Research Article

The *E*/*Z* isomer ratio of lycopene in foods and effect of heating with edible oils and fats on isomerization of (all-*E*)-lycopene

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Abbreviations: DIPEA, *N*,*N*-diisopropylethylamine; **IV**, iodine value; **SV**, saponification value

Abstract

Since *Z*-isomers of lycopene are more bioavailable and show a higher antioxidant capacity than the (all-*E*)-isomer, it is important to understand foods containing high amount of the *Z*-isomer and develop practically feasible method for *Z*-isomerization of (all-*E*)-lycopene. First, we investigated the *E*/*Z* isomer ratio of lycopene in raw and commercially available processed tomato products using an improved normal-phase HPLC method. The tomato products contained 4.6–33.4% of *Z*-isomers to the total lycopene, (5*Z*)-lycopene being the most abundant *Z*-isomer. The oil-containing products like tomato sauce and tomato soup suffered heat processing contained a higher percentage of *Z*-isomers of lycopene (27.4–33.4%). Subsequently, the impact of the amount and types of oils added on thermal *Z*-isomerization of (all-*E*)-lycopene contained in tomato puree was investigated. Increased addition of olive oil to tomato puree increased the production of lycopene *Z*-isomers upon heating at 120 °C. (all-*E*)-Lycopene contained in tomato puree was converted to *Z*-isomers in the range of 39.2–50.7%, when 5% of vegetable oil (linseed, soybean, corn, sesame, rapeseed, rice bran, safflower seed, olive, sunflower seed, or coconut oils) or animal fat (beef tallow and pork lard) was added before heating at 120 °C for 30 min. When sesame oil was employed, the total *Z*-isomerization ratio and (5*Z*)-lycopene content were significantly increased.

Practical applications

The dietary intake of lycopene offers many health benefits such as decreased risk of cancer and arteriosclerosis. Lycopene has a large number of geometric isomers caused by *E*/*Z* isomerization at arbitrary sites within the 11 conjugated double bonds, and the functionalities such as antioxidant capacity and bioavailability of the *Z*-isomers are higher than those of the all-*E*-isomer. This study clarified the foods richly containing *Z*-isomers of lycopene and demonstrated thermal *Z*-isomerization of (all-*E*)-lycopene contained in tomato puree with edible oils and fats. These findings will contribute to effective intake of lycopene and the development of facile isomerization of (all-*E*)-lycopene to *Z*-isomers in the fields of food, drink, and dietary supplement manufacturing, as well as for daily cooking at home.

1 Introduction

Lycopene is one of the more widespread and important carotenoids ($C_{40}H_{56}$). It is found abundantly in vegetables and fruits with a bright-red color, such as tomatoes, guava, and gac (*Momordica cochinchinensis*) [1, 2]. Lycopene has strong antioxidant properties and can significantly lower the risk of cancer and atherosclerosis [3, 4]. While lycopene in fresh tomato occurs predominantly in the (all-*E*)-configuration, *Z*-isomers of lycopene are primarily found in the human body; for example, more than 50% of total lycopene in serum and tissues is present as *Z*-isomers [5, 6], and these are probably safe for humans [7]. Because of their abundance in the human body, the *Z*-isomers of lycopene may have a greater potential for bioavailability than the (all-*E*)-isomer. In fact, both *in-vitro* tests using cultured small intestinal cells and *in-vivo* tests using ferrets strongly support these suggestions [8, 9]. Moreover, in humans, the ingestion of tomato sauce rich in *Z*-isomers of lycopene resulted in the measurable increase in plasma lycopene concentrations compared to a sample abundant in the (all-*E*)-isomer [10]. The lycopene *Z*-isomers are also expected to show higher antioxidant activity than the (all-*E*)-isomer [11, 12]. For these reasons, the intake of *Z*-isomers of lycopene, rather than the (all-*E*)-isomer, is preferable for human health, and appropriate methods are required to enable efficient *Z*-isomerization of (all-*E*)-lycopene.

