to the economy. As a processing crop, it takes first rank among the vegetables.

Though the tomato was not recognized as a valuable food until about a century ago, its merit is now universally accepted. It is often referred to as 'the poor man's orange' because of its high vitamin, malic acid, and citric

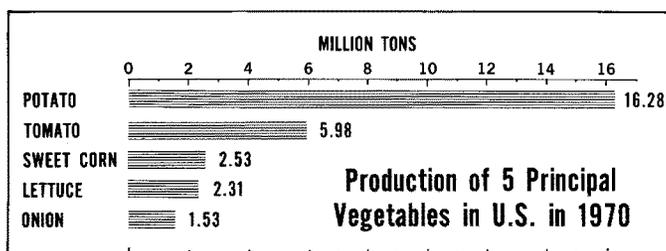


Fig. 1. Yield of the 5 most prevalent vegetables in the United States of America in 1970

acid contents, and the fact that it serves as a fine appetizer. The tomato is also popular because it is a most rewarding crop for the home garden since it grows well practically everywhere, and it provides high nutrition in many forms such as raw in salads; cooked in soups, preserves, catsups, sauces; pickled; and in other forms.

Demand for and acceptance of fresh tomato fruit are based largely on the flavor. Flavor is a composite of taste and odor (aroma), which are entirely different from physiological and chemical points of view. Taste is a function of the taste buds in the mouth; which constitute a selective mechanism. A relation exists between the kind of taste that a substance has and its chemical constitution. On the basis of psychological studies, the four primary sensations of taste are: sourness of acids; saltiness of ionized salts; sweetness of sugars, glycols, alcohols, aldehydes, ketones, amides, esters, amino acids, sulfonic acids, and halogenated acids; and bitterness of long chain organic substances and alkaloids. Salty and sour tastes show a much better correlation with structure than do sweet and bitter tastes.

From the consumer's point of view, odor or aroma excites sensation in the brain when the aroma compounds contact the nasal cavity. The sensation depends upon the aroma substance fitting the olfactory cells in the nose. Fruit aroma is generally considered to consist of various volatile substances such as esters, aldehydes, ketones, alcohols, lactones, hydrocarbons, acids, etc., which exist in minute quantity in the fruit.

Tomato fruit quality is determined mainly by color, texture, and flavor. Among those, color and flavor are probably the most useful criteria for estimating maturity of tomato fruit. High quality is associated with redness of color and prominence of flavor. The flavor of a fruit becomes pronounced when the sugar content is at its maximum, at which time the skin acquires its richest color.

Studies of fruit volatiles have greatly increased during the last decade with advances in analytical techniques, as well as in instrumentation. Gas-liquid chromatography, coupled with infrared or mass spectrometry, has given flavor chemists a versatile tool with which to study the volatiles of fruit and other food commodities.

In view of the important role that the tomato plays in the diet of a common man, certain chemical and physiological aspects influencing its quality are discussed in this paper.

ANATOMY AND MORPHOLOGY OF FRUIT

By use and culture, the tomato is considered a vegetable. Botanically, however, it is a fruit, and among fruits it is a berry, since it is indehiscent (non-shedding), pulpy, and has one or more seeds that are not stones. The

principal commercial cultivars of tomato fruit are globular or oblate in shape, but some of the special types may be elongated or pear-shaped. The weight of the fruit may be a fraction of an ounce in cherry tomatoes, 4½ to 6 or 7 ounces in table and market cultivars, and 9 to 12 ounces in the largest canning types. In transection, the fruit has from 2 to 25 locules.

The quality of fruit depends upon the relative amounts of outer and inner wall tissue. MacGillivray & Ford (1928) divided the tomato into five fractions, such as outer and inner wall, inner locule tissue, gelatinous pulp, skin, and seed. On the basis of amount of each fraction, they concluded that the outer and inner wall regions play an important role in the quality of the tomato because of the highest contents of dry matter, insoluble solids, and reducing sugars.

Structurally, the fruit is composed of pericarp, placental tissue, and seeds. Groth (1910) showed that the skin of tomato pericarp consists of an epidermal layer followed by three or four well-defined layers of collenchymatous tissue. The epidermis is covered by a thin cuticle and the polyhedral cells are without sinuous outlines. The size and number of epidermal cells increase greatly with the growth of the fruit. The epidermis develops hairs and glands that are shed as the fruit matures. The hairs are unbranched and consist of three to five cells, while the glands have a unicellular basal stalk and a top of two or four cells. Rosenbaum & Sando (1920) noted a complete absence of stomata in the epidermis of tomato fruit and observed a thickening of the cuticular layer during the fruit's ageing process.

The pericarp is mainly composed of large thin-walled cells with numerous intercellular spaces, and it continues to thicken 60 hours after pollination (Smith & Cochran, 1935). During development, the cells enlarge enormously. As the fruit matures, some of the cells in the inner and central portions of the carpels may partially disintegrate.

During the development of ovules, there is an outward growth of the parenchymatous cells of the placenta which surround their bases. The parenchyma increases until it completely encloses the developing seeds in a homogeneous tissue of twin-walled cells. The cells do not unite with the carpellary walls, but press against them and the surfaces of the seeds. At first, the tissue is firm and compact, but as the fruit matures the walls become thinner and the cells partially collapse. Large numbers of round starch grains are included in the gelatinous contents. The mature seeds are oval in outline and flattened laterally, and vary considerably in size. The surface is covered with gray hairs and scales which are the remains of the lateral walls of the outermost cell layer of the integument. The integument is divided into four regions out of which the innermost layer or epidermis is highly pigmented and imparts color to the mature seed.

CHEMICAL CHANGES DURING GROWTH AND MATURATION

The chemical composition of fresh tomato fruits depends upon factors such as cultivars, maturity, light, temperature, season, climate, soil fertility, irrigation, and cultural practices.

The relative concentrations of the chemical constituents of tomato fruit are important in assessing the quality in respect to color, texture, appearance, nutrient value, taste, and aroma. Yu et al. (1967) showed that Fireball and V.R. Moscow tomatoes contained 94% moisture at the red stage of maturity. Compositional changes associated with ripening of tomato fruit are presented in Table 1.

