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Changes in Contents of Carotenoids and Vitamin E during Tomato Processing

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The aim of this study was to investigate the effect of different types of tomato processing on contents of lycopene, β-carotene, and α-tocopherol. Samples of tomato sauce, tomato soup, baked tomato slices, and tomato juice were taken at different times of heating, respectively, after each step of production. HPLC was used to analyze contents of carotenoids and vitamin E. Due to the loss of water during thermal processing, contents of lycopene, β-carotene, and α-tocopherol on a wet weight basis increased. On a dry weight basis, contents of lycopene increased or decreased depending on the origin of the tomatoes used, whereas the β-carotene contents decreased or were quite stable. In contrast to lycopene, β-carotene isomerized due to thermal processing. The α-tocopherol contents significantly rose during short-term heating. The increase was not caused by release of α-tocopherol from the seeds containing predominantly γ-tocopherol and accounting for 2% of total α-tocopherol content only.

KEYWORDS: Carotenoids; vitamin E; tocopherols; tomato

INTRODUCTION

Processing of food is often considered to cause losses of micronutrients. Nevertheless, it can also have positive effects. Several studies have shown an enhanced bioavailability of carotenoids from processed vegetables (*1*−*5*). Possible explanations for this result are the mechanical and thermal disruption of the cell matrix and the carotenoid−protein complexes.

In diverse studies, carotenoids showed antioxidant, antimutagenic, and anticarcinogenic properties and were effective in immunoenhancement (*6*−*10*). In contrast, supplemental β-carotene increased the risk of lung cancer incidence in a large intervention trial with smokers (*11*). Lycopene, giving tomatoes their red color, had the highest antioxidant activity in quenching singlet oxygen as well as in reacting with the $ABTS^{\bullet+}$ radical cation and the phenoxyl radical (*12*−*15*). Furthermore, it implicated the potential of preventing cardiovascular disease and cancer (*16*).

In human nutrition, the most important sources of lycopene are tomatoes and tomato-based products. Among 72 epidemiologic studies reviewed by Giovannucci (*17*), 57 reported inverse associations between tomato intake or blood lycopene level and the risk of cancer at a defined anatomic site. The evidence for a benefit was strongest for cancers of the prostate, lung, and stomach (*17*). Apart from lycopene, the presence and synergy of a multitude of nutrients found in tomatoes may have contributed to these benefits. Tomatoes contain modest to high amounts of vitamin C, vitamin E, folates, phenolic compounds, and other carotenoids such as β-carotene (*18*). All of them are relevant to the prevention of chronic diseases (*19*).

Like lycopene, vitamin E belongs to the lipophilic fraction of the tomato fruit. In diverse studies, it showed antiatherosclerotic and anticarcinogenic properties involving inhibition of LDL oxidation, modulation of cellular signaling, transcriptional regulation, and induction of apoptosis (*20*).

Investigations into the effects of tomato processing on the content of vitamin E were scarcely conducted (*21*). Mostly, only the fate of lycopene and other carotenoids was evaluated during processing of tomatoes (*21*−*28*). In addition, the role of the loss of water during processing was rarely mentioned (*26*).

The aim of the present study was to investigate the effect of processing on contents of carotenoids and vitamin E in common tomato products. For this, tomato juice was produced under industrial-like conditions, whereas tomato sauce, tomato soup, and baked tomato slices were prepared under household conditions. To discuss the loss of water during thermal treatment, the results were calculated on a wet weight basis as well as on a dry weight basis.

MATERIALS AND METHODS

Chemicals. All chemicals used were of analytical grade. All carotenoids investigated were identified using reference materials, which were a kind gift of F. Hoffmann-La Roche, Basel, Switzerland, as well as UV−vis data. Standard solutions in cyclohexane/toluene (8+2, v/v) containing 2−10 mg/100 mL of the carotenoids investigated were

