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Biochemical Parameters in Tomato Fruits from Different Cultivars as Functional Foods for Agricultural, Industrial, and Pharmaceutical Uses

Pranas Viskelis, Audrius Radzevicius, Dalia Urbonaviciene, Jonas Viskelis, Rasa Karkleliene and Ceslovas Bobinas

Abstract

Tomato and tomato based products are an important agricultural production worldwide. More than 80 % of grown tomatoes in the worldwide are processing in the products such as tomato juice, paste, puree, catsup, sauce, and salsa. Tomato fruit is rich in phytochemicals and vitamins. Tomato nutritional value, color, fruit and flavor of their products depends mainly on lycopene, β-carotene, ascorbic acid and sugars and their ratio in fruits. Epidemiological studies and the results associated with the consumption of tomato products against the prevention of chronic diseases such as cancer and cardiovascular disease, confirming the tomato products as a functional food, and show that lycopene and β-carotene acts as an antioxidant. In order to increase the amount of these elements in tomato fruit, it is important to evaluate and investigate tomato genotypes influence to the carotenoids accumulation. Studies have confirmed that the carotenoid content in tomato fruits is determined by genotypic characteristics. In this work the main attention will be focused on from the biochemical and physical properties in tomato of different varieties, chemical and physical properties, to functional properties of supercritical fluid extraction of lycopene from tomato processing by products supercritical fluid tomato extracts.

Keywords: biochemical composition, physical properties, phytochemicals, nondestructive analysis, supercritical fluid extraction
1. Introduction

Tomato is one of the most valuable and popular vegetables worldwide. It is desirable that tomatoes are fertile and disease resistant, and each cultivar differs in fruit size, shape, taste, colour, and skin and flesh firmness. Tomatoes must also be resistant to transportation conditions to meet market requirements and consumer needs, as there is an increased demand for large-fruit salad-type tomato varieties. Tomatoes and tomato-based products are an important agricultural commodity worldwide. More than 80% of tomatoes grown worldwide are processed into products such as tomato juice, paste, puree, catsup, sauce, and salsa. Tomato fruit is rich in organic acids, sugars, dietary fibre, pectic substances, proteins, fats, minerals (potassium, phosphorus, sulphur, magnesium, calcium, iron, copper, and sodium), vitamins (B1, B2, B3, PP, C, provitamin A, I, and H), and carotenoids possessing antioxidant qualities (lycopene, β-carotene, etc.). Due to the importance of vegetables in the human diet, it is recommended to consume 400-500 grams daily, 140 to 150 kg per year of various vegetables, including 25 to 32 kg of tomatoes for an adult human [1, 2]. The nutritional value, colour, and flavour of tomatoes and their products depend mainly on lycopene, β-carotene, ascorbic acid and sugars, and their ratios in the fruits. The two most important carotenoids in tomato fruits are lycopene, which determines the fruit’s red colour, and β-carotene, which accounts for approximately 7% of tomato carotenoids [3]. Therefore, tomato products and their quality can be characterised by the contents of these elements. Humans get 85% of their lycopene from tomatoes and tomato products [4], which is the reason why tomatoes are used in functional food products [5], and sometimes as functional foods [2, 6]. Epidemiological studies and other studies associated with the consumption of tomato products for the prevention of chronic diseases, such as cancer and cardiovascular disease, confirm that tomato products are functional foods and show that lycopene and β-carotene act as an antioxidant [7, 8]. In order to increase the amounts of these elements in tomato fruits, it is important to evaluate and investigate the influence of tomato genotypes on carotenoid accumulation. Previous studies have confirmed that the carotenoid content in tomato fruits could be determined by genotypic characteristics [9, 10]. This paper focuses on the biochemical and physical properties of tomatoes of different varieties, their chemical and physical properties, and the functional properties of supercritical fluid extraction of lycopene from tomato processing.

2. Tomato biochemical composition

Currently, the food industry advocated increasingly in synthetic antioxidants changes by the ‘safer natural mixtures’. This option has been made available through the worldwide consumer preference for natural antioxidants, some of which are added intentionally during processing and some exist inherently in foods. Between them, carotenoids comprise the group of the most abundant micronutrients in fruits and vegetable; also, their dietary consumption is related with a lower frequency of some cancer types of as well as reinforces prevention against the cardiovascular diseases [11-13].
Flower and fruit colour is caused by different types of pigments belonging to the terpenoid and phenylpropanoid classes. Carotenoids, chlorophylls, and anthocyanins are the main three groups of pigments. Colour characteristics, in some plants, can be determined by domestication of agronomic traits, while in others, the increase of these pigments in tissues can occur naturally. This could be applied to tomato (*Solanum lycopersicum* L.), which has several carotenoids, such as lycopene and β-carotene, among others. The amount of these carotenoids is principally determined by the tomato cultivar and genotype [14, 15]. It has been established that carotene, nitrates, and sugar amounts in fruits and root crop vegetables depend on plant genotype, meteorological conditions, fertilisation, and soil composition [16-19]. The levels of the essential antioxidant vitamins, in contrast with other antioxidative defences, are determined mainly by the plant’s dietary supply. One major vitamin for enriching human diets is the antioxidant vitamin C (ascorbic acid). This vitamin can counteract the oxidising effects of lipids by scavenging free radicals that have been found to be major promoters of certain diseases. Recently, it has been demonstrated that carotenoids react cooperatively and synergistically with vitamin C, serving to regenerate a pro-oxidant radical carotenoid following the antioxidant reduction of a radical species [11]. Vitamin C usually found in vegetables and fruits, and it is a natural antioxidant. Ascorbic acid plays an important role in biochemical processes such as the formation of collagen, absorption of iron, and its involvement in the immune response and the synapses. However, a high amount of this antioxidant for human could be painful and cause adverse effect. Thus, the precise determination of ascorbic acid in various plant species or cultivars is very important [21-25]. There seems to be little doubt that acids and sugar not only contribute to the sweetness and sourness of tomatoes but are also major factors in overall flavour intensity. Since the lack of flavour is a common complaint about fresh market tomatoes, increases in sugar and acid contents could make a contribution to improve tomato flavour [16].

Nitrate is very important for plant functions and nutrition. It is a part of the nitrogen cycle and occurs naturally. Human exposure to nitrate is mainly exogenous through the consumption of vegetables, and to a lesser extent through water and other foods. Vegetables are the major vehicles for the entry of nitrate into the human body. Ever-increasing concerns over nitrate toxicity have directed a number of countries to institute maximum allowable threshold concentrations of nitrate-N in vegetables [26].