Sugars

The soluble solids of tomatoes are predominantly sugars, which in turn are important contributors to flavor. In general, the flavor of a fruit becomes

Table 1. *Some compositional changes of tomato fruit^d associated with ripening*

Composition ^b	Stage of maturity				
	Large green	Breaker	Pink	Red	Red-ri ripe
Dry matter (%)	6.40	6.20	5.81	5.80	6.20
Titratable acidity (%)	0.285	0.310	0.295	0.270	0.285
Organic acids (%)	0.058	0.127	0.144	0.166	0.194
Ascorbic acid (mg %)	14.5	17.0	21.0	23.0	22.0
Chlorophyll (mg %)	45.0	25.0	9.0	0.0	0.0
β -Carotene (mg %)	50.0	242.0	443.0	10.0	0.0
Lycopene (mg %)	8.0	124.0	230.0	374.0	412.0
Reducing sugars (%)	2.40	2.90	3.10	3.45	3.65
Pectins (%)	2.34	2.20	1.90	1.74	1.62
Starch (%)	0.61	0.14	0.136	0.18	0.07
Volatiles (ppb)	17.0	17.9	22.3	24.6	31.2
Volatile reducing substances (μ eq. %)	248	290	251	278	400
Amino acids (μ mole %)	- ^c	2358	3259	2941	2723
Protein nitrogen (mg N/g dry wt.)	9.44	10.00	10.27	10.27	6.94

^aFireball cultivar, except V. R. Moscow cultivar for amino acid contents.

^bExpressed on the basis of fresh weight unless specified.

^cValue not reported.

Source: Dalal et al. (1965), except dry matter, starch, amino acids, and protein nitrogen from Yu et al. (1967).

pronounced when its sugar content peaks. The free sugars, representing more than 60% of the solids in tomatoes, are mainly D-glucose and D-fructose, with trace amounts of sucrose, a ketoheptose, and raffinose. Although the glucose and fructose are present in approximately equal amounts, the fructose contributes more maximum sweetness. In general, the sugar content of tomato fruit is a function of the stage of maturity. It increases uniformly from small and green mature to large and red-ripe tomatoes (Dalal et al., 1965). Similar results were reported by Rosa (1925), Winsor et al. (1962a), and Lambeth et al. (1964).

Starch

The starch content of tomato fruit depends upon maturity, cultivar, and ripening conditions, and varies from 1–1.22% in immature fruit to 0.1–0.15% in red-ripe fruit. Yu et al. (1967) studied the composition of tomato fruit at nine different stages of maturity and observed that starch accumulated until nearly the large-green stage and then rapidly decreased. Relatively low starch contents in the last stage of fruit maturation were noticed by Sando (1920), Rosa (1925), Saywell & Cruess (1932), and Davies & Cocking (1965). Yu et al. (1967) observed that the increases and decreases in free reducing sugar and starch contents were not parallel as the maturation progressed.

Pectins

The texture of the fruit is satisfactory only when pectase, calcium, and pectin are in sufficient quantities. Appleman & Conrad (1927) reported that the pectic substances changed with maturation, with protopectin predominating in green fruit; but as ripening progressed, partial enzymatic hydrolysis resulted in a decrease of protopectin and a corresponding increase in soluble pectin. The loss of pectate from the middle lamellae is considered to cause softening of the fruit as maturation progresses. Kattan (1957) reported a significant difference in firmness between fruits harvested at the green-mature stage and fruits harvested at the pink or red stage. Dalal et al. (1965) showed that protopectin increased up to the large-green stage and then progressively decreased. Increases in soluble pectins during maturation coincided with a progressive softening of fruit. Although Woodmansee et al. (1959) found no consistent changes in the soluble pectin fractions of unripe, ripe, and overripe fruits, a number of researchers (Haber & LeCrone, 1933; Luh et al., 1960) have demonstrated a gradual increase in this fraction, and its subsequent slight decline with fruit deterioration.

Ascorbic acid

Tomato fruit is a rich source of ascorbic acid (vitamin C). On the basis of fresh weight, vitamin C content averages about 25 mg/100 g (Olliver, 1967); however, the values vary with the cultivars. The effect of light on the ascorbic acid content during growth is well reviewed by Hobson & Davis (1971). The ascorbic acid content changes little during fruit maturation and ripening according to several reports (MacLinn & Fellers, 1938; Wokes & Organ, 1943; Kaski et al., 1944). On the contrary, increases in ascorbic acid concentrations during maturation were reported by Brown & Moser (1941), Fryer et al. (1954), and Dalal et al. (1965). Tomato cultivars ripening at a faster rate were shown to contain higher amounts of vitamin C as compared to those that ripened at a relatively slower rate (Clutter & Miller, 1961).

Organic acids

Citric and malic acids are organic acids that contribute most to the typical taste of tomato fruit. Other acids such as acetic, formic, trans-aconitic, lactic, fumaric, galacturonic, and α -oxo acids have been detected. As whole fruit ripens from mature green to red, acidity increases to a maximum value and then decreases (Janes, 1941; Rosa, 1925; Winsor et al., 1962a; Dalal et al., 1965). Maximum acidity was found at breaker (Winsor et al., 1962a) and at pink stages (Janes, 1941; Rosa, 1925; Dalal et al., 1965).

Acidity of tomato fruit is very important for flavor. It is also important to the processor because butyric, thermophyllic, and putrefactive anaerobic microorganisms cannot thrive when the pH is below 4.3. If the pH is over 5, however, the spores of the microorganisms are difficult to kill.

Amino acids

In addition to small amounts of tryptamine, 5-hydroxy tryptamine, and tyramine (Udenfriend et al., 1959; West, 1959a, 1959b), 20 other amino acids have been reported in ripe tomatoes (Carangal et al., 1954; West, 1959b; Burroughs, 1960; Freeman & Woodbridge, 1960; Wong & Carson, 1966; Davies, 1966; Yu et al., 1967). Concentrations of these materials are higher in the pulp than in the walls of the fruit (Carangal et al., 1954; Davies, 1966). Freeman & Woodbridge (1960) observed that glutamic and aspartic acids increased markedly; while alanine, arginine, leucine, and valine decreased with ripening. Davies (1966) reported that glutamic acid increased approximately 10-fold and aspartic acid more than doubled as tomatoes passed from the mature green to the red stage of ripeness. In their studies of eight varieties of tomatoes, Hamdy & Gould (1962) noted that glutamic

acid peaked at the ripe stage. Yu et al. (1967) reported comparable results. However, Yu et al. (1967) found that glutamic acid doubled as the fruit passed from breaker to pink stages of development. Total amino acid content was shown to be constant throughout the ripening process (Freeman & Woodbridge, 1960; Yu et al., 1967). Environmental factors such as application of fertilizers affected the amino acid composition of the tomato fruit (Carangal et al., 1954; Saravacos et al., 1958; Davies, 1964).

On the basis of the patterns of changes noted for the volatile (aroma) components (Dalal et al., 1965) and amino acids during maturation, Yu et al. (1967) hypothesized that certain amino acids could serve as precursors of volatile compounds in tomato fruit. This was further verified by using crude preparations from tomato fruits for the enzymatic degradations of amino acids (Yu et al., 1968a, 1968b, 1968c; Yu & Spencer, 1969, 1970). Nitrogen fertilization (Saravacos et al., 1958), the α -amino acid-citric acid ratio (Hamdy & Gould, 1962), and the dicarboxylic amino acid-soluble carbohydrate ratio (Taverna, 1965) all seem to affect the flavor of raw or processed tomatoes.