Several processed tomato products contain a relatively high percentage of *Z*-isomers of lycopene such as tomato sauce (33%) and tomato soup (21%) [5, 13, 14]. Thus, a good understanding of *Z*-isomers-rich foods and their intake would offer health

benefits. However, only a few reports summarized the *Z*-isomers contents in foods cyclopedically. In addition, there are several areas to be improved in the analytical methods of lycopene isomers using conventional methods; the separation of lycopene isomers with HPLC is currently insufficient. A number of studies have been performed to analyze lycopene isomers using reversed- [15–18] or normal-phase [5, 19, 20] HPLC with a UV detector. Comparing the normal- and reversed-phase methods, the latter method shows a better separation than the former, but the separation of the peaks remains insufficient, e.g., between (13*Z*)- and (15*Z*)-isomer, which are the major isomers found in tomato products and live animals [5, 19, 20].

In this study, we improved the normal-phase analytical methods for lycopene isomers by examining the length of the column, column temperature, and mobile phase, which greatly affect the separation of compounds in HPLC [21]. The *E*/*Z* isomer ratio of lycopene in various processed tomato products (including raw tomatoes) was investigated using the improved analytical method. In addition, Schierle et al. [5] reported that when tomato materials were heated with olive oil, the *Z*-isomerization of (all-*E*)-lycopene was promoted. However, few studies have focused on the impact of the amount and types of oils added on *Z*-isomerization of (all-*E*)-lycopene. We have previously reported that thermal *Z*-isomerization of (all-*E*)-lycopene was promoted in vegetable oils, especially sesame oil, but the study was a basic model using purified lycopene [18]. Therefore, we also investigated the effect of the above additives (1–10% of commonly used vegetable oils and animal fats) in tomato puree to model practical applications. These data will contribute to the understanding of the foods containing

high-functional lycopene, and will be an effective tool for understanding the *E*/*Z* isomerization of lycopene.

2 Materials and methods

2.1 Materials

Analytical grade acetone, ethanol, benzene, and chloroform ($CHCl_3$), and high-performance liquid chromatography (HPLC)-grade hexane were obtained from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). *N*,*N*-Diisopropylethylamine (DIPEA) was purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). The suppliers of the tomato-based foods and some raw materials other than tomato are summarized in Supporting Information Table S1. The suppliers of the vegetable oils (linseed, soybean, corn, sesame, rapeseed, rice bran, safflower seed, olive, sunflower seed, and coconut oils) and animal fats (beef tallow and pork lard) are summarized in Supporting Information Table S2 along with some of their chemical properties [22–28].

2.2 Preparation of (all-*E*)-lycopene

(all-*E*)-Lycopene was obtained from tomato oleoresin (Lyc-O-Mato® 15%, LycoRed Ltd., Beer-Sheva, Israel) by purification according to the previous description with some modifications [16, 18]. The oleoresin (3 g) was dissolved in 100 mL of benzene, and insoluble substances were collected by suction filtration on a Kiriyama funnel (number 5B filter paper). Then, the residue was rinsed sequentially with 50 mL of benzene, 100 mL of acetone, and 50 mL of ethanol, and dried *in vacuo*: 304 mg of fine

red crystalline (all-*E*)-lycopene (normal-phase HPLC, ≥98.2% purity) was obtained.

2.3 Thermal isomerization of (all-*E*)-lycopene

The mixture of lycopene isomers used in the experiments for optimizing the separation method was prepared according to the previous description [16, 20]: purified (all-*E*)-lycopene (13 mg) was dissolved in 130 mL of $CHCl_3$ and transferred into a 200-mL brown glass bottle, purged with nitrogen, and then heated at 50 °C for 24 h in a hot-water bath. The yield of the *Z*-isomers was estimated to be nearly 70% of all lycopene isomers.

2.4 HPLC analysis

Several studies have performed normal-phase HPLC analysis to separate lycopene isomers under the following conditions: three Nucleosil 300-5 columns (250 mm in length, 4.6-mm inner diameter, 5-µm particle size; GL Sciences Inc., Tokyo, Japan) connected in tandem; column temperature of 30 °C; hexane mobile phase containing 0.1 or 0.15% DIPEA; flow rate of 1.0 mL/min; and detection wavelength 460 or 470 nm [5, 16–20]. However, the above analytic conditions are insufficient for the separation of lycopene isomers, especially between (13*Z*)- and the other *Z*-isomers such as (15*Z*)-isomer. Thus, we optimized the following analytical conditions: the column length (number of the Nucleosil 300-5 columns), column temperature, and mobile phase. Namely, we examined them in the following range: the number of columns connected in tandem, 1–5 columns; column temperature, 25–45 °C; mobile phase component;