Tomatoes and tomato products are major sources of lycopene compounds and are also considered an important source of carotenoids and vitamins in the human diet [27, 28]. Therefore, considerable work has been conducted to increase their levels in tomatoes through breeding programmes [29]. The amount of carotenes and their antioxidant activity as well as their biochemical composition are significantly influenced by the tomato variety and maturity [20, 30]. The importance of genotype selection for high nutritional value is outlined first, followed by the optimisation of environmental conditions and agricultural practices [31]. Normalised values for lycopene contents of different tomato cultivars in California ranged from 8.4 to 17.2 mg 100 g\(^{-1}\), representing a 100% difference from the lowest to the highest values [32]. According to Viskelis, the highest amount of lycopene (over 10 mg 100 g\(^{-1}\)) was found in the Lithuanian cultivar ‘Rutuliai’, which was 1.6 times higher than that of the hybrid ‘Admiro’ and twice as high as the hybrid ‘Kassa’ [33].
Based on the multiannual data [34] of 10 cultivars (‘Viltis’, ‘Milžinai’, ‘Skariai’, ‘Laukiai’, ‘Veža’, ‘Pažar’, ‘Vilina’, ‘Ruža’, ‘Ranij 310’, and ‘Elbrus’) investigated in Lithuania (Fig. 1), the highest level of lycopene was established in cultivars the ‘Ranij 310’ (13.56 mg 100 g\(^{-1}\)) and ‘Elbrus’ (12.57 mg 100 g\(^{-1}\)).

The least amount of lycopene was found in the fruits of the cultivars ‘Skariai’ (8.55 mg 100 g\(^{-1}\)) and ‘Milžinai’ (8.75 mg 100 g\(^{-1}\)). In other cultivars, the lycopene amount had varied from 9.57 (‘Veža’) to 12.08 mg 100 g\(^{-1}\) (‘Laukiai’). Lycopene is the most abundant carotene in red tomato fruits and accounts for up to 90% of the total carotenoids. Typical red-pigmented tomato fruits also contain a lesser amount of β-carotene and other carotenoids. β-Carotene occurs in tomato fruits in various amounts from 0.23 to 2.83 mg 100 g\(^{-1}\) [35]. Our studies showed (Fig. 2) that significantly higher amounts of β-carotene were accumulated by two cultivars, ‘Ranij 310’ and ‘Elbrus’, with 2.34 and 2.16 mg 100 g\(^{-1}\), respectively. The least amount of β-carotene was found in the cultivar ‘Veža’ (1.33 mg 100 g\(^{-1}\)). Most of the investigated cultivars had similar amounts of β-carotene, which varied from 1.43 to 1.70 mg 100 g\(^{-1}\).

Figure 1. The amount of lycopene in tomato fruits.

Figure 2. The amount of β-carotene in tomato fruits.
Tomatoes are a good dietary source of ascorbic acid (vitamin C); however, the ascorbic acid content in tomatoes varies greatly. Many factors contribute to this variation, and environmental growing conditions and cultivar genotype have been reported as having major effects on ascorbic acid composition [21, 22]. There is a wide variation of ascorbic acid content in different cultivars. According to Mathews, the vitamin C values for 41 cultivars ranged from 10.7 to 20.9 mg 100 g⁻¹ (23). Ten years of data presented by a Lithuanian scientist showed that the average amount of ascorbic acid was 16.20 mg 100 g⁻¹ in different tomato cultivars [36]. According to our data (Fig. 3), the cultivar ‘Vilina’ had a significantly higher amount (15.9 mg 100 g⁻¹) of ascorbic acid compared with the other eight cultivars, except for the value of the cultivar ‘Laukiai’, which was not significantly different (12.2 mg 100 g⁻¹). The least amount of ascorbic acid was found in the cultivar ‘Viltis’ (7.8 mg 100 g⁻¹).

Figure 3. The amount of ascorbic acid in tomato fruits.

Sugars and acids are particularly important taste constituents of tomatoes. The sugar content of ripe tomatoes averages 3% [37], but in Lithuanian-grown tomatoes, the average amount of total sugar is 4.37% [2]. Other researchers have reported that the amounts of total sugar varied little for different cultivars and ranged from 4.01% to 4.17% [33]. In our research, the total sugar content had a small amount of variation, from 4.32% in cultivar ‘Viltis’ to 5.03% in cultivar ‘Elbrus’ (Fig. 4).

The nitrate content in vegetables may range from 1 to 10000 mg kg⁻¹. The various reasons for this wide range are the excessive use of fertilisers, crop variety, types of N-fertilisers, light and temperature conditions, and lack of water [26]. A combination of these factors accounts for the different nitrate values reported for vegetables in different countries. A complicating factor for the nutritional exploitation of vegetables is the presence of nitrate (nitrite), which is antinutritional and toxic in nature. Nitrate content is an important quality characteristic of vegetables [38]. Amr and Hadidi reported that cultivar had a significant effect ($P \leq 0.05$) on the nitrate content of greenhouse grown tomatoes [39]. Tomatoes accumulate low contents (100 -150 mg kg⁻¹) of nitrates. This was demonstrated in our investigation (Fig. 5); all cultivars had a low content of nitrates compared with other vegetables, and the amount of nitrates ranged from 55 (‘Vilina’) to 91 mg kg⁻¹ (‘Elbrus’).
2.1. Fruit biochemical composition of organic tomato

Consumers are becoming more interested in the environmental problems caused by agricultural activities, and there is an increased focus on the health risks resulting from the use of various chemicals. The growing phytosanitary problems and the unrelenting use of pesticides has led to new challenges in food safety. The sustainability of conventional agriculture is being questioned, and changes are needed in agricultural sciences. Currently, the development of organic growing systems is rapidly emerging as a national priority, and many countries have certified organic agriculture programs. The organic food market is developing dynamically in many countries, and therefore, studies concerning the nutritive value of organically grown products are becoming increasingly important [40, 41].

Tomatoes are an excellent plant for the comparison of fruit quality attributes between conventional and organic systems due to their global value and popularity. Unfortunately, organic cultivation has a markedly negative effect on yield, and organic fruits have more visible defects compared with conventionally grown fruits [42]. However, consumers expect organic food to have a higher nutritional value, to be healthier, or simply to be safer and less risky. Scientists

Figure 4. The amount of total sugar in tomato fruits.

Figure 5. The amount of nitrates in tomato fruits.
have reported that conventional crops have higher levels of protein and vitamin E, carotenoids, and alkaloids, while organically grown crops tend to have more phytic acid, phenolic compounds, glucosinolates, and vitamin C. However, studies have shown that the relative impact of adopting organic production methods on food quality and safety may change over time, according to changes of soil characteristics and plant cultivars [43]. Organic foods are perceived by many consumers as safer and healthier compared with conventional ones. Organic farming enhances the long-term natural fertility of the soil, minimises soil pollution, and avoids the use of mineral fertilisers and pesticides, which lead to positive health effects for livestock and humans consuming organic foods. Fruits and vegetables have positive health benefits and contain significant amounts of biologically active compounds that may be responsible for these effects [44].

Tomato fruit quality composition varies due to a wide variety in species, stage of ripeness, year of growth, climatic conditions, light, temperature, soil, fertilisation, irrigation, and other conditions of cultivation. The amount of total and soluble solids in tomato fruits are a major economic parameter for their nutrition value. The average dry matter content of a ripe fresh fruit ranges between 5.0% and 7.5% [45]. Earlier studies noticed statistically significant differences in the content of dry matter in organic tomato fruits. Studies have reported that organic tomatoes contain, on average, 7.86% dry matter in fresh tomato fruits, compared with 5.07% dry matter in conventionally grown tomatoes. An investigation of different cultivars showed that cherry tomato contained the highest levels of dry matter compared with other tomatoes [42].