Proteins and enzymes

The results of Sando (1920), Rosa (1925), and Yu et al. (1967) on the total nitrogen content of tomato fruit during ripening are inconsistent. Yu et al. (1967) showed that the initial high level of total nitrogen gradually decreased to a minimum at the large green stage of maturity and then increased steadily up to the red stage, followed by a rather gradual decline at the red-ripe stage. Non-protein nitrogen increased with advancing maturity of the fruit. A gradual decrease in the protein content was correlated with the increased production of volatile compounds.

All biological reactions are controlled by enzymes. The effective amount of enzyme present at any given stage of maturity of tomato is generally determined by the relative rates of synthesis and degradation, and by environmental conditions. Yu et al. (1968a) demonstrated that the degradation of amino acids to carbonyl compounds was higher when catalyzed by enzyme extracts from field-grown tomatoes than by those from greenhouse-grown tomatoes. This degradation increased with the maturity of the fruit. The nature and amounts of volatile compounds produced also depended on the maturity stage of the tomato fruit (Yu et al., 1968b, 1968c). An intimate association of the rate of degradation of unsaturated fatty acids with the production of carbonyls by enzyme extracts from ripe fruits has been reported recently by Jadhav et al. (1972). It is generally agreed that several compositional changes accompanied by the development of the typical aroma upon ripening due to catalytic actions of various enzymes

ultimately reflect on the quality of the fruit.

Steroids

Tomato fruits contains tomatine, a glycosidic steroidal alkaloid (Fig. 2). Traces of solanine were also found. By definition, an alkaloid is an alkali-like, poisonous, nitrogenous, physiologically active, and bitter-tasting plant product. According to Kajderowicz-Jasosinska (1965), the largest amount of tomatine, 0.087%, was found in green fruits. In yellowish fruits, the level was reduced to nearly half. Artificially ripened fruits contained relatively higher amounts of tomatine than did those that matured on the plants. Red-ripe tomatoes lose almost all their tomatine when left on the plants for two to three days. Besides alkaloids, stigmasterol and β -sitosterol are two main sterols of the tomato fruit.

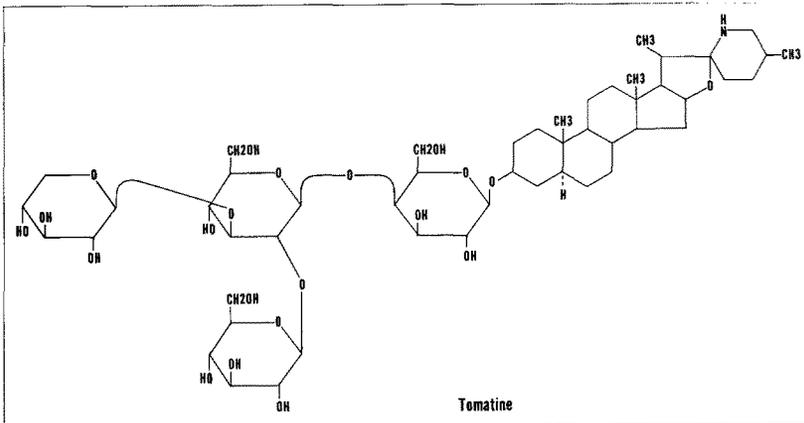


Fig. 2. Structural formula of tomatine

Pigments

Consumers buy tomatoes by 'eye' judgment. Color is perhaps the most important and reliable index of tomato maturity. Consequently it contributes significantly to the grade of both raw and processed products. Chlorophyll *a* and *b*, the major green pigments of tomato fruit until the mature green stage of development, take part in the photosynthetic process during growth and maturation (Boe & Salunkhe, 1967a). As destruction of chlorophyll progresses during ripening, different shades of color such as

green-yellow, yellow-orange with some trace of green, orange-yellow, orange-red, and red develop in sequence.

According to Ferrari & Benson (1961), β -carotene and lycopene contribute 7% and 87% of the carotenoids in a normal red tomato. Curl (1961) reported isolating 22 xanthophyll components (yellow pigments) from the tomato fruits of which the major proportion consisted of lutein, violathin, and neoxanthin; while Edwards & Reuter (1967) detected mainly lutein, lutein 5,6-epoxide, lycoxanthin, and lycophyll. Carotenoids of tomatoes have been found to consist predominantly of carotenes (Kuhn & Grundmann, 1932). Trombly & Porter (1953) listed 19 carotenes obtained from tomato extracts. The two colorless carotenoids, phytoene and phytofluene, are common to tomatoes (Porter & Zscheile, 1946; Rabourn & Quackenbush, 1953; Tomes, 1963). McCollum (1955) showed that the color of red tomatoes depended upon the total carotenoids as well as the ratio of the dominant pigments, lycopene (red color) and β -carotene (yellow color). He also noted that although β -carotene represented only 2 to 10% of the total carotenoids, it exerted a pronounced effect on color. Meredith & Purcell (1966) detected only α - and β -carotenes in mature green tomatoes.

Pigment distribution studies indicated that the concentration of total carotenoids was highest in the outer pericarp, while β -carotene quantities were greatest in the locular region (McCollum, 1955). Ellis & Hamner (1943) and McCollum (1955) studied polar differences and found that although coloration was initiated in the apical end, carotene content was greatest in the proximal region of the ripe fruit.

The report of several workers (Biswas & Das, 1952; Goodwin & Jamikorn, 1952; Tarnovska, 1961; Thompson et al., 1965; Edwards & Reuter, 1967; Czygan & Willühn, 1967) demonstrated that quantities of β -carotene usually increased during ripening. Meredith & Purcell (1966) showed a small decrease in β -carotene after the light-red stage, while Dalal et al. (1965, 1966) found very rapid decreases after a pink stage of ripeness. Other carotenes such as phytoene, phytofluene, ζ -carotene, and γ -carotene increased during ripening (Meredith & Purcell, 1966; Edwards & Reuter, 1967). It is agreed that the β -carotene contribution to the yellowness of the fruit decreases as lycopene concentration increases with further ripening (Dalal et al., 1965, 1966; Meredith & Purcell, 1966).

On the basis of structural similarity and high correlation between the high boiling volatiles (terpenoids) of tomato, Stevens (1970b) hypothesized the production of such volatiles from oxidation of the polyene-carotenes.