hexane containing 0.15–0.025% of DIPEA. The detection wavelength of the compounds was set at 460 nm using a photodiode array detector (MD–2010 Plus, Jasco Co., Ltd., Tokyo, Japan), where the differences in molar extinction coefficients among lycopene isomers are relatively small [19, 20]. Column temperature was kept at prescribed temperatures by a column heater (U-620, Sugai, Tokyo, Japan), and the analysis was done isocratically at a constant flow rate of 1 mL/min by a PU-980 pump (Jasco Co., Ltd., Tokyo, Japan). The peaks of lycopene isomers obtained by the thermal isomerization of (all-*E*)-lycopene in $CHCl_3$ were identified according to their HPLC retention times, visible spectral data, and the relative intensities of the *Z*-peak as % D_B/D_{II} previously described [19, 20, 29–31].

2.5 Extraction of lycopene isomers from tomato-based foods

All procedures were carried out at room temperature, unless otherwise indicated, and light exposure was kept to a minimum throughout the extraction. A defined amount of the material corresponding to lycopene content was weighed into a 50-mL volumetric flask and approximately 30 mL of acetone was added [5, 32]. Lycopene was extracted from the tomato material by ultrasonic treatment for 5 min at ice temperature (approximately 4 °C) in order to prevent thermal *Z*-isomerization of lycopene [5, 20]. After diluting the mixture in a measuring flask to 50 mL with acetone, lycopene was once again extracted by ultrasonic treatment for 10 min at ice temperature. The residue was removed by suction filtration on a Kiriyama funnel (number 5B filter paper). If any color remained in the residue, it was rinsed by acetone

until the filtrate was colorless. The collected solution containing lycopene was evaporated to dryness under reduced pressure at 35 °C, dissolved in 5–10 mL of hexane, and then filtered through a 0.2-μm polytetrafluoroethylene membrane filter (Advantec Co., Ltd., Tokyo, Japan). The above method was applied to all tomato samples other than a tomato oleoresin and tomato supplements: the former sample was directly diluted in hexane to a concentration of 0.2 mg/mL and the latter was directly diluted only the content of the capsule in hexane to a concentration of 0.5 mg/mL, and filtered through the membrane filter. Samples of raw tomatoes, a whole tomato, and a cut tomato were homogenized by a food processor before lycopene extraction. A dried tomato was homogenized with an equal weight of water before the extraction.

2.6 Thermal isomerization of (all-*E*)-lycopene contained in tomato puree with oils

Olive oil was added to tomato puree to a final concentration of 1, 3, 5 or 10% (w/w). Each mixture was homogenized by a food processor, and then 30 g of each sample was transferred into a 100-mL glass bottle. This mixture was heated in an oil bath at 120 °C. Heating was continued for two different durations: 30 min and 1 h. Similarly, the other vegetable oils (linseed, soybean, corn, sesame, rapeseed, rice bran, safflower seed, olive, sunflower seed, and coconut oils) and animal fats (beef tallow and pork lard) were each separately added to tomato puree to a final concentration of 5%. The sample (30 g) was transferred into a 100-mL glass bottle and heated at 120 °C. As before, the heating was performed for either 30 min or 1 h. Contents of lycopene *Z*-

isomers in the obtained samples were analyzed in the same manner as mentioned above.

3 Results and discussion

3.1 Optimized HPLC conditions for the analysis of *Z*-isomers of lycopene

The normal-phase HPLC chromatogram of the *Z*-isomers of lycopene generated by thermal isomerization in $CHCl_3$ analyzed by the traditional protocol (the number of columns connected in series, three; column temperature, 30 °C; mobile phase component; hexane containing 0.1% of DIPEA) [19, 20] is shown in Figure 1A. The peak numbers in the figure are corresponding to Table 1. Since (5*Z*)-, (9*Z*)-, (13*Z*)-, and (15*Z*)-lycopene are observed widely in foods and animals, clear separation is required. However, as observed in Figure 1A, the separations between (13*Z*)- and (15*Z*)-lycopene, and between (9*Z*)-lycopene and peak 13, putative (5*Z*,9*Z*,5′*Z*)-lycopene (Table 1), were insufficient. When the number of columns was increased, detectable peaks of lycopene isomers increased, while the number of detectable peaks did not increase further when using more than four columns (Supporting Information Figure S1). Thus, the column number was set to four. With this modification, (5*Z*)-, (9*Z*)-, and (13*Z*)-lycopene could be separated clearly from the other *Z*-isomer peaks. When varying the column temperature, the separations between peaks 4 and 5, and (13*Z*)- and (15*Z*)-lycopene were improved at more than 40 °C (Supporting Information Figure S2). However, at 45 °C, the separations between peak 6 and (13*Z*)-lycopene, and peak 15 (putative (5*Z*,5′*Z*)-lycopene, (Table 1)) and (all-*E*)-lycopene were worsened. Based on the above