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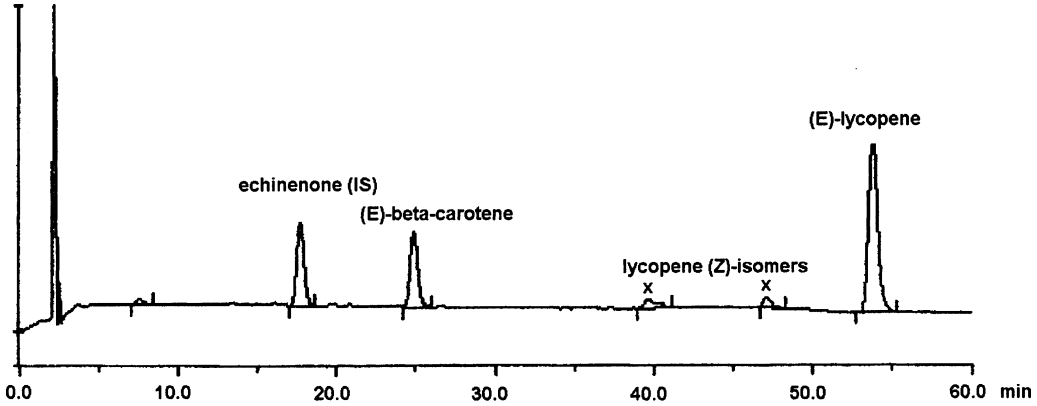

Figure 1. Chromatographic separation of carotenoids in a tomato extract (for HPLC conditions see text).

diluted daily 1:10−1:500 with a mixture of methanol and methyl *tert*-butyl ether (1+1, v/v) to get the working solutions. The lycopene (*Z*)-isomers were quantified using the (*E*)-lycopene for calibration. Structural elucidation of the main lycopene (*Z*)-isomers by using different spectroscopic techniques is under investigation and will be reported separately. Tocopherol reference materials were from Calbiochem (no. 613424, Calbiochem, Darmstadt, Germany). Standard solutions in hexane containing 1 mg/mL were diluted daily 1:200−1:5000 with hexane to prepare the working solutions.

Samples. Fresh tomatoes (origin: Holland and Spain) were bought at a local supermarket.

Sample Preparation. Tomato juice was produced from canned tomatoes in a pilot plant at the University of Applied Sciences Lippe & Höxter. Samples were taken after (i) extraction, (ii) homogenization (70 bar, 62.5 kg/h), (iii) sterilization (121 °C, 2 min), and (iv) filling into bottles and pasteurization (80 °C, 20 min). The other tomato products were prepared from fresh tomatoes. Tomatoes from Holland were used for tomato sauce 1, tomato soup, and baked tomato slices. Spanish tomatoes were taken for tomato sauce 2. The tomatoes were washed and cut into equal pieces (cubes for sauce and soup, slices for baked tomatoes). No spices were added. The same temperature of the hotplate was chosen for cooking the sauces and the soup (i.e., medium heat). Tomato sauce 1 was heated for 50 min. Samples were taken after 0, 5, 25, and 50 min. Tomato sauce 2 was cooked for 210 min. Samples were taken after 0, 5, 30, 60, 90, 120, 150, 180, and 210 min. To prepare the tomato soup, the tomatoes were peeled before cutting and cream was added after 25 min of heating. Samples were taken after 0, 25 (still without cream), 35, and 50 min. The baked tomato slices were prepared in a preheated oven at three different oven temperatures (180, 200, and 220 °C). Samples were taken after 0, 15, 30, and 45 min, respectively. For comparison of stability, standards of lycopene and β-carotene were dissolved in sunflower oil and heated at 180 °C in the oven. Samples were taken after 0, 15, 30, 45, and 60 min. The stability of vitamin E was tested by heating pure sunflower oil and pure tomato juice as well as a mixture of tomato juice and 10% sunflower oil at 180 °C in the oven. Samples were taken after 0, 15, 30, 45, and 60 min, respectively. Furthermore, the distribution of vitamin E throughout the tomato fruit was determined. For this purpose, the fruit was divided into three different fractions: the outside layers (peel, pericarp), the inside layers (flesh, central axis), and the seeds. All samples were homogenized prior to analysis and stored at −18 °C until analysis.