Phenolics

Flavonoids and some other phenolic compounds constitute the total phen-

olics of tomato fruit. A commercially important function of flavonoids follows from the fact that fruit color gives immense aesthetic pleasure to man. Wu & Burrell (1958) postulated that the previously conjectured citrinin of tomato is quercetin or a flavonoid mixture. They subsequently isolated naringenin and quercetin from the fruit skins of three varieties of tomatoes. No flavonoids were detected in the peeled fruit. p-Coumaric, ferullic, caffeic, and chlorogenic acids are other phenolics found in tomato fruit. Walker (1962) found increasing concentrations of these compounds, except p-coumaric acid, during ripening. Despite this, phenolic compounds do not produce astringency in tomato fruits. In general, polyphenolics decrease while total phenolics increase during ripening.

Lipids

Lipid fraction of tomatoes is composed of triglycerides, diglycerides, sterols, sterol esters, free fatty acids, and hydrocarbons. Kapp (1966) initiated investigations on the total lipids in the pericarp of tomatoes but found no definite relationship with color development. He reported that total lipids varied with cultivar, fruit maturity at harvest, and storage treatment. A total of 33 saturated and unsaturated fatty acids were found in the pericarp of all tomato varieties tested. Linoleic, linolenic, oleic, stearic, palmitic, and myristic acids comprised the major portion of the fatty acid fraction and increased during the period of greatest color development. During the same period, linoleic and palmitic acids decreased in percent of total fatty acids.

Ueda et al. (1970) found considerable amounts of total lipids in green tomato fruits on plants and lesser amounts in fruits harvested at the breaker stage. A slight increase in neutral lipids occurred at the full ripe stage. The fatty acid composition of triglyceride showed a decrease in linoleic and oleic acids at the stage of color development. According to Jadhav et al. (1972), contents of linoleic and linolenic acids decreased with advancing maturity of tomato fruits. The unsaponifiable fraction of tomato skin contains hydrocarbons plus α and β amyrin, while the alkali soluble fraction contains long-chain organic acids (Brieskorn & Reinartz, 1967a, 1967b).

Minerals

Mineral content increases during growth and maturation of the tomato fruits because of increased cell organization and permeability, acid-base balance, and control or activation of enzyme systems. Although mineral elements represent a small fraction of the dry matter of fruit, they all play an important role in the nutritional composition and final quality of the product.

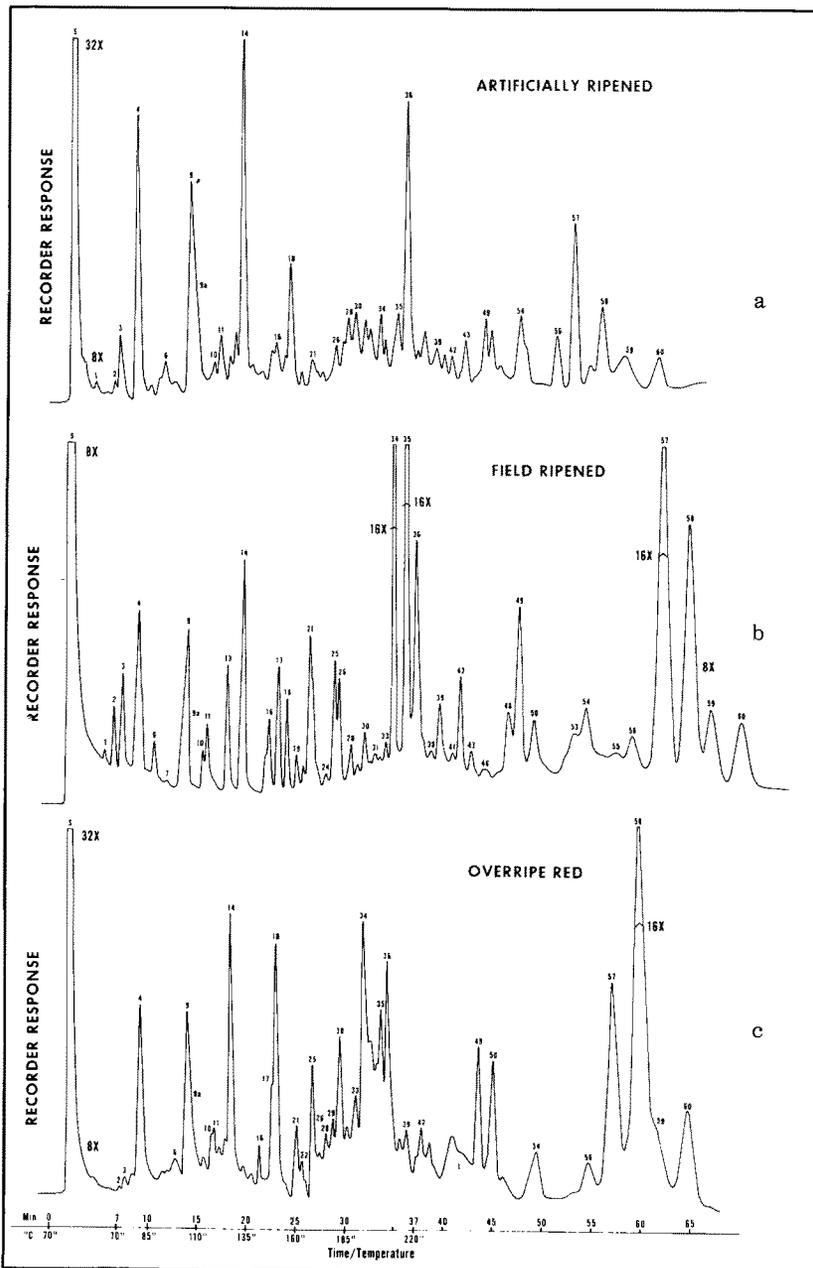


Fig. 3. Gas-chromatograms of volatiles from artificially ripened, field ripened, and overripened tomatoes Source: Shah et al. (1969).

Volatiles

There are numerous volatiles or aroma components in a tomato fruit. Johnson et al. (1971) surveyed the volatile compounds in tomato fruit that have been identified by several workers. Altogether 65 carbonyls, 34 hydroxy compounds (alcohols), 19 esters, 18 acids, 14 hydrocarbons, 6 nitrogen compounds, 5 lactones, 4 acetals and ketals, 4 sulfur compounds, 3 ethers, and 3 chlorine compounds have been reported. According to Shah et al. (1969) a typical aroma of field-ripe tomato is due to carbonyls (32%), short-chain (C_3-C_6) alcohols (10%), hydrocarbons, long-chain alcohols, and esters (58%).

Quality of fruit depends upon environmental conditions such as light, temperature, nutrient availability during growth and maturation, post-harvest treatments, and storage conditions. Consequently, concentrations of aroma components may change with changes in enzymatic activities.