results, the column temperature was set to 40 °C. Modifying the mobile phase component, the detectable peaks were maximized when the content ratio of DIPEA was less than 0.075% (Supporting Information Figure S3). However, when less than 0.05%, the separations among peaks 5, 6, and (13*Z*)-lycopene worsened. Thus, the content ratio of DIPEA was set to 0.075%. When the above set column number, column temperature, and mobile phase components were combined, the separation of lycopene isomers was markedly improved compared with previous conditions (Figure 1B) [5, 19, 20]. The above analytical conditions were used in subsequent analyses of lycopene isomers.

3.2 Content of lycopene *Z*-isomers in foods

Lycopene isomer contents in commercially available processed tomato products including raw tomatoes were investigated using the improved normal-phase HPLC method (Table 2). Schierle et al. [5] reported that processed tomato products that used oils during manufacture contain a higher percentage of *Z*-isomers of lycopene: for example, *Z*-isomers of lycopene constituted 33% of the total lycopene in tomato sauce. Also in this study, the oil-free tomato products such as tomato juice (Ripe tomato, Ito En, Ltd.; Figure 2A) and tomato ketchup (Kagome tomato ketchup, Kagome Co., Ltd.; Figure 2B) contained a low percentage of the *Z*-isomers: 8.3% and 11.9%, respectively. On the other hand, except the tomato supplements, the samples including oils such as tomato sauce (Basic tomato sauce, Fresh Del Monte Japan Co., Ltd.; Figure 2C) and pasta sauce (Olive and tomato, St.Cousair Ltd.; Figure 2D) had a relatively higher level

of *Z*-isomers: 22.4% and 32.3%, respectively. Although oils were added during manufacture of the tomato supplements, the *Z*-isomer contents were no more than approximately 10% of total lycopene. This indicated that *Z*-isomerization of (all-*E*)-lycopene needs both heating and the presence of oils. Tomato sauce and pasta sauce are heated after the addition of oils in order to cook and sterilize. There would be no heating during manufacture of tomato supplements as they do not need to be sterilized due to their low water activity.

To verify the above hypothesis, tomato samples, some of which contained oils, were heated at 120 °C for 1 h, and then the contents of lycopene *Z*-isomers among them were compared. The samples chosen for this study are tomato juice (Tomato juice; Kagome Co., Ltd.), tomato ketchup (Tomato ketchup; H. J. Heinz Company), tomato oleoresin (Lyc-O-Mato® 15%; LycoRed Ltd.), pizza sauce (Ripe tomato pizza sauce; Kagome Co., Ltd.), and tomato supplement (Lycopene; DHC Co., Ltd.). Lycopene *Z*-isomer contents of tomato juice and tomato ketchup – which include no oils – hardly increased after the heat treatment, whereas those of pizza sauce and tomato supplement – which include oils – increased significantly (Figure 3). The tomato oleoresin is extracted by organic solvents from tomato materials, and although oils are not added in its manufacturing process, the (all-*E*)-lycopene markedly isomerized to *Z*-isomers (Figure 3). The reason for this is that the oleoresin contains glycolipids and phospholipids from the tomatoes [33]. Thermal *Z*-isomerization of (all-*E*)-lycopene in tomato oleoresins has also been observed in previous studies [7, 34]. These results strongly support the hypothesis that *Z*-isomerization of (all-*E*)-lycopene needs both

heating and the presence of oils. In addition, the fact that the (all-*E*)-lycopene in the tomato supplement isomerized to *Z*-isomers efficiently by heating (Figure 3) indicates that tomato supplements could be enhanced in their bioavailability and antioxidant ability [8–12], by heating before capsulation.