Analysis of Carotenoids. Contents of carotenoids were analyzed by using C_{30}-HPLC with diode array detection according to the method of Böhm (*29*) after three extractions with methanol/tetrahydrofuran (1+1, v/v) containing 0.1% BHT. In particular, 400 mg of MgO, 500 μL of echinenone (i.e., internal standard solution), and 35 mL of methanol/tetrahydrofuran were added to 2 g of sample. The mixture was homogenized on ice for 5 min using an Ultra Turrax (IKA-Labortechnik). The resulting solution was filtered through no. 1390 paper on a Büchner funnel. The extraction was repeated twice until the residue was colorless. The combined extracts were dried under vacuum at 30 °C in a rotary evaporator (Büchi). The residue was redissolved in methanol/tetrahydrofuran (1+1, v/v), containing 0.1% BHT, until the solution reached the defined volume of 10 mL. The solution was centrifuged (5000 rpm, 5 min) and then used for HPLC analysis, which was done with 1.3 mL min^{-1} methanol and methyl *tert*-butyl ether by using a gradient procedure at 23 ± 1 °C on a YMC C30 column (YMC, Schermbeck, Germany) with diode array detection at 450 nm (**Figure 1**). All extractions were carried out in the dark and were done three times for each sample. Recovery of the internal standard was 101 ± 7%.

Analysis of Vitamin E. Two grams of sample was weighed into centrifuge tubes. Successively, 1 mL of distilled water, 1 mL of ethanol, 1 mL of methyl *tert*-butyl ether (MtBE), and 1 mL of petroleum ether were added. After each addition, the tubes were shaken for 30 s. Then, the samples were centrifuged (5000 rpm, 5 min), and the upper layer was transferred into a flask. The extraction with 1 mL of MtBE and 1 mL of petroleum ether was repeated twice. The combined extracts were dried under vacuum at 30 °C in a rotary evaporator (Büchi). The residue was dissolved in 2 mL of mobile phase (*n*-hexane/MtBE; 96+4, v/v) and then centrifuged (14000 rpm, 5 min). The resulting solution was analyzed for vitamin E by using Diol-HPLC at 50 °C (**Figure 2**) with 1.5 mL min^{-1} hexan/MtBE (96+4, v/v) with fluorescence detection (*30*). All analyses were done in duplicate.

Total Solids. The content of total solids was gravimetrically analyzed. For this purpose, the samples were dried at 103 ± 2 °C. All determinations were carried out in duplicate.

Statistical Analysis. All results are presented as means ± standard deviation. Differences between variables were tested for significance by using Tukey, a one-way analysis of variance procedure (SPSS for Windows 11.0). Differences were considered to be significant at $p < 0.05$.

RESULTS

Carotenoids. (*all-E*)-Lycopene was the most abundant carotenoid in each of the various tomato samples. As its main isomer, (15*Z*)-lycopene was identified. In addition, (*E*)-β-carotene, (9*Z*)-β-carotene, and (13*Z*)-β-carotene were found in the samples. Continuous thermal treatment under household conditions led to an increase in contents of (*E*)-lycopene and (*E*)-β-carotene on a wet weight basis (data not shown). Calculations using dry matter as a basis showed different results. During the preparation of tomato soup and tomato sauce 1 (data not shown) from Dutch tomatoes, contents of (*E*)-lycopene and (*E*)-β-carotene on a dry weight basis significantly decreased. **Table 1** shows the comparison of (*E*)-lycopene and (*E*)-β-carotene contents on a wet weight basis with the contents on dry weight basis during the preparation of tomato soup. In contrast, cooking of tomato sauce 2 from Spanish tomatoes led to a significant rise of (*E*)-lycopene contents on a dry weight basis within the first 30 min (**Table 2**). In the same samples, the contents of (*E*)-β-carotene did not significantly change during the first 30 min, but thereafter a significant decrease followed (data not shown). Unlike processing under household conditions, the production