An investigation of different farming systems was carried out by the Institute of Horticulture Lithuanian Research Centre for Agriculture and Forestry [46]. Tomatoes were grown using two different farming systems (organic and conventional) in unheated greenhouses in natural soil, using the tomato cultivar ‘Vilina’ and two tomato hybrids, ‘Benito’ and ‘Tolstoi’. Organic tomato plants were sprayed twice (on the 7th and 21th of July) with an organic fertiliser based on seaweed extract (Ascophyllum, 15% w/w). Conventional tomatoes were grown under conventional tomato growing technologies adopted by the Institute of Horticulture [46].

The results of this research agreed with previous data that higher amounts of dry matter and soluble solids were present in the organically grown tomatoes of all investigated cultivars compared with the conventionally grown fruits (Fig. 6) but determined that the differences were not statistically significant. The amount of dry matter varied from 6.64 (cv. ‘Vilina’) to 9.06% (cv. ‘Benito H’) in organically grown tomato fruits and from 6.37 (cv. ‘Vilina’) to 8.44% (cv. ‘Benito H’) in conventionally grown tomatoes. The highest amount of soluble solids (4.47%) was detected in fruits of the tomato hybrid ‘Tolstoi’ grown using the organic system. In organic tomatoes, the average amount of dry matter was 7.77%, and the amount of soluble solids was 4.40%, while conventional fruits had 7.30% dry matter and 4.30% soluble solids.

Previous studies noted that the lycopene content in organic tomatoes was lower than in conventional ones, but found a significantly higher level of β-carotene in organic fruits [42]. Schulzova and Hajsova [47] investigated the impact of fertilisation systems on biologically active compounds in tomatoes and determined that the amounts of carotenoids varied depending on the farming system and cultivar. In their experiment, levels of β-carotene ranged...
from 5.4 to 9.8 mg kg$^{-1}$ and levels of lycopene ranged from 137 to 286 mg kg$^{-1}$. However, Riahi and colleagues [48] investigated the impact of conventional and organic production systems on the quality of field tomatoes and did not find any significant differences in the amount of lycopene for all cultivars.

The data (Fig. 7) from this study show that tomato hybrids, grown organically, accumulated significantly higher amounts of lycopene in their fruits compared with those under conventional farming, but there were no significant difference in the amount of lycopene in cv. ‘Vilina’ fruits. The organic fruit of the tomato hybrid ‘Tolstoi’ had 5.85 mg 100 g$^{-1}$ of lycopene, while conventional tomato fruits had 4.58 mg 100 g$^{-1}$ of lycopene. The average amount of lycopene in organic fruits was significant higher compared with conventional tomatoes. A comparison of β-carotene in organic and conventional tomatoes showed that a significant higher amount (0.21 mg 100 g$^{-1}$) was found only in organic fruits of the hybrid ‘Tolstoi’.

Figure 6. The influence of farming systems on the amount of dry matter and soluble solids in tomato fruits.

Figure 7. The influence of farming systems on the amount of carotenoids in tomato fruits.
2.2. Tomato ripening impact on fruit biochemical composition

The fruit quality and biochemical composition of tomatoes can be determined by fruit maturity at harvest. That is particularly problematic when tomatoes are picked green because it is difficult to distinguish between mature and immature green tomatoes. Thus, the chosen harvest time determines tomato fruit quality and biochemical composition. Normally, advanced mature green tomatoes will usually achieve much better flavour at the table-ripe stage compared with fruits picked at the immature or partially mature stages, which are more susceptible to physical injuries and water loss because of their thin skin. During ripening on the vine, tomato fruits accumulate sugars, carotenoids, and ascorbic acid [1, 49]. Fruit texture is another very relevant attribute of tomato quality in common with biochemical composition. Tomato firmness is closely related to the susceptibility of fruit to physical damages at harvest time and during storage. In addition, this characteristic can be tested very easy, by human fingers, and that can be the most important factor for consumer [49, 50].

Plant genotype, growing conditions, and fruit ripeness can have a major influence on carotenoids content in tomato fruits [2, 34, 51]. On the basis of scientific data, the lycopene amount can vary widely in fully ripened tomatoes. For example, Heinonen and colleagues [52] detected 3.1 mg 100 g\(^{-1}\) lycopene, while others reported that the average amount of lycopene was 9.27 mg 100 g\(^{-1}\) [7], or varied from 3.1 to 7.7 mg 100 g\(^{-1}\) in fresh tomato fruits [3]. The investigation of the impact of tomato ripening on fruit biochemical composition was carried out at the Lithuanian Research Centre for Agriculture and Forestry [53]. To evaluate the impact of fruit ripening on tomato quality, tomatoes were picked at different ripening stages: I—100% green tomato fruits, II—early stage of ripeness (10% -30% coloured tomato fruits), III—tomato fruits gained colour specific to the cultivar (60% -90% coloured tomato fruits), and IV—fully ripened (over 90% coloured tomato fruits). The research was conducted on 5 tomato (Lycopersicon esculentum Mill.) varieties: ‘Aušriai’, ‘Skariai’, ‘Milžinai’, ‘Vilina’, and ‘Vėža’. It was found that the highest amount of accumulated lycopene was detected in fully ripened fruits and varied from 9.21 (‘Milžinai’) to 12.69 mg per 100 g\(^{-1}\) (‘Vilina’) (Fig. 8). In the green tomato fruits detected, lycopene levels were the lowest ones and varied from 0.25 (‘Milžinai’) to 0.72 mg 100 g\(^{-1}\) (‘Vėža’).

The similar tendencies were observed with β-carotene content (Fig. 9). In the green tomato fruits detected, β-carotene amount was lowest and ranged from 0.20 (‘Milžinai’) to 0.47 mg 100 g\(^{-1}\) (‘Vėža’), while in fully ripened tomatoes, detected β-carotene levels were highest and varied from 1.40 (‘Vėža’) to 1.69 mg 100 g\(^{-1}\) (‘Vilina’). According to these experiment, it is possible to make conclusion that levels of lycopene and β-carotene increase sequentially in tomato fruits during their ripening, except in varieties ‘Vilina’ (between II and III stages) and ‘Milžinai’ (between III and IV stages) fruits where a small increase in lycopene and β-carotene was detected, but these values were not statistically insignificant.

Fruit flavour of tomato is mainly determined by acids and sugars quantity and the ratio of the two. The flavour is more enjoyable with more sugars and less acids [54, 55]. Tomato quality changes during the fruit ripening time. There are less ascorbic acid and more organic acids in the tomatoes at the beginning of the fruit ripening, and there are the high levels of total sugar and dry matter in fruits at the end of tomato ripening. However, data regarding total sugar...
and ascorbic acid amount in tomatoes within their ripening vary greatly; some authors say that tomato ascorbic acid levels increase rapidly throughout ripening [33], while others report that there were no significant differences [56].

Figure 8. Amount of lycopene in different cultivars at different tomato ripening stages.

Figure 9. Amount of β-carotene in different cultivars at different tomato ripening stages.