Since sulfhydryl compounds are more readily oxidized than ascorbic acid, they play the role of antioxidant in solutions containing the vitamin and consequently the sulfhydryl content of the fruit decreases during storage (Zuman, 1951). Oxidative breakdown of sulfur compounds leads to the generation of sulfurous volatiles that generally cause off-flavor.

Dalal et al. (1968) observed that isopentanal and hexanol increased with maturation up to the breaker and large green stages, respectively. Both these components decreased considerably at the breaker, pink, and red stages and then increased slightly at the red-ripe stage. The concentration of all volatiles except for isopentanal and hexanol increased during ripening. Shah et al. (1969) evaluated volatiles of field-ripened, artificially-ripened, and overripened tomato fruits (Fig. 3). In artificially ripened (20-22°C) fruits the concentrations of butanol, 3-pentanol, 2-methyl-3-hexanol, isopentanal, 2,3-butanedione, propyl acetate, isopentyl butyrate (peaks 10, 13, 14, 4, 30, 6, 18, respectively), and other unidentified carbonyls were higher than those observed in field-ripe fruits. The concentrations of nonanal, decanal, dodecanal, neral, benzaldehyde, citronellyl propionate, citronellyl butyrate, geranyl acetate, and geranyl butyrate were higher in field-ripened tomatoes than in the artificially ripened ones (peaks 21, 26, 35, 34, 25, 57, 58, 59, and 60, respectively).

A visual comparison of the chromatograms from the field-ripened and overripened fruits indicated an increase in concentrations of isopentyl butyrate, citronellyl butyrate, and geranyl butyrate (peaks 18, 58, 60 respectively).

Yu et al. (1968a, 1968b, 1968c) found that the crude enzyme preparations from green tomatoes synthesized short-chain carbonyls when alanine, leucine, and valine were used as substrates. The enzyme preparations at this

stage were inactive with other amino acids. At a later stage of maturation, however, the enzyme preparations were active with a greater number of amino acids. This shows that as the fruit ripens, more intricate enzyme systems become operative and utilize more substrates for synthesizing volatile compounds. Shah et al. (1969) hypothesized that the short-chain compounds, especially C_4 - C_6 moieties, were formed in their maximum concentrations during the early stage of maturation. Under conditions such as a lack of sunlight, restricted nutrient availability, and limited enzymatic activity during artificial ripening, the long-chain compounds may not be synthesized appreciably. Formation of various groups of volatiles is schematically presented in Fig. 4.

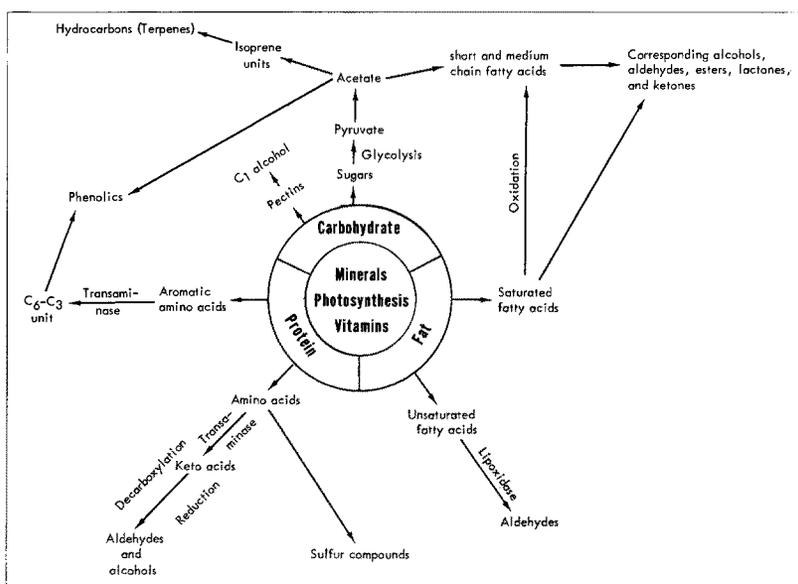


Fig. 4. Degradation of chemical constituents to volatiles

Quantitative differences in volatile compounds between three different cultivars of unprocessed tomatoes were studied by Nelson & Hoff (1969). The results are presented in Table 2. Acetaldehyde, methyl sulfide, methanol, ethanol, and isopentanal were found in Rutgers in greatest quantities in processed tomatoes. The cultivar H 1350, on the other hand, contained the smallest amounts of methyl sulfide, acetone, and methanol. Acetone and methanol occurred in Roma at higher concentrations. Similar results were reported by Johnson et al. (1968). Additionally, differences caused by harvest dates were apparent (Table 3). Stevens (1970a) examined

the volatiles from Campbell 146 and Campbell 1327 cultivars and found differences in the concentrations of 2-isobutylthiazole, methyl salicylate, and eugenol. All of these when present at threshold measurements probably contribute to maximum tomato flavor. Genetic factors play an important role in controlling the concentration of these components.

The remarkable advances made in analytical instrumentation have aided flavor chemists in the successful separation and identification of trace amounts of aroma compounds. A complete analysis of volatiles requires a three-step procedure: extraction, fractionation, and identification. A simple method for the extraction of tomato volatiles is by use of a proper solvent.

Table 2. *Average concentration of selected components in three cultivars of unprocessed tomatoes*

Compound	Cultivar		
	H1350	Roma	Rutgers
	ppm	ppm	ppm
Acetaldehyde	0.92	0.21	0.48
Acetone	0.76	0.64	1.03
Methanol	229	125	177
Ethanol	62	14	56
Isopentanal	0.42	0.44	0.87
Hexanal	3.44	2.82	1.32

Source: Nelson & Hall (1969).

Table 3. *Average concentration (ppm) of two volatiles in three selected tomato cultivars harvested at different dates*

Cultivar	Volatile	Harvest date		
		Sept. 6	Sept. 12	Sept. 19
ES 24	<i>cis</i> -3-Hexenol	19.85	9.26	9.7
	Pentanol	1.64	0.7	0.57
Heinz 1350	<i>cis</i> -3-Hexenol	30	— ^a	15
	Pentanol	1.79	— ^a	1.35
Heinz 1370	<i>cis</i> -3-Hexenol	9.7	8.82	8.38
	Pentanol	0.82	0.68	0.85

^aValues not reported.

Source: Johnson et al. (1968).