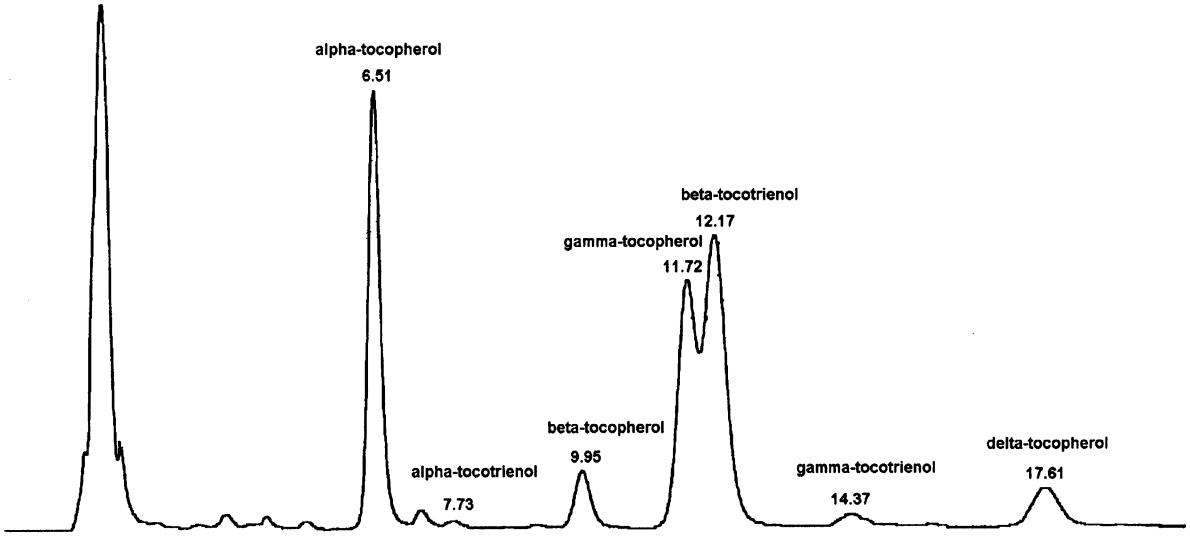

Figure 2. Chromatographic separation of tocopherols and tocotrienols in a tomato extract (for HPLC conditions see text).

Table 1. Changes in Contents of (*E*)-Lycopene, (*E*)-β-Carotene, and α-Tocopherol during Preparation of Tomato Soup[a]

sample	content of (*E*)-lycopene (mg/100 g)	content of (*E*)-β-carotene (mg/100 g)	content of α-tocopherol (mg/100 g)
	Wet Weight Basis		
0 min	5.26 ± 0.30A	0.35 ± 0.05A	0.061 ± 0.001A
25 min	5.70 ± 1.28A	0.44 ± 0.02B	0.570 ± 0.032B
35 min	6.41 ± 0.76A	0.41 ± 0.02B	0.402 ± 0.025C
50 min	11.40 ± 0.94B	0.57 ± 0.01C	0.613 ± 0.097B
	Dry Weight Basis		
0 min	122.9 ± 6.4A	7.45 ± 1.01A	1.30 ± 0.02A
25 min	79.7 ± 17.9B	6.21 ± 0.25B	7.97 ± 0.45B
35 min	63.6 ± 7.6B	4.09 ± 0.20C	3.99 ± 0.25C
50 min	64.2 ± 5.3B	3.26 ± 0.08C	3.95 ± 0.55C

[a] Values within columns with the same letter are not significantly different ($p > 0.05$).

Table 2. Changes in Contents of (*E*)-Lycopene and α-Tocopherol, Each on Dry Weight Basis, during Preparation of Tomato Sauce 2[a]

sample	content of (*E*)-lycopene (mg/100 g of dm[b])	content of α-tocopherol (mg/100 g of dm)
0 min	99.7 ± 4.5A	4.8 ± 0.1A
5 min	98.5 ± 8.9A,B	7.7 ± 0.4B
30 min	120.5 ± 12.0C	9.6 ± 0.1C
60 min	79.5 ± 1.2B	9.9 ± 0.2C
90 min	101.6 ± 9.1A	9.3 ± 0.5C,D
120 min	93.9 ± 1.0A,B	8.4 ± 0.6B,D
150 min	99.7 ± 3.1A	7.3 ± 0.3B
180 min	87.4 ± 2.4A,B	7.3 ± 0.1B
210 min	91.7 ± 3.4A,B	8.0 ± 0.1B,D

[a] Values within columns with the same letter are not significantly different ($p > 0.05$). [b] Dry matter.