(5*Z*)-Lycopene was the most prevalent isomer over most of the processed tomato products, including raw tomatoes (Table 2). Computational studies report that the activation energy of isomerization from (all-*E*)-lycopene to each mono-*Z*-isomer follow the following order: (5*Z*)- > (9*Z*)- > (13*Z*)- > (15*Z*)-lycopene, and the relative potential energy of (mono-*Z*)-lycopene on the basis of (all-*E*)-lycopene was in the order: (15*Z*)- > (13*Z*)- > (9*Z*)- > (5*Z*)- ≈ (all-*E*)-lycopene [35–37]. Thus, the reason why (5*Z*)-lycopene is present in the largest amount among *Z*-isomers in the processed tomato products would be its high storage stability due to its low potential energy and its inherent presence in the raw tomatoes. On the other hand, (13*Z*)- and (15*Z*)-lycopene were found widely in the tomato products in spite of their low storage stabilities (due to elevated potential energies) because of their ease of generation due to their low activation energies.

3.3 *Z*-Isomerization of (all-*E*)-lycopene by heating with vegetable oils and animal fats

The effects of the amount and the types of oils (or fats) added to tomato puree on thermal *Z*-isomerization of lycopene were investigated. Although (all-*E*)-lycopene in neat tomato puree did not isomerize to *Z*-isomers upon heating at 120 °C for 1 h, the thermal *Z*-isomerization was enhanced significantly when olive oil was added at more

than 1% to the puree (Figure 4). Further, as the amount of olive oil added and heating period were increased, the total amount of *Z*-isomers of lycopene increased. The commercially available oil-containing processed tomato products used in this study contain 1–5% of vegetable oils. This oil amount is considered sufficient to thermally isomerize (all-*E*)-lycopene to *Z*-isomers during a heating process such as cooking or sterilization. The isomerization was mainly observed as an increase in levels of (9*Z*)- and (13*Z*)-lycopene (Supporting Information Table S3). This is similar to the thermal isomerization of purified (all-*E*)-lycopene in organic solvents, which has been previously described [20]. (5*Z*)-Lycopene, which is the most common *Z*-isomer in tomato products, slightly decreased (Supporting Information Table S3). This indicates that further thermal energy is required to increase (5*Z*)-lycopene because of its high activation energy of isomerization from (all-*E*)-lycopene [35–37], and the isomer would isomerize to di-*Z*-isomers such as (5*Z*,9′*Z*)- and (5*Z*,13′*Z*)-lycopene. In fact, the peaks, putative (5*Z*,9′*Z*)- and (5*Z*,9*Z*)-lycopene, increased slightly in this test. The reason why (15*Z*)-lycopene increased slightly (Supporting Information Table S3), despite the low activation energy of isomerization from (all-*E*)-lycopene compared with (9*Z*)- and (13*Z*)-isomers, is its low storage stability due to its high potential energy [35–37].

Thermal isomerization of (all-*E*)-lycopene to *Z*-isomers was conducted in ten vegetable oils (linseed, soybean, corn, sesame, rapeseed, rice bran, safflower seed, olive, sunflower seed, and coconut oils) and two animal fats (beef tallow and pork lard) as per the procedure outlined above. These oils and fats have different iodine values (IV), saponification values (SV), and fatty acid (FA) compositions (Supporting

Information Table S2). Table 3 lists the contents of the isomers obtained. The isomerization ratios of the *Z*-isomers increased in all the tests in the range from 39.2% to 50.7% by heating for 30 min and from 46.7% to 55.0% for 1 h. The total content of the *Z*-isomers attained in the ten vegetable and two animal oils were higher in the order corresponding to sesame (50.7%) > linseed (48.6%) > safflower seed, beef tallow (46.9%) > pork lard (46.5%) > rice bran (46.1%) > soybean (45.6%) > corn (45.3%) > coconut (44.0%) > olive (43.7%) > sunflower seed (41.0%) > rapeseed oil (39.2%) after 30 min of heating, and safflower seed (55.0%) > sesame (54.5%) > pork lard (54.4%) > olive (53.6%) > corn (53.0%) > rice brain (52.6%) > linseed (52.3%) > soybean (51.6%) > beef tallow (51.4%) > sunflower seed (51.2%) > rapeseed (50.5%) > coconut oil (46.7%) after 1 h. Over both heating durations, the total *Z*-isomerization ratio and (5Z)-lycopene content, which has higher bioavailability [38] and antioxidant capacity [10] as well as greater storage stability among the *Z*-isomers [35–37], increased notably when sesame oil was employed. This *Z*-isomerization promoting effect of sesame oil was also observed previously [18]. There was no definite correlation between the *Z*-isomerization promoting effect and the IV, SV, or FA compositions of oils in this test. Thus, the cause of the differences in the isomerization tendencies of lycopene among oils is considered to be the presence of specific minor components contained in the oil. One such minor component is iron, which increases the content of (5*Z*)-isomer possibly by preferentially lowering the activation energy during isomerization [18].