Studies have shown that amounts of ascorbic acid (Fig. 10) and total sugars (Fig. 11) throughout tomato ripening increased in some investigated cultivars, while in others decreased. In fully ripened tomato fruits, the average amount of ascorbic acid varies from 10 to 20 mg 100 g⁻¹. However, some scientists note that the average amount of ascorbic acid is 25 mg 100 g⁻¹ in fresh tomatoes [57]. According to this study, it was found that ascorbic acid increased rapidly within tomato ripening only in cv. ‘Vilina’ fruits and the highest amount of ascorbic acid was accumulated in fully ripe tomatoes and reached 20.4 mg 100 g⁻¹. Throughout the ripening period of tomatoes, there were no trends found of ascorbic acid accumulation in other cultivars. The lowest levels of ascorbic (in all ripening stages) were found in cv. ‘Milžinai’ and varied from 3.8 to 4.2 mg 100 g⁻¹. It is possible to make a conclusion that the amount of ascorbic acid mainly depends on tomato genotype and less influenced by fruit ripening stage. Thus, the
amount of total sugar varied independently of the tomato ripening stage. The highest levels of total sugar were detected in fully ripe tomatoes in three of the five investigated cultivars, and the established amount varied from 4.71% to 5.14%.

Figure 10. Ascorbic acid content in different tomato cultivars at different ripening stages.

Figure 11. Total sugar content in different tomato cultivars at different ripening stages.

3. Tomato physical properties

In addition to chemical composition, texture and fruit colour are also very important quality attributes of fruit vegetables. Firmness is related to the susceptibility of fruit to physical damage within harvest and storage. For fresh tomatoes, the two quality attributes—texture and skin colour—are very important to buyers and consumers. Texture is influenced by flesh firmness and skin strength. The degree of fruit firmness has been used as an indication of fruit quality, and firmness may be the final index by which the consumers decide to purchase a given batch of tomatoes [14, 58, 59]. Therefore, fruit firmness and colour are the main elements for external tomato quality evaluation. According to provisions, All marketable tomatoes
should have firmness over 1.45 N mm\(^{-1}\), but the means of fruits for home use should be higher 1.28 N mm\(^{-1}\) [60]. Thus, there are two possible minimum limits for tomato fruit firmness considering to market regulations and for home use. Previous investigations have shown that the growing system affected fruit firmness, but only in some tomato cultivars [48].

3.1. Fruit physical properties of organic tomato

Experimental evidence (Fig. 12) has indicated that higher tomato fruit skin and flesh firmness were found in hybrids grown conventionally [44]. Conventional tomato fruits of hybrid ‘Benito’ had significant stronger skin (294.3 N cm\(^{-2}\)) and flesh (53.8 N cm\(^{-2}\)) firmness, meanwhile organic fruits skin firmness reached 273.1 N cm\(^{-2}\) and flesh firmness — 41.5 N cm\(^{-2}\). There were no significant differences found in tomato cv. ‘Vilina’ skin and flesh firmness between organic and conventional fruits, but skin and flesh firmness of organic tomato fruits was slightly stronger. Average data of fruit firmness showed that conventional tomato fruits had stronger skin and flesh compared with organic ones, but difference was not significant.

![Figure 12. The influence of farming systems on tomato fruit skin and flesh firmness.](image)

People identification of colours is sufficiently complex where sensations like brightness, intensity, lightness, and others modify the perception of the primary colours (red, blue, and yellow) and their combinations, meaning that in many ways colour definition is a matter of subjective interpretation. Colour scale gives measurements of colour in units of approximately visual uniformity across the colour solid. According to the Hunter scale, lightness measured by value \(L^*\) and varies from 100 for perfect white to 0 for black, approximately as the human eye would appreciate it. Value \(a^*\) measures greyness when zero, greenness when negative, and redness when positive; value \(b^*\) measures greyness when zero, blueness when negative, and yellowness when positive. \(C\) indicates colour pureness, and \(h^\circ\) indicates colour tone [61].

Colour development in tomato fruits is temperature sensitive with better plastid conversion occurring above 12°C and below 30°C [62]. Scientists found that index \(b^*\) suffered big changes
if tomatoes were ripened to high temperatures (over 30°C) and yellowing took place due to the inhibition of lycopene synthesis and the accumulation of yellow/orange carotenoids. Otherwise, at low temperatures (below 12°C), chlorophyll is not degraded and lycopene accumulation does not start. This could be related to abnormal ripening conditions; changes in the $b^*$ values may compensate $a^*$ magnitudes, depending on their mathematical relationship, leading to misleading results [14, 63]. According to average data of colour indexes (Table 1), it was established significant increase in tomato fruit colour tone (by 4.78 U) and pureness (by 2.46 U) in conventional tomato, meanwhile organic tomato fruits distinguished with significant higher value of colour index $a^*$ (redness) by 4.18 U. There were no significant differences found in colour index $b^*$ and chroma ($C$) values between organic and conventional tomato fruits.

<table>
<thead>
<tr>
<th>Cultivar</th>
<th>$L^*$ ± SE</th>
<th>$a^*$ ± SE</th>
<th>$b^*$ ± SE</th>
<th>$C$ ± SE</th>
<th>$h^*$ ± SE</th>
</tr>
</thead>
<tbody>
<tr>
<td>'Vilina' (organic)</td>
<td>39.65 ± 1.05</td>
<td>29.05 ± 2.02</td>
<td>28.12 ± 2.90</td>
<td>40.55 ± 1.62</td>
<td>43.99 ± 2.38</td>
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<tr>
<td>'Vilina'</td>
<td>38.50 ± 1.15</td>
<td>28.41 ± 2.10</td>
<td>26.95 ± 1.91</td>
<td>39.20 ± 2.28</td>
<td>43.50 ± 2.43</td>
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<tr>
<td>'Benito H' (organic)</td>
<td>42.36 ± 1.25</td>
<td>34.29 ± 1.67</td>
<td>32.38 ± 2.58</td>
<td>47.23 ± 1.94</td>
<td>43.31 ± 1.86</td>
</tr>
<tr>
<td>'Benito H'</td>
<td>49.64 ± 1.40</td>
<td>24.70 ± 1.72</td>
<td>36.49 ± 1.69</td>
<td>44.11 ± 1.19</td>
<td>55.88 ± 2.81</td>
</tr>
<tr>
<td>'Tolstoi H' (organic)</td>
<td>43.12 ± 1.25</td>
<td>28.36 ± 1.34</td>
<td>30.50 ± 2.22</td>
<td>41.67 ± 2.22</td>
<td>47.03 ± 1.84</td>
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<tr>
<td>'Tolstoi H'</td>
<td>44.36 ± 1.24</td>
<td>26.06 ± 2.57</td>
<td>30.19 ± 1.18</td>
<td>39.39 ± 2.11</td>
<td>49.30 ± 2.72</td>
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<tr>
<td>Organic (average)</td>
<td>41.71 ± 1.18</td>
<td>30.57 ± 1.68</td>
<td>30.33 ± 2.57</td>
<td>43.15 ± 1.93</td>
<td>44.78 ± 2.03</td>
</tr>
<tr>
<td>Conventional (average)</td>
<td>44.17 ± 1.26</td>
<td>26.39 ± 2.13</td>
<td>31.21 ± 1.59</td>
<td>41.08 ± 1.82</td>
<td>49.56 ± 2.65</td>
</tr>
</tbody>
</table>

Table 1. Farming systems influence on colour indexes in tomato fruits

3.2. Tomato fruit colour and firmness changes during ripening

Tomato fruit ripening provides positive and negative features to the final product. Even if ripening provides desired taste, texture and colour, considerable costs, and harvest losses result from negative ripening features. The increase of fruit pathogen susceptibility related with ripening is a main factor to production losses before and after harvest. This change is genetically regulated fruit physiology, and it necessitates use of various fumigants and pesticides in attempts to minimise losses. In addition to being potentially harmful and wasteful of energy and to the environment, such practices represent main costs in agricultural output. Eventually, ripening imparts abundant nutritional and quality parameters upon a very important component of the human diet, fruit [1, 64, 65].