of tomato juice scarcely affected the contents of total solids. On wet as well as dry bases, contents of (*E*)-lycopene and (*E*)-β-carotene significantly decreased following the step of homogenization (**Table 3**). Unprocessed tomatoes contained a lower relative amount of (*Z*)-isomers of β-carotene than the final products (<1 vs ~27%). (*E*)-Lycopene was not susceptible to thermal isomerization in tomato products, but it also readily

Table 3. Changes in Contents of (*E*)-Lycopene and (*E*)-β-Carotene during Production of Tomato Juice[a]

sample	content of (*E*)-lycopene (mg/100 g)	content of (*E*)-β-carotene (mg/100 g)
	Wet Weight Basis	
after extraction	8.91 ± 0.55A	0.24 ± 0.02A
after homogenization	6.70 ± 0.22B	0.21 ± 0.01A,B
after sterilization	7.66 ± 0.22C	0.19 ± 0.00B
after pasteurization	7.49 ± 0.24B,C	0.19 ± 0.01B
	Dry Weight Basis	
after extraction	214.1 ± 13.3A	5.77 ± 0.46A
after homogenization	133.6 ± 4.3B	4.22 ± 0.12B
after sterilization	159.4 ± 4.6C	4.03 ± 0.04B
after pasteurization	150.7 ± 4.9B,C	3.76 ± 0.30B

[a] Values within columns with the same letter are not significantly different ($p > 0.05$).

Table 4. Contents of (*E*)-Lycopene and Share of (*E*)-Lycopene in Total Lycopene Content of Standard Solutions Dissolved and Heated in Sunflower Oil[a]

sample	content of (*E*)-lycopene (mg/100 g of fm[b])	share (%) of (*E*)-lycopene in total lycopene content
0 min	0.976 ± 0.008A	96.3
15 min	0.388 ± 0.021B	57.0
30 min	0.272 ± 0.006C	49.8
45 min	0.213 ± 0.007D	49.0
60 min	0.203 ± 0.005D	50.2

[a] Values with the same letter are not significantly different ($p > 0.05$). [b] Fresh matter.

isomerized in a model reaction, when a standard solution of (*E*)-lycopene was dissolved and heated in sunflower oil (**Table 4**).

Vitamin E. Vitamin E in tomatoes is predominantly represented by α-tocopherol. Homogenization and sterilization of tomatoes during production of tomato juice resulted in significant losses of contents of α-tocopherol on wet as well as dry weight bases (data not shown). In contrast, short-term heating of tomato sauce, tomato soup, and baked tomato slices led to a significant rise of α-tocopherol contents on wet as well as dry

Table 5. Changes in Contents of α-Tocopherol during Preparation of Baked Tomato Slices[a]

sample	content of α-tocopherol (mg/100 g of fm[b])	content of α-tocopherol (mg/100 g of dm[c])
	Tomatoes Baked at 180 °C	
0 min	0.111 ± 0.005A	2.50 ± 0.12A
15 min	0.346 ± 0.020B	5.07 ± 0.29B
30 min	0.408 ± 0.030B	5.44 ± 0.40B
45 min	0.543 ± 0.038B	6.45 ± 0.45B
	Tomatoes Baked at 200 °C	
0 min	0.111 ± 0.005A	2.50 ± 0.12A
15 min	0.459 ± 0.009B	8.07 ± 0.15B
30 min	0.592 ± 0.072B,C	9.24 ± 0.15B
45 min	0.772 ± 0.064C	9.30 ± 0.77B
	Tomatoes Baked at 220 °C	
0 min	0.111 ± 0.005A	2.50 ± 0.12A
15 min	0.429 ± 0.027B	8.19 ± 0.52B
30 min	0.512 ± 0.031B	7.30 ± 0.44B,C
45 min	0.674 ± 0.032B	6.74 ± 0.32C

[a] Values within columns with the same letter are not significantly different ($p > 0.05$). [b] Fresh matter. [c] Dry matter.