4 Conclusions

The separation of lycopene isomers using normal-phase HPLC was improved. (all-*E*)-, (5*Z*)-, (9*Z*)-, (13*Z*)- and (15*Z*)-Lycopene, which are observed widely in tomato products and living animals, were clearly separated from the other *Z*-isomers when compared with the previously reported method. Using the improved analytic method, the amounts of lycopene *Z*-isomers in processed tomato products were measured more accurately and cyclopedically. The tomato products cooked with oils – such as tomato sauce and pizza sauce – contained higher levels of the *Z*-isomers. Furthermore, we found that increasing the added amount of oil increased the production of *Z*-isomers of lycopene when heating. When sesame oil was used, the total *Z*-isomerization ratio and (5*Z*)-lycopene content were notably increased. These findings are important, not only for the food and drink manufacturing industries, but also for daily cooking at home.

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The authors have declared no conflicts of interest.

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Tables

Table 1. Absorption maxima (λ_{max}) and relative intensities of the *Z*-peak (%D_B/D_{II}) for geometrical lycopene isomers separated and observed using normal-phase high-performance liquid chromatography[a]

		λ_{max} (nm)		% D_B/D_{II}	
Peak	Lycopene isomer[b]	In-line	Reported[b]	In-line	Reported[b]
1	(9*Z*,13′*Z*)	359, 431, 455, 487	360,433,457,487	30.8	30.4
2	UZ	359, 431, 455,487	–	29.4	–
3	(9*Z*,9′*Z*)	359, 432, 459, 488	360, 433, 459, 490	12.0	9.5
4	UZ	359, 439, 463, 495	–	67.5	–
5	UZ	359, 427, 455, 483	–	22.5	–
6	UZ	359, 447, 463, 495	–	61.0	–
	(13*Z*)	359, 435, 463, 495	361, 437, 463, 494	56.4	52.4
	(15*Z*)	359, 439, 467, 499	360, 441, 468, 499	72.5	70.0
7	UZ	359, 427, 455, 483	–	23.4	–
8	(9*Z*, 13*Z*)	359, 431, 455, 487	361, 433, 456, 488	27.7	26.2
9	UZ	359, 439, 459, 491	–	22.9	–
10	UZ	359, 435, 455, 487	–	31.2	–
11	(5*Z*,9′*Z*)	359, 439, 463, 495	361, 438, 464, 495	13.4	13.4
12	UZ	359, 431, 455, 487	–	11.6	–
	(9*Z*)	359, 439, 463, 495	361, 438, 464, 495	11.2	12.7
13	(5*Z*,9*Z*,5′*Z*)	359, 439, 463, 495	361, 438, 463, 495	13.0	12.6
14	(5*Z*,9*Z*)	359, 439, 463, 495	361, 438, 464, 495	9.6	11.8
15	(5*Z*,5′*Z*)	443, 471, 499	443, 470, 502	ND	ND
	(all-*E*)	443,471, 499	444, 470, 502	ND	ND
	(5*Z*)	443, 471, 499	444, 470, 502	ND	ND

[a]Values and peak designations were obtained from the chromatograms in Figure 1B, with a mobile phase of hexane containing 0.75% *N,N*-diisopropylethylamine for lycopene isomers generated during heating at 50 °C for 24 h in chloroform. UZ, unidentified *Z*-isomer of lycopene. –, not assigned. ND, not detected substantially.