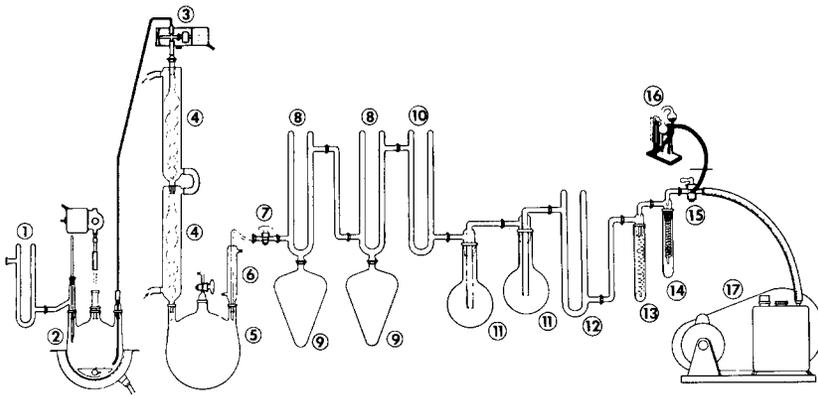


Fig. 5. An apparatus for the isolation of volatiles from solid or aqueous foods by evaporation from a continuous thin heated film under vacuum.

- 3. Pump for feeding the food material.
- 4. Vaporizer under high vacuum heated by circulating glycerine (105°C) through the outer jacket.
- 9-14. Series of cooled traps.
- 17. Vacuum pump.

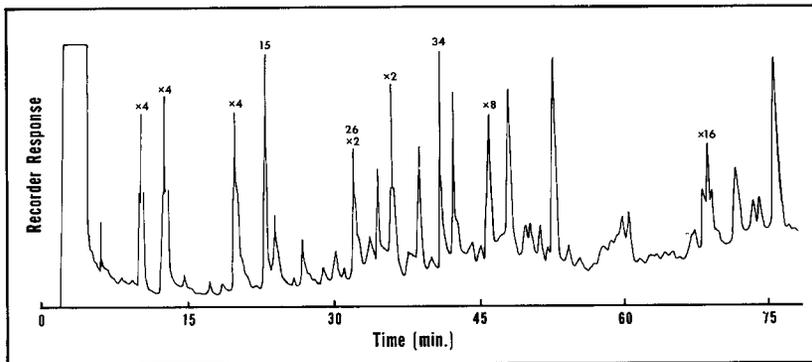


Fig. 6. A gas chromatographic pattern of tomato volatiles. Peak 15 is 2-isobutylthiazole. Source: Stevens (1970 a).

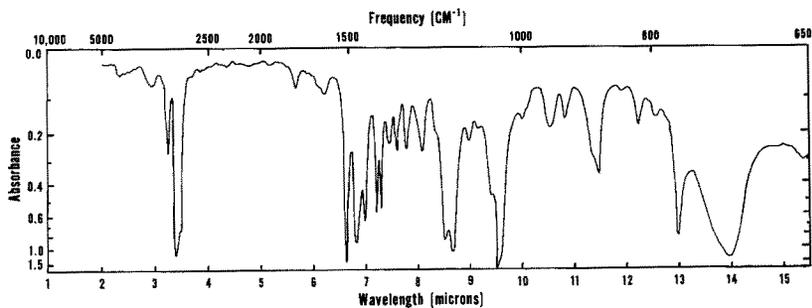


Fig. 7. Infra-red spectrum of 2-isobutylthiazole. Source: Kazeniac & Hall (1970).

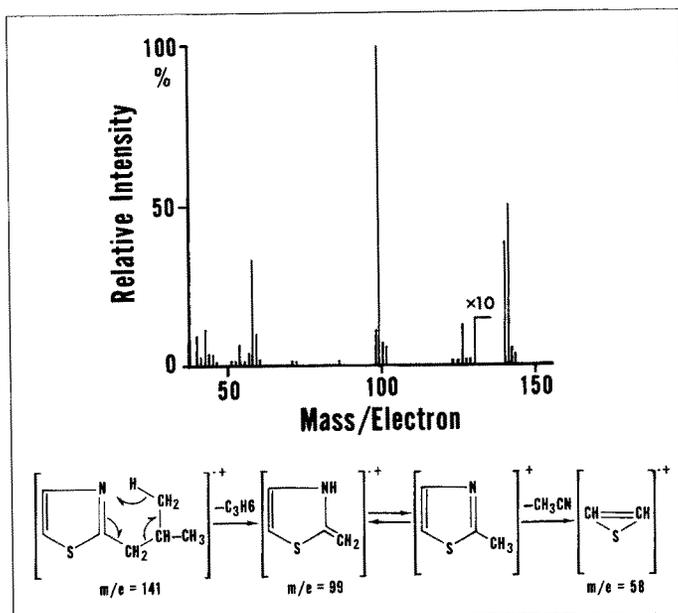


Fig. 8. Mass spectrometric data of 2-isobutylthiazole. Source: Viani et al. (1969).

Inclusion of non-volatile compounds such as pigments, however, makes the analysis complex. Steam distillation often causes chemical changes in the aroma. Distillation under reduced pressure coupled with low temperature condensation appears to be the most desirable means of obtaining the volatile fraction. An apparatus used by Chang (1973) for isolation of volatiles from solid or aqueous foods under vacuum is shown in Fig. 5.

The concentrated essence obtained by one of the preceding methods can be separated into its components by various types of chromatography. Gas chromatography has facilitated the separation of very small quantities of mixtures. A typical gas chromatographic pattern of tomato volatiles is presented in Fig. 6. The problems encountered in gas chromatography of volatiles has been thoroughly discussed by Jennings (1972).

Identification of individual components of a tomato essence can be accomplished by comparing chemical and physical properties of that compound with those of an authentic compound. Rigorous methods of identification range from determination of physical constants (boiling point, melting point, chromatographic R_f values, retention time) to ultraviolet, infra-red, and mass spectrometric analyses. Nuclear magnetic resonance (NMR) could be applicable if a large sample of aroma component is available. High sensitivity of these instruments has made the identification of flavor components possible. By applying the present knowledge of spectroscopic characterization of organic compounds, the identity of 2-isobutylthiazole (Fig. 6) separated on a GLC column could be further confirmed by data obtained from infra-red (Fig. 7) and mass spectrometries (Fig. 8).

PHYSIOLOGICAL CHANGES DURING GROWTH AND MATURATION

Respiration

Tomato fruit passes through successive stages of growth and maturation before ripening. Metabolic activities associated with such changes require uptake of oxygen. Although the tomato fruit has stomata, gaseous exchange takes place through the stem end of the fruit.

The respiratory activity of the tomato can be divided into two parts: pre-climacteric and climacteric. The rate of respiration declines continuously from an initial high, during the first few weeks, to a stage of maturation, especially degradation of starch and changes in the sugar-acid ratio (Beadle, 1937; Winsor et al., 1962a; Davies & Cocking, 1965; Boe, 1966). Mitochondrial oxidation of succinate, malate, and α -deoxoglutarate becomes enhanced during this period of maturation. Dickinson & Hanson (1965) found that mitochondria isolated from mature green tomatoes were

more active than those isolated at other stages.