weight bases. In these samples, the contents of α-tocopherol on a dry weight basis decreased only after tomatoes had baked for 45 min at an oven temperature of 220 °C and sauce had cooked for >60 min. Furthermore, the addition of cream to the soup resulted in a reduction of the α-tocopherol content (**Table 1**). **Table 5** shows the changes in contents of α-tocopherol of the baked tomato slices on wet as well as dry weight bases, and **Table 2** shows the α-tocopherol contents of sauce 2 on a dry weight basis. The increase in α-tocopherol contents due to thermal treatment was not caused by the release of tocopherols from the seeds, as they contained mainly γ-tocopherol and accounted for merely 2% of total α-tocopherol content, whereas the major part of the α-tocopherol is situated in the outside layers (59%) as well as in the inside layers (39%) of the tomato fruit. In a model reaction, α-tocopherol was proven to be very stable against thermal treatment. Tomato juice, sunflower oil, and a mixture of both were heated at 180 °C in the oven for 60 min. No significant changes in α-tocopherol content were observed (data not shown).

DISCUSSION

For our investigations, tomatoes from Holland and Spain were taken. Their (*E*)-lycopene content (5.51 ± 0.15 vs 4.97 ± 0.22 mg/100 g of fresh matter) was comparable to existing data and was affected by cultivar, ripening stage, and growing conditions (*31*). The ripening stage had the greatest influence on the carotenoid content (*31*). The (*E*)-β-carotene content of the tomatoes used (0.48 ± 0.01 vs 0.40 ± 0.02 mg/100 g of fresh matter) was similar to existing data (*21*, *22*, *32*, *33*). Several publications mention inconsistent results for the behavior of carotenoids during thermal processing of tomatoes. Some differences might be explained by the fact that not all authors took into account the loss of water during heating. Still, contradictory results exist. For example, Takeoka et al. (*26*) and Abushita et al. (*21*) investigated the production of tomato paste. Takeoka et al. found (*E*)-lycopene losses on a soluble solids basis that ranged from 9 to 28% (*26*), whereas in the study of Abushita et al. a rise of (*E*)-lycopene contents on a dry weight basis was reported during the same process (*21*). Likewise, our own results were not consistent. In all samples prepared from tomatoes from Holland, the (*E*)-lycopene content on a dry weight basis significantly decreased within 25 min. Differently, during the cooking of the sauce from Spanish tomatoes, the (*E*)-lycopene content on a dry weight basis significantly increased within the first 30 min. The latter is in good agreement with data presented by Graziani et al. (*28*), who showed that the content of (*E*)-lycopene significantly rose during heating of tomatoes in an oil bath at 100 °C for 2 h. Longer heating led to a decrease in carotenoid content (*28*). They suggested that lycopene was released from its binding sites during heating and that within the first 2 h the release exceeded the thermal degradation (*28*). The differences in the behavior of (*E*)-lycopene depending on the origin of the tomatoes gave rise to the idea that the choice of raw tomatoes affected the alterations of carotenoid contents. Ripening stage, firmness, and genotype could have influenced the extractability of carotenoids. The cultivar of the tomatoes employed in the presented study was unknown; only the origin was known. Nevertheless, it could be assumed that they were of different genotypes. Depending on the variety of the tomato fruit, the carotenoids were associated with different proteins and appeared mainly in lipid droplets or mainly in crystalline structures. Such differences in structure might have caused a release of lycopene or prevented it. The possible influence of ripening stage, firmness, and genotype on the behavior of carotenoids during tomato processing could also serve as an explanation for the inconsistent results found in the literature. Further studies are necessary to support this hypothesis.

Apart from thermal treatment, the carotenoids were affected by mechanical treatment and the addition of cream. Both the (*E*)-lycopene and the (*E*)-β-carotene contents decreased following the step of homogenization during the production of tomato juice. It could be assumed that the pressure of 70 bar led to a destruction of carotenoid−protein complexes and membranes of chromoplasts. The carotenoids then could be degraded by oxygen and high temperature. The addition of cream to the tomato soup is a common practice in some recipes. Our results on a dry weight basis solely show a significant reduction of the (*E*)-β-carotene content after the addition of cream. It is well-known that carotenoid−protein complexes are denatured by the cooking of vegetables (*21*). The addition of proteins might anew lead to the formation of such complexes. Free (*E*)-β-carotene was presumably bound to milk proteins, after the cream was added. Further investigations should clarify why only β-carotene and not lycopene was affected by this practice.