One of the most important parameter of all complex attributes of fruit quality is fruit colours. The complexity of tomato fruit colour is subject of both environmental and genetic regulation due to the presence of a various carotenoid pigment system with appearance conditioned by pigment types and quantity [30].

Tomato fruits are generally consumed at their last ripening stage, which appears when fruit reach the full red colour but before it softening. Thus, it is possible to say that tomato colour
is one of the most important external parameter to appreciate ripeness level and postharvest life and is a main contributor in the final consumer’s purchase [49, 50, 66].

Thompson and coworkers [67] compared the colour measurements of tomato fruits (measurements were taken at fruit equatorial) with the homogeneous ones from the same region and reported that the hue ($h^*$) of homogeneous tomatoes was a better indicator for lycopene content than fruit surface hue. The earlier colorimetric investigation showed that the ratio between the chromatic coordinates ($a^*/b^*$) separated better than the tomato colour index in the fruits of the different varieties as a function of their external colour [49, 60, 68].

The study of tomato fruit colour changes during ripening [69, 70] revealed that colour index $L$ has a tendency to decline (Table 2) from 49.5 till 44.7 (after 10 days) in tomato fruits during ripening on vine. The polynomial trendline of fruit ripening time and colour index $L$ revealed that the determination coefficient ($R^2$) was 0.9504.

### Table 2. Tomato fruit colour changes during ripening on vine

<table>
<thead>
<tr>
<th>Period (days)</th>
<th>$L$</th>
<th>$a^*$</th>
<th>$b^*$</th>
<th>$C$</th>
<th>$h^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>49.65 ±2.11</td>
<td>-3.23 ±4.16</td>
<td>27.54 ±1.06</td>
<td>27.99 ±0.98</td>
<td>96.67 ±4.57</td>
</tr>
<tr>
<td>2</td>
<td>49.50 ±2.57</td>
<td>-3.42 ±4.29</td>
<td>27.39 ±1.95</td>
<td>27.87 ±2.02</td>
<td>96.87 ±4.94</td>
</tr>
<tr>
<td>4</td>
<td>49.58 ±2.38</td>
<td>-0.87 ±8.88</td>
<td>26.92 ±1.35</td>
<td>28.05 ±2.57</td>
<td>92.75 ±6.99</td>
</tr>
<tr>
<td>6</td>
<td>48.12 ±3.66</td>
<td>5.41 ±11.62</td>
<td>31.85 ±2.84</td>
<td>34 ±2.82</td>
<td>81.23 ±5.21</td>
</tr>
<tr>
<td>8</td>
<td>45.32 ±3.02</td>
<td>7.43 ±10.26</td>
<td>24.54 ±1.95</td>
<td>27.29 ±2.08</td>
<td>74.53 ±6.42</td>
</tr>
<tr>
<td>10</td>
<td>44.68 ±3.52</td>
<td>11.2 ±11.55</td>
<td>24.13 ±1.99</td>
<td>28.61 ±2.20</td>
<td>66.92 ±5.38</td>
</tr>
</tbody>
</table>

At the beginning of tomato ripening, colour index $a^*$ was negative. Positive value of index $a^*$ was detected only on the 6th day of experiment. Hence, colour index $a^*$ has a tendency to increase during tomato ripening and that was expressed by a polynomial trendline where the coefficient of determination ($R^2$) reached 0.9592. Colour index $b^*$ has distinguished on the 6th day when reached 31.9 value, but there were no significant differences between the rest measurements. A significant increase in chroma value ($C$) on the 6th day was established, and it reached 34.0. The comparison of the rest measurements showed that chroma had varied in small range, and there were no big differences. The experiment showed that hue angle has a tendency to decline during tomato fruit ripening on vine from 96.80 to 66.92, and it was expressed by polynomial trendline where the coefficient of determination ($R^2$) reached 0.9739. Previous studies showed that tomato fruit lightness ($L^*$), at different ripening stage, varied from 42.3 to 50.7, chroma ($C^*$) — from 32.5 (‘Brooklyn H’) to 44.1 (‘Benito H’), colour index $b^*$ (yellowness) — from 28.8 (‘Rutulaii’) to 36.5 (‘Benito H’), colour index $a^*$ (redness) — from 12.9 (‘Brooklyn H’) to 26.1 (‘Tolstoi H’), and hue angle ($h^*$) — from 49.3 (‘Tolstoi H’) to 66.6 (‘Brooklyn H’) [70].

Maturation of tomato fruits continues after their harvest, so they may quickly overripe, which affects fruit quality and reduce their realisation time. The quality of tomato texture is determined by tomato skin and flesh firmness and their relationship. Tomato fruit firmness is
strongly correlated with fruit quality parameters (colour, shape, appearance, etc.). Fruit firmness is used as a parameter in determining the quality of tomatoes. The hardness of the fruit can be a crucial factor to the consumer choice. The transportability of fruit is very important factor because the stronger fruits are less vulnerable to harvesting, sorting, packaging, and transporting production [71]. The assessment of data showed that the skin (Fig. 13) and fruit flesh (Fig. 14) firmness value of tomato fruits went down throughout ripening period.

Figure 13. Fruit skin firmness of different cultivars at different tomato ripening stages.

Fruit skin firmness varied from 109 N cm\(^{-2}\) in fully ripened tomatoes (cv. ‘Milžinai’) to 303 N cm\(^{-2}\) in green fruits of the cv. ‘Aušriai’. Tomato flesh firmness varied from 6.0 N cm\(^{-2}\) (fully ripened cv. ‘Vilina’) to 68.0 N cm\(^{-2}\) (green tomatoes cv. ‘Milžinai’). The comparison of fully ripened tomatoes revealed that fruits of cv. ‘Vėža’ had the strongest skin and fruits of cv. ‘Aušriai’ had the strongest flesh. A significant increase of tomato flesh firmness between the III and the IV ripening stages in ‘Skariai’ fruits was also found.

Figure 14. Tomato flesh firmness in different tomato cultivars at different ripening stages.
4. Nondestructive determination of tomato fruit in different ripening stages — Techniques to analyse properties and quality of plants

From an agricultural point of view, the optimal picking time for tomatoes is when 85% -90% of the fruits are red or almost red. Typically, tomato fruits are harvested when they are light red in colour. Such fruits are less injured mechanically during the harvesting process. It is known that tomato colour depends on the pigment (lycopene, carotene, xanthophylls, and chlorophyll) concentration and distribution, so the proper time of tomato picking affects the overall fruit and yield quality. The optimal colour of tomato fruits is when they are rich in carotenoids and low in carotene. Fruits that are harvested too early have a poorer quality because organic and mineral accumulation in their tissues is not finished. Such fruits are entirely unsuitable for storage. Therefore, fruit picking time is determined by the size, colour, texture and flesh firmness [2, 72].