A climacteric rise in respiration occurs during ripening (Winsor et al., 1962a; Pratt et al., 1965) and is considered a turning point in the life of the fruit in regards to quality. The climacteric maximum may occur either before or after the fruit is removed from the plant, depending upon the harvesting procedures. Compositional changes associated with ripening are discussed in the previous section. Mitochondria show reduced rates of oxidation of organic acids at this stage of respiration (Dickinson & Hanson, 1965). A progressive decrease in the oxidative capabilities of mitochondria isolated from fruits during successive stages of ripeness was also reported by Abdul-Baki (1964), Lyons et al. (1964), and Drury et al. (1968).

Pigment development

Pigment alterations during ripening change the appearance of the tomato fruit. Color is a most important and complex attribute of quality and hence it has received substantial attention in breeding programs. Lycopene and carotene pigments are unmasked as chlorophyll gradually disappears during ripening. Pigmentation first appears in the semi-liquid material surrounding the seeds when the tomato fruit reaches its climacteric peak.

MacGillivray (1934) studied the temperature of fruit in the field. He observed that the temperature of the fruit varied from 15°C in well shaded fruit to 38°C on plants with poor foliage. Rose (1926) reported that increased temperature affected final color and speed of ripening and that optimum color resulted at temperatures between 23 and 25°C. He further noted no color above 30°C.

Specific gravity

Maturity can be determined on the basis of specific gravity, besides by size and color. Applying this criterion, Salunkhe et al. (1971) found that the specific gravity of tomatoes increased up to the breaker-turner stage. However, no information is available on the specific gravity of fruits during ripening. Assuming no significant change in the size after the breaker-turner stage, specific gravity would probably decline during ripening as a result of respiration losses.

CHEMICAL AND PHYSIOLOGICAL CHANGES DURING RIPENING

Field and greenhouse conditions

Today, greenhouse tomato production is a major enterprise in agriculture.

Of all the food crops grown under glass, plastic, or fiberglass, tomatoes exceed all others combined in value and acreage. Until recently, however, little attention has been given to the quality of tomatoes grown under greenhouse conditions.

Non-uniform environmental conditions, mainly light, have been considered the primary reason for inadequate color development in greenhouse tomatoes (McCollum, 1946). Forshey & Alban (1954) indicated that restricted photosynthetic activity due to shading lowers the sugar concentration in greenhouse tomatoes. Lack of sunlight during the growing period, resulting in fruits of low concentrations of sugars and soluble solids, has been correlated with softer fruit. Frazier et al. (1954), McCollum (1946), and Somers et al. (1945) have all indicated that light energy impinging directly on the fruits determines their ascorbic acid contents. Brown & Moser (1941) reported that greenhouse fruit had only about half the vitamin C concentration of field-grown tomatoes.

Dalal et al. (1965, 1966) reported data on field and greenhouse-grown tomatoes of V. R. Moscow and Fireball cultivars with regards to total titratable acidity, color development, free reducing sugars, pectins, volatile reducing substances (VRS), organic acids, and ascorbic acid. Concentrations of all non-volatile attributes except total titratable acidity were low in greenhouse-grown tomatoes. These authors concluded that such tomatoes suffered a considerable loss in quality (color and taste) because of lower concentrations of VRS, organic acids, and sugars.

To evaluate the aroma, Dalal et al. (1967) analyzed by gas chromatography the volatile compounds present in an ethyl chloride extract of red-ripe tomatoes (cv. V. R. Moscow). Except for isobutanol, hexanol, and hexanal, concentrations of the aroma components in the field-grown tomatoes were higher than those in the greenhouse-grown tomatoes. Fruits harvested at different stages of maturation were also analyzed for volatile components (Dalal et al., 1968). Gas-liquid chromatograms were consistent for both field and greenhouse-grown tomatoes at all stages of maturity. The production of volatiles increased along with the growth of fruit.

Artificial ripening

Extensive studies were conducted by Boe et al. (1968) to assess the quality of artificially ripened tomatoes. He showed that such tomatoes were higher in acid content and lower in sugars than field-ripened tomatoes. Tomatoes ripened under the conditions of magnetic fields had the characteristics of fruit ripened in the dark. Dalal et al. (1967) used tomatoes for artificial ripening that were taken from the field at the large green stage and maintained at 15-20°C until they were red-ripe. Such fruits contained less

volatile compounds than did field-ripened tomatoes.

STORAGE AND POST-HARVEST PHYSIOLOGY

Temperature

The life processes occurring in harvested produce are essentially destructive. Cold storage is designed to reduce these destructive processes to a minimum. According to Van 't Hoff's Law, the rate of chemical reaction is doubled for every 10°C (18°F) increase in temperature. The optimum storage temperature required to increase shelf-life without loss in quality will vary with the commodity.

Storage temperature should not be so low that it causes chilling injury. Mature green tomatoes will suffer cold injury and not ripen properly if held at 0°C to 4.4°C for longer than 3 to 5 days, although the freezing point of the tomato is about -0.55°C. The proper temperature conditions for storing green or red tomatoes have been established by several workers (Haber, 1931; Tomkins, 1963; Truscott & Brubacher, 1964; Truscott & Warner, 1967), and vary from 8°C to 21°C depending upon the objectives of storage.

Rosa (1926) determined compositional changes at 4-day intervals in green tomatoes stored under various constant temperatures. He noted that total solids and total acids decreased rapidly in fruit held at 25°C, while sugars increased slightly during the first time interval and then gradually decreased. At 19°C, compositional changes were less rapid and less extensive. At 4°C and 12°C, total solids and total acids showed little change with time, but sugar concentrations slowly increased throughout the treatment period. Similar results were observed by Haber (1931) relative to total acids and pH of green mature tomatoes following 4 to 5 weeks storage at either low (2.4, 4.4, and 10°C) or high (21.1°C) temperatures. However, Craft & Heinze (1954) concluded that temperature and duration of storage had little or no effect on total acidity, soluble solids, and pH. Hall (1968), using tomato fruits at the incipient color stage, found that the titratable acidity of pericarp portions of fruit held at 3.3°C was significantly higher than that of fruits held at 7.2 or 10°C. Acidities of pericarp and locular portions of fruit chilled for 4 or 8 days followed by 6 days at 21.1°C were higher than those of control fruits ripened without prior chilling.

Light

Visible spectrum of light has long been known to accelerate the color of

tomato fruits. McCollum (1954) and Nettles et al. (1955) observed significantly redder color and higher carotenoids in tomato fruits when illuminated with light as compared to tomatoes ripened in the dark. Shwefelt and Halpin (1967) used three kinds of fluorescent lamps to accelerate color development of green tomatoes and found the standard Grow-Lux lamp to be the most effective in enhancing the color. Boe et al. (1968) showed the effect of light frequency and concluded that red light was nearly as effective as full light to increase the color in tomatoes.