In accordance with our results, Nguyen and Schwartz (*34*) reported a significant isomerization susceptibility of (*E*)-β-carotene in contrast to (*E*)-lycopene during processing of tomatoes to different products. These results were supported by the studies of Abushita et al. (*21*) and Nguyen et al. (*35*). Both described no alterations of the isomeric composition of lycopene and a significant increase in the (*Z*)-isomers of β-carotene as a consequence of thermal processing of tomatoes (*21*, *35*). Likewise, Lessin et al. (*23*) reported an increase in (*Z*)-isomers of β-carotene during the process of canning tomatoes. In agreement with our results, they identified the (13*Z*)-isomer as the predominant (*Z*)-isomer of β-carotene followed by smaller quantities of the (9*Z*)- and (15*Z*)-isomers (*23*). Nguyen et al. (*35*) explained the differences in thermal isomerization susceptibility of lycopene and β-carotene by the different physical structures of crystals and membranes associated with these carotenoids. This also could account for the outcome of the model reaction. Without protection by the tomato matrix, (*E*)-lycopene quickly isomerizes.

The α-tocopherol content of different fresh tomatoes has been analyzed as 0.001−1.164 mg/100 g of fresh matter (*21*, *33*, *36*−

38). In the present study, the α-tocopherol content amounted to 0.111 ± 0.005 mg/100 g of fresh matter (Dutch tomatoes) and 0.239 ± 0.005 mg/100 g of fresh matter (Spanish tomatoes), respectively. Ripening stage and cultivar affected the α-tocopherol content (*33*, *38*). Short-term heating led to an increase in α-tocopherol contents of tomatoes on wet as well as dry weight bases. Longer heating resulted in a decrease of α-tocopherol contents on a dry weight basis. Possibly, α-tocopherol was released from its binding sites as a consequence of thermal treatment, and only heating for >1 h or at oven temperatures >200 °C led to a thermal degradation exceeding the release. Furthermore, the α-tocopherol contents decreased during production of tomato juice. We assumed that this was due to the fact that the juice was produced from preheated tomatoes. Probably, the complete release of α-tocopherol by thermal processing had already been reached. Abushita et al. (*21*) reported significant losses of α-tocopherol on a dry weight basis due to the production of tomato paste. The α-tocopherol content of the final paste was ∼20% lower than the content of the raw material (*21*). However, a value of the α-tocopherol content of an intermediate product was mentioned, which was ∼13% higher than the value of raw tomatoes (*21*). This could explain why the possibility of a release reaction of α-tocopherol during tomato processing has been found before, but never been mentioned or discussed.

The analysis of the distribution of tocopherols among the different fractions of tomato fruit showed that the increase of α-tocopherol was not caused by release from the seeds containing predominantly γ-tocopherol (3.61 mg/100 g of fresh matter = 65% of total γ-tocopherol content). The α-tocopherol content of the seeds amounted to 0.16 mg/100 g of fresh matter and accounted for only 2% of the total α-tocopherol content. A similar distribution of tocopherols was found by Biacs et al. among the paprika fruit (*39*)—like tomatoes belonging to the nightshade family. As the seeds could be excluded as a reservoir of α-tocopherol, further studies are necessary for a better understanding of possible causes of the increase in α-tocopherol contents due to tomato processing. For this, the physical structure of tocopherols in tomatoes needs to be enlightened. In samples of tomato soup, α-tocopherol presumably was bound to milk proteins, as the addition of cream resulted in a decrease of α-tocopherol content. In tomatoes, the tocopherols also might be complexed with proteins, which could be denatured as a consequence of thermal processing. α-Tocopherol itself was proven to be rather stable against heating. In a model reaction, it was not affected by a temperature of 180 °C for 60 min.

In conclusion, the experiments showed that losses of carotenoids and vitamin E were masked by the evaporation of water during thermal processing. Consequently, processed tomatoes still contained high amounts of the investigated parameters, which is one reason for recommending the intake of these products. New results in the field of release reactions underscored the importance of careful selection of raw material and showed that thermally treated tomatoes contain more bioaccessible vitamin E than fresh tomatoes.

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