Producers focus their attention on fruit and vegetable quality and aim to avoid poor quality production. The genotype of selected cultivars has a great influence on fruit quality, but the degree of maturity is also very important. Packaging factories use ethylene gas (natural fruit hormone) to speed up the tomato ripening processes. It has been established that during the fruit ripening process, ethylene gas is produced naturally. It increases the permeability of the cell protoplasm. Ethylene then enters the cell, and the air activates the biochemical processes of ripening. Therefore, in order to speed up the ripening of fruit, ethylene gas is employed. The action of ethylene helps to ripen tomatoes within 4-6 days, under the same conditions without ethylene gas fruit maturation time is nearly three times longer [73, 74].

Growers select commercial tomato varieties and hybrids that are resistant to diseases and pests in order to obtain more high-quality fruits. However, picking tomato fruits before they are technically mature may have a decisive influence on their final quality and taste. Commercial growers are concerned with producing adequate amounts of high-quality products, but they are not as concerned about fruit taste; however, tomato flavour is one of the most important indicators for consumers [2, 69].

In tomatoes, individual elements of biochemical composition are typically determined by chemical analysis methods (spectroscopy, high performance liquid chromatography, thin layer chromatography, and so on). Carotenoid (lycopene and β-carotene) extraction from tomato as well as its biochemical analysis requires a large quantity of various organic solvents. Lycopene extraction with organic solvents is a good method for qualitative and quantitative analysis, but this extraction method is not cost-efficient and is time consuming [75, 76]. To facilitate and simplify the determination of biochemical substances without tomato damage, it may be possible to use nondestructive methods, such as colour coordinate spectrophotometry and near-infrared (NIR) spectroscopy method based on the transmittance principle, using near-infrared wavelength spectrophotometer.

Biochemical analyses using modern detection methods require not only specialised and expensive equipment but also professional and technical personnel, causing many inconveniences for growers, producers, and researchers. Agriculture, plant breeding, and food industry
should use a simple, inexpensive, reliable, and rapid method for the detection of biochemical substances in tomatoes \[77, 78\]. Therefore, attention has been given to three-dimensional colorimetry, where the assessment of reflection values is rescaled and compared with the values of biochemical elements. The nondestructive prediction of individual biochemical elements is very important in tomato breeding and in the development of new varieties to improve fruit quality, because it is possible to predict the amount of biochemical elements on the plant without fruit damage. This could significantly speed up the process of selection and hybridisation \[79, 80\].

Prediction accuracy depends on the amount of accurate accumulated data, which is obtained by chemical analysis. Therefore, it is important to collect a large database of research results so that predicted data would more closely resemble observed data \[75, 79\].

For that reason, a study of tomato fruit ripening processes was conducted, and calibration curves for dry matter, soluble solids, organic acids, skin and flesh firmness, lycopene and β-carotene, ascorbic acid, and sugar content were created according to data from NIR and biochemical analysis methods. The investigation looked at different tomato cultivars of different fruit ripening stages. The study examined 10 different tomato cultivars and hybrids including ‘Tamina’, ‘Money Maker’, ‘Saint Pierre’, ‘Tocayo H’, ‘Polfast H’, ‘Brooklyn H’, ‘Tolstoi H’, ‘Benito H’, ‘Tourist H’, and ‘Rutuliai’. In order to get more and varied types of data, the dynamics of biochemical elements during fruit ripening were also observed. Therefore, the tomato fruit investigations were made with fruits of six different ripening stages \[80\].

During the investigation, tomato fruit biochemical composition and texture analysis were conducted using near-infrared (NIR) spectroscopy performed in parallel with normal biochemical and texture analyses. It assessed the values of reflection (nondestructive method) compared with the biochemical and fruit texture values (destructive methods).

During the first year of the experiment, calibration graphs were created, and the statistical reliability of these graphs was evaluated during the second year.

Biochemical analyses were conducted using the following methods. Ascorbic acid was determined by titration with 2,6-dichloroindophenol sodium salt solution, soluble solids were determined with a digital refractometer (ATAGO, PAL-1, Japan), dry matter by gravimetrically after drying at 105°C to a constant weight, and sugars by the AOAC method. Organic acid content, expressed as citric acid, was determined by titration with a 0.1-N sodium hydroxide solution, and carotenoids were measured using HPLC.

Tomato texture was measured using a texture analyser (TA.XTPlus, Stable Micro Systems, Godalming, United Kingdom). To pierce the tomato peel and the pulp of the fruit (unpeeled skin), a P/2 probe (2 mm diameter flat probe tip) was used, and the data were processed using ‘Texture Exponent’ software.

The near-infrared (NIR) spectroscopy method, based on transmittance, was used for nondestructive measurements, using a near-infrared wavelength spectrophotometer (NIR Case NCS001A, SACM SCImola Imola, Italy).
Calibration graphs were created using ‘SACM NCS (NIR Calibration Software) Vers. 3.0 RC I’ software.

Calibration graphs of dry matter, soluble solids, organic acids, skin and flesh firmness, lycopene and β-carotene, ascorbic acid, and sugar content were created according to NIR and chemical analysis data. The created graphs make it possible to determine the amount of these elements in a nondestructive manner. The tomato skin firmness calibration graph is shown in Fig. 15.

![Figure 15. Calibration graph of tomato skin firmness.](image)

Such calibration graphs allow the determination of the strength of the tomato fruit and amount of biochemical elements very quickly and inexpensively, and also offers great opportunities to producers, manufacturers, and food industry.

On the second year of the study, the reliability of the newly created calibration graphs was assessed. Again, normal biochemical analysis and nondestructive measurements using near-infrared (NIR) spectroscopy were performed. The reliability of the obtained results was evaluated statistically (Table 3).

Based on the obtained results, a strong correlation between normal and nondestructive analytical methods in measuring of soluble solids ($r = 0.9251$), lycopene ($r = 0.8701$), β-carotene ($r = 0.9486$), ascorbic acid ($r = 0.8052$), skin strength ($r = 0.9906$) and the pulp strength ($r = 0.9369$) was found. The average correlation was observed in dry matter ($r = 0.6480$), titratable acidity ($r = 0.5800$), and total sugars ($r = 0.5982$). Consequently, based on the created calibration graphs, nondestructive measurements of tomato fruit quality parameters using near-infrared spectroscopy (NIR) can be carried out. The reliability assessment of the obtained results and comparison of nondestructive techniques and traditional methods showed that there is a strong correlation between them by measuring soluble solids, lycopene, β-carotene, ascorbic acid, skin firmness and strength of the flesh, and average correlation by determining dry matter, titratable acidity, and total sugar content of tomato fruits.
5. Tomato as the functional food ingredients

Fresh vegetables are an essential source of minerals, dietary fibres, and especially vitamins. Humans get 90% of their vitamin C from vegetables, which are also rich in B group vitamins. Vegetables stand out from other food products due to their high energy value. They are very important for human nutrition, and they supplement the human body with minerals, vitamins, proteins, fats, and carbohydrates [2, 81, 82]. Due to their biochemical composition, tomatoes are very valuable vegetables. Their fruit is prized for its good taste and its nutrition value. Tomato fruit contains soluble sugars, organic acids, fibre, pectins, proteins, fats, minerals (potassium, phosphorus, sulphur, magnesium, calcium, iron, copper, and sodium), many vitamins (B1, B2, B3, PP, C, A, I, and H), and the alkaloid tomatine with phytoncide properties. The greatest influences on both valuable and harmful substances in tomato fruits are environmental and growing conditions, fruit ripening stage, and cultivar characteristics [70, 83, 84]. Tomatoes can be eaten fresh, fried, boiled, or pickled in various salads and other dishes. In addition, processed tomatoes (paste, juice, sauce) retain all nutritional characteristics of the fresh fruit [2, 85].