At least two pigment systems are involved in color changes of tomato ripening-biodegradation of chlorophylls and synthesis of carotenoids. Jen (1974) showed that white fluorescent light and color filter with maxima at 650, 570, and 500 nm corresponding to red, green, and blue, respectively, were compared at the same radiant energy level with dark controls for their effects on the pigment systems of tomato fruits ripened under controlled environments. Degradation of chlorophylls was faster in tomatoes illuminated with light than the control, with red light yielding the highest degradation rate. No change in chlorophylls a/b ratio was observed. The carotenoid levels after 10 days illumination in Mg/g were 136, 117, 81, 72 and 42 for blue, red, green, white, and dark control, respectively. Illumination of red and yellow lutescent tomatoes produced similar results. This indicates that red light is most effective in accelerating the biodegradation of chlorophylls and blue light is most effective in enhancing the biosynthesis of carotenoids in tomato fruits during ripening. The explanations for these results could be that phytochrome requires red light for activation of ripening process (Khudairi, 1972) and the absorption maxima of the carotenoids are in the blue region of light, hence blue lights accelerates biosynthesis of carotenoids in tomato fruits.

Controlled atmosphere storage

In a controlled atmosphere (CA), the concentrations of oxygen and carbon dioxide are decreased and increased, respectively, from their normal values in the air, and nitrogen is used to maintain the new composition. Fruits under CA storage respire at an even lower rate than do fruits under conventional cold storage in normal air, which also reduced the respiration rate. With a lower respiration rate, fruits do not age as rapidly, less sugar has to be used in respiration, and the fruits taste sweeter at the end of the storage period.

The effects of controlled atmospheres with low oxygen and high carbon dioxide concentrations on the storage life and biochemical changes of the tomato fruit have been well documented. An atmosphere with 5% O₂ and 5% CO₂ at 12°C retarded ripening and fungal growth in tomatoes (Kidd &

West, 1933). Exposing tomatoes to more than 5% CO₂ delayed ripening but increased rotting (Tomkins, 1963). The best storage atmosphere at 12.8°C was a mixture containing 2.5% O₂ and 5% CO₂ (Eaves & Lockhart, 1961). According to Parsons et al. (1970), tomatoes could be stored best in an atmosphere with 3% O₂ and zero CO₂. Salunkhe & Wu (1973) found that low O₂ atmospheres (1% or 3% O₂) inhibited the degradation of chlorophyll and starch, and the synthesis of lycopene, β-carotene, and soluble sugars in green-wrap tomatoes.

Hypobaric storage

Hypobaric or sub-atmospheric storage is a recent approach of increasing the storage life of horticultural produce (Burg & Burg, 1966; Tolle, 1969; Wu et al., 1972). This type of CA storage includes a reduction of atmospheric pressure, and has the same sort of effects as standard CA storage. In the sub-atmospheric storage, however, the ethylene and other gases produced by the respiring fruits are removed by a continuous evacuation of air. Since ripening fruits produce ethylene in the presence of an adequate oxygen supply, removal of oxygen as well as ethylene delays ripening and extends the marketable life of the produce. Green-wrap tomatoes subjected to hypobaric storage evidenced a delay in the physiological changes (losses of chlorophyll, starch, and the formation of lycopene, β-carotene, flavor, and sugar) associated with ripening (Wu et al., 1972).

Packaging

Packaging fruits in polyethylene provides modified atmospheres and consequently reduces fruit decay, softening, and loss of soluble solids during storage. Reductions in transpiration and respiration losses increase the shelf life and retain quality.

Growth regulators

Basically, the ripening process is associated with the production of ethylene gas, which acts as a ripening hormone. In general, the rate of ripening depends upon the amount of ethylene produced indigenously. Ethylene gas has been used commercially to accelerate ripening of fruits. Ethylene in the order of 1 ppm is enough to induce color change in many fresh fruits.

Boe & Salunkhe (1967b) reported biochemical changes associated with ethylene and oxygen treatments. They observed increased concentration of citric acid in the fruits ripened in ethylene (100 ppm). Treatments with oxygen decreased reducing sugars and high concentrations had no effect on

the rate of lycopene synthesis. Boe et al. (1968) noted that ethyl, hexylalcohols, kinetin, 2,4-dichlorophenoxyacetic acid, and naphthaleneacetic acid (NAA) increased the ripening rate of tomato fruit. Injury to fruit was observed with treatment by acetaldehyde, dextrose, fructose, pyruvic acid, octyl, dodecyl, heptyl, hexadecyl alcohols, and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T). No injury was noticed with citric and malic acid; however, ripening induction was apparent with citric acid.

Ethrel, Amchem Product No. 68–240, contains ethephon (2-chloroethylphosphonic acid) and is known to induce earlier and more uniform ripening when applied either to the foliage of the tomato plant or to the harvested mature green fruits. The results of Salunkhe et al. (1971) indicated no significant differences in quality factors such as color, acidity, and sweetness between the control fruits and those treated with 1,000 ppm Ethrel. A new compound, CPTA [Amchem Product No. 70–334 containing 2-(p-chloroethylthio)-triethylamine hydrochloride] accelerates change in surface color of green tomatoes (Rabinowitch & Rudich, 1972). When tomato fruits were dipped in solutions of CPTA (1200, 2400, or 4800 ppm), red color was developed in the exocarp – not because of initiation of ripening, but only due to the synthesis of lycopene and its accumulation in carotenogenic tissues. However, a treatment of CPTA in combination with Ethrel caused higher color grades when compared with the Ethrel treatment. Jadhav & Salunkhe (1972) found that tomato fruits treated with Amchem 72-A42 (CPTA amine) alone or in combination with Ethrel developed pink and red colors without prior accumulation of yellow color because of acceleration of lycopene synthesis. In processing tomatoes, the combined treatment of Ethrel and CPTA or CPTA amine might bring about improved fruit color and uniform ripening.

Available evidence indicates a delay of tomato ripening by ethylene oxide (Lieberman & Mapson, 1962) and a retardation of chlorophyll breakdown by gibberellic acid which is reversible by ethylene (Khudairi, 1972).

ZUSAMMENFASSUNG

Die Qualität der Tomatenfrucht wird chemisch bestimmt durch Farbe, Festigkeit, durch Geruch und Geschmack, durch Nährwert und Bekömmlichkeit. Im allgemeinen korrelieren hoher Zuckergehalt, intensive Rotfärbung und Festigkeit der Frucht mit Vorhandensein eines vollen Armas.

Biochemische Veränderungen bedingt durch Wachstums, Reife und Umwelt der Tomatenfrucht werden diskutiert.

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