Long ago, it was believed that tomatoes contained oxalic acid, which adversely affects metabolic processes; therefore, older people were advised not to eat them. It has been confirmed that the amount of oxalic acid in tomatoes is less than in lettuce, potatoes, or red beets, and the influence of purines (protein metabolic products that lead to gout (podagra)) is less than in many other plant products. Tomatoes can be eaten by children, adults, and the elderly. If someone’s stomach is very sensitive, fresh tomatoes should be peeled first because the skin can stick to the stomach walls and cause inflammation. Vitamins and other valuable nutritional compounds found in tomatoes not only improve human nutrition but also prevent various diseases. Ascorbic acid directly removes free radicals of oxygen and superoxides. The human body does not synthesise ascorbic acid, so it must be obtained from food. Ascorbic acid is one
of the most important antioxidants found in tomato fruits [86, 87]. It is believed that carotenoids, found in tomato fruits (which can reach 3.67 mg 100 g⁻¹), may reduce the risk of human diseases, in particular cardiovascular diseases and prostate cancer [88, 89]. Epidemiological studies have shown the existence of an inverse relationship between lycopene intake and prostate cancer risk. Patients with prostate cancer had lower lycopene levels in their blood plasma than control patients [90]. The inverse relationship is also expressed in aggressive prostate cancer cases. Prostate cancer risk was lowered by 83% for the patient group with the highest lycopene plasma levels (0.40 µmol l⁻¹) compared to the lowest concentration (0.18 µmol l⁻¹) group [91]. Similar results were obtained in other studies, where it was found that two or more tomato dishes per day can reduce the risk of developing prostate cancer [89, 92].

There have been several epidemiological studies that have outlined the relationship between lycopene concentrations in the blood plasma and cardiovascular disease risk. One found that men who had coronary disorders had lower lycopene levels in their plasma compared to men without coronary disorders [35]. Alternatively, a study of the relationship between the lycopene level in fatty tissues and heart disease showed that an increased lycopene concentration had a protective effect against cardiac dysfunction [93, 94].

Lycopene consumption efficiency is determined by lycopene (the active principle compound of tomatoes, which acts as an antioxidant) bioavailability. Unfortunately, the mechanism of lycopene uptake remains unclear. It is known that absorption of consumed lycopene reaches only 10% (in some cases can increase up to 30%). Furthermore, lycopene absorption from fresh tomatoes is less than from the processed products (tomato paste or sauce) [7] because the mechanical and thermal treatment of tomatoes enhances lycopene uptake. There are other factors that affect the process of lycopene absorption. It has been found that the addition of oils in tomato dishes enhances carotenoid absorption [95], but the addition of various fibre substances can reduce absorption [96].

It is believed that processed fruits and vegetables are less valuable than fresh, but lycopene is better absorbed from processed tomatoes. Heat-treated tomatoes can have more bioavailable lycopene, and this justifies tomatoes as a functional food [2, 5, 6]. Undoubtedly, the effect will be negligible or absent, if the consumed amount of lycopene is 6-8 mg per day. It has been reported that 25-35 mg of lycopene should be consumed daily, that is, approximately 200 g tomatoes per day [97].

Thus, tomatoes, as a source of various antioxidants and vitamins, can increase the human’s body resistance to the impact of radiation, reduce cholesterol accumulation, heal some skin diseases, and prevent cardio diseases and prostate cancer [8, 98].

6. Lycopene in tomatoes: Chemical and physical properties affected by food processing

The importance of lycopene is mainly due to its beneficial properties for human health. Lycopene protects humans from attack by pathogenic agents responsible for a number of
chronic diseases, such as cardiovascular disease, different types of cancer (digestive tract, cervix, breast, skin, bladder, and prostate), hypertension, osteoporosis, neurodegenerative diseases, male infertility, and even the transmission of immunodeficiency syndrome from mothers to babies [99].

The availability of lycopene in food may depend on several factors. First, the carotenoid content of food may be increased by mechanical processing. Food processing may be beneficial because it disrupts food matrices, facilitating the release and solubilisation of carotenoids, resulting in increased carotenoid bioavailability, including lycopene bioavailability [100]. Within the plant, lycopene is part of the matrix in chloroplasts or chromoplasts, and the absorption of lycopene from raw tomatoes is low because it is occurs mostly in the trans-isofrom and is tightly bound within the matrix [101]. Second, the bioavailability of lycopene is greatly increased by thermal (cooking or by commercial) processing, such as conversion to soups, sauces, and catsup [102]. Nevertheless, increased uptake or higher blood levels of lycopene have been achieved predominantly by the intake of tomatoes or tomato products rather than by the intake of purified lycopene [8, 103]. In synthetic nutritional supplements, lycopene is in the form of an oleoresin embedded in phospholipid complexes and oils. Third, the addition of lipids, such as vegetable oils, increases lycopene absorption [101]. For example, it has been reported that lycopene is more efficiently absorbed when tomato juice is warmed with a supplemental lipid. Moreover, lycopene is lipophilic, and the dissolution of carotenoids in a lipid phase occurs in the stomach and the duodenum. Roldan-Gutiérrez and de Castro [104] reported that, due to the action of bile salts and pancreatic lipases, carotenoids in a lipid phase (droplets) enter the duodenum and form multilamellar lipid vesicles. During intestinal absorption, carotenoids and lycopene incorporate into chylomicrons and interact with other carotenoids [104]. Interactions with other carotenoids are complex and have not been fully studied. For example, β-carotene in the same dish as lycopene causes an increase in the absorption of lycopene [102].

Moreover, during exposure to thermoenergy, oxygen, and light, lycopene can undergo isomerisation and degradation. Isomerisation converts all-trans-isomers to cis-isomers and results in a reduction of the biological properties of lycopene [99]. Red tomatoes normally contain 94%-96% all-trans-lycopene. All-trans-lycopene is thermodynamically the most stable form. Some authors have reported that the formation of cis-isomers of lycopene may increase biological activity. Cis-isomers are more soluble in bile acid micelles and may be preferentially incorporated into chylomicrons compared with trans-isomers [105]. Cis-isomers of lycopene have distinct physical characteristics and chemical behaviours from all-trans-isomers, including decreased colour intensity, greater polarity, lesser tendency to crystallise, and greater solubility in oil and hydrocarbon solvents. However, these physical characteristics have a direct impact on the sensory qualities and consumer health benefits of food. The determination of the degree of lycopene isomerisation during processing and storage would provide a measurement of the potential health benefits of tomato-based foods [99].

An overview of the observed results of Haymann and colleagues [106] during the isomerisation processes of lycopene is given in Fig. 16. The study demonstrated that various cis-isomers (predominantly 5-cis- and 9-cis-lycopene) were formed during energy-rich irradiation, whereas at the same time degradation of all-trans-, 15-cis-, 13-cis-, and 7-cis-lycopene occurred.
A theoretical study on the cis-trans isomerisation of lycopene revealed that 5-cis- and 9-cis-lycopene are more stable than other isomers since their rotational barrier to reisomerise the all-trans configuration is higher ($\Delta E_r = 35.2$ kcal/mol and 23.1 kcal/mol, respectively) than that of all other isomers ($\Delta E_r = 16.8$ to 19.9 kcal/mol) [106]. Furthermore, the stability of 5-cis-lycopene and 9-cis-lycopene is also induced by their much lower relative energy compared to other isomers. Those effects lead to the accumulation of the 5-cis- and 9-cis-isomers during irradiation with halogen lamp. In contrast, low rotational barrier ($\Delta E_r = 22.1$ kcal/mol) and one of the highest potential energies of all mono-cis-isomers results in a dominant degradation of 7-cis-lycopene during energy-rich irradiation [106, 107]. All-trans-lycopene underwent degradation, while the concentration of cis-isomers, mainly 13-cis and 9-cis, increased. The investigation showed that the 5-cis-isomer changed distinctively during lycopene storage compared to the other lycopene isomers [106].

Figure 16. Thermal and photoinduced isomerization leads to degradation and formation of lycopene isomers in lycopene extract [106].

After intestinal absorption, carotenoids are carried to the blood stream by chylomicrons via the lymphatics. Concerning transport in the plasma, carotenoids are transported by lipoproteins, and transport depends on the carotenoid structure. Therefore, lycopene is found in the aqueous interface at the lipoprotein surface. For this reason, lycopene is transported in low-density lipoproteins, and oxygenated carotenoids are transported in both low-density and high-density lipoproteins [104].

It is important to develop more attractive ready-to-eat products to contribute to the increased consumption of fruit and vegetable products and their health benefits for consumers. Food processing should be adapted to enhance the bioavailability of nutrients [108]. Additional information needs to be collected on the thermal behaviour of lycopene before we can have
definitive answers regarding its physical state and stability during processing and cooking. Little is known about the stability of lycopene in supplemental form [109].

7. Tomato plants in agricultural, industrial, and pharmaceutical applications

As was previously mentioned, tomatoes are one of the most widely produced and consumed ‘vegetables’ in the world, both for the fresh fruit market and the processed food industries. The tomato industry is one of the most globalised and advanced horticultural industries. Furthermore, tomato production has historically been located in temperate zones that have long summers and winter precipitation, but now, with new modern technologies (greenhouse structures, climate control, and crop protection), tomato production has expanded and is focused on the production of fresh tomatoes. However, cultivation practices, the ratio between production for processing or fresh consumption, and the organisation and structure of the industry and markets differ widely among countries. Further, tomatoes are harvested at different stages of ripeness for different purposes. Processing tomatoes are mechanically harvested red-ripe and immediately transported to a processing plant. Fruit destined for the fresh market is hand harvested at the mature green, partially ripe or fully ripe stages. Mature green fruits are picked because they are firm enough and have a sufficient shelf-life to survive the stress of being shipped considerable distances, and they are ripened to acceptable levels of quality at distant markets. Quality characteristics of fresh-market fruits are similar to those of processing tomatoes, but the characteristics that are readily apparent to the consumer (colour, size, shape, firmness, and aroma) dominate the others [110].

The industrial processing of tomato products produces waste such as tomato skins and seeds. Ripe tomato skins contain approximately five times more lycopene than the pulp. The largest portion of tomato waste is the peals which are the most abundant sources of lycopene. The lycopene content is over 90% in ripe tomato skin [106, 110]. Tomato waste is a potential natural source for lycopene extraction. One of the most important trends in the food industry is the demand for all-natural food ingredients that are free of toxic solvents and chemical additives. A unique process for the nontoxic, safe, and inexpensive extraction, separation, and concentration of lycopene is supercritical fluid extraction with carbon dioxide (SCF CO₂). SFE adds value to agricultural waste by extracting lycopene from tomato skins and using it for the fortification of foods and in pharmaceutical applications [110].

Studies have proposed that lycopene may work synergistically with other carotenoids, vitamins, and minerals present in the diet. Lycopene extracts and concentrates could be used not only in traditional food products but also as functional ingredients in specifically formulated foods and dietary supplements that enhance human health and wellbeing. Growth in consumer demand for healthier food products provides an opportunity for food industry to develop new functional foods enriched with natural lycopene, as well as for pharmaceutical industry to develop new nutraceutical products comprising pharmaceutical-grade lycopene [111, 112].
8. Conclusions

Tomato biochemical composition, nutritional value, colour, and flavour of tomato products depend mainly on lycopene, β-carotene, ascorbic acid, sugars, dry matter, and their ratios in fruits. The two most important carotenoids in tomato fruits are lycopene and β-carotene. Therefore, tomato products and their quality can be characterised by the contents of these elements. It has been established that tomato fruit quality varies due to species, stage of ripeness, farming system, climatic conditions, growing area, fertilisation, and other conditions of cultivation.

In addition to chemical composition, texture and fruit colour are also very important quality attributes of vegetables. Firmness is related to the susceptibility of fruit to physical damage during harvest and storage. For fresh tomatoes, two quality attributes, texture and skin colour, are very important to buyers and consumers. Texture is influenced by flesh firmness and skin strength, which can be used as an indication of fruit external quality.

To facilitate and simplify the determination of biochemical substances without tomato damage, it might be possible to use nondestructive methods, such as colour coordinate spectrophotometry and the near-infrared (NIR) spectroscopy method (based on the transmittance principle, using a near-infrared wavelength spectrophotometer). A reliability comparison of nondestructive techniques and traditional methods showed that there was a strong correlation between them for measuring soluble solids, lycopene, β-carotene, ascorbic acid, skin firmness, strength of the flesh, dry matter, titratable acidity, and total sugar content of tomato fruits.

Tomato fruits have positive health benefits and contain significant amounts of biologically active compounds, which are responsible for positive health effects. Epidemiological and other studies associated with the consumption of tomato products for the prevention of chronic diseases, such as cancer and cardiovascular disease, confirm that tomato products are a functional food and show that lycopene and β-carotene act as antioxidants. The growing interest and demand for healthy, environmentally safe, and cost-efficient products has driven the research of new technologies in the food, pharmaceutical, and cosmetic industries. Therefore, bio compounds, such as lycopene from tomato plant material, are important for agricultural, industrial, and pharmaceutical applications. However, the levels of lycopene and other biological compounds in plant material depend on the species, growing conditions, and climate trends.

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