[b]Tentatively assigned by the literature [5, 19, 29–31]

Table 2. Contents of lycopene isomers in tomato products[a]

Sample	Product name	Supplier	Content (%)						
			(all-*E*)	Total *Z*[b]	(5*Z*)	(9*Z*)	(13*Z*)	(15*Z*)	Other *Z*[c]
Raw tomato	Round tomato	Kagome	91.9 ± 0.1	8.1 ± 0.1	4.1 ± 0.0	1.0 ± 0.1	2.4 ± 0.2	0.6 ± 0.0	ND
	Mini tomato	Feel	94.3 ± 1.2	5.8 ± 1.2	2.4 ± 0.9	0.2 ± 0.2	2.3 ± 0.2	0.5 ± 0.1	0.4 ± 0.0
Tomato juice	Tomato juice	Kagome	94.0 ± 0.8	6.0 ± 0.8	3.5 ± 0.3	0.8 ± 0.1	0.2 ± 0.2	1.2 ± 0.8	0.2 ± 0.4
	Ripe tomato[d]	Ito en	91.7 ± 0.0	8.3 ± 0.0	4.1 ± 0.1	0.9 ± 0.0	1.1 ± 0.2	1.8 ± 0.1	0.4 ± 0.2
Whole tomato	Ripe whole tomato	Memo's	95.4 ± 0.1	4.6 ± 0.1	1.7 ± 0.1	0.7 ± 0.0	1.3 ± 0.1	0.9 ± 0.0	ND
Cut tomato	Ripe cat tomato	Memo's	94.4 ± 0.4	5.6 ± 0.4	2.3 ± 0.5	0.8 ± 0.3	1.9 ± 0.7	0.6 ± 0.6	ND
Tomato puree	Tomato puree	Kagome	90.9 ± 2.9	9.2 ± 2.9	4.0 ± 0.2	1.4 ± 0.9	1.2 ± 0.0	0.9 ± 0.1	1.6 ± 1.6
	Organic tomato puree	Del monte	88.0 ± 0.3	12.0 ± 0.3	5.0 ± 0.6	2.0 ± 0.3	1.7 ± 0.2	2.3 ± 0.0	1.0 ± 0.2
Tomato paste	Tomato paste	Kagome	90.8 ± 0.5	9.2 ± 0.5	3.4 ± 1.0	1.6 ± 0.7	2.2 ± 0.3	1.2 ± 0.3	0.9 ± 0.2
Tomato oleoresin	Lyc-O-Mato® 6%	LycoRed	83.6 ± 1.5	16.4 ± 1.5	6.4 ± 0.4	2.4 ± 0.3	2.8 ± 0.1	0.6 ± 0.2	4.2 ± 0.5
	Lyc-O-Mato® 15%	LycoRed	90.4 ± 1.5	9.6 ± 1.5	4.2 ± 0.5	1.5 ± 0.0	1.2 ± 0.8	1.5 ± 0.1	1.3 ± 0.3
Dried tomato	Sun dried tomato	Chichukai foods	91.6 ± 0.4	8.4 ± 0.4	4.7 ± 0.2	ND	3.7 ± 0.6	ND	ND
Tomato ketchup	Tomato ketchup[d]	Kagome	88.1 ± 1.6	11.9 ± 1.6	6.7 ± 0.2	0.8 ± 0.8	0.7 ± 0.7	3.4 ± 0.3	0.2 ± 0.2
	Tomato ketchup	Heinz	88.8 ± 0.1	11.2 ± 0.1	6.5 ± 0.0	1.2 ± 0.4	2.5 ± 0.1	1.0 ± 0.4	ND
Salsa sauce	Salsa	Kagome	88.8 ± 0.8	12.0 ± 0.8	5.1 ± 0.3	0.6 ± 0.0	5.5 ± 0.3	0.6 ± 0.6	0.1 ± 0.1
Tomato sauce	Basic tomato sauce	Kagome	67.5 ± 0.7	32.5 ± 0.7	8.0 ± 0.3	2.9 ± 0.5	6.9 ± 0.2	3.0 ± 0.0	11.7 ± 0.6
	Basic tomato sauce[d]	Del monte	77.6 ± 1.5	22.4 ± 1.5	6.6 ± 0.3	3.5 ± 0.0	2.9 ± 0.4	1.5 ± 0.0	7.9 ± 0.9
Pasta sauce	Olive and tomato[d]	St.Cousair	67.7 ± 1.9	32.3 ± 1.9	9.0 ± 0.5	5.6 ± 0.5	6.1 ± 1.2	2.2 ± 0.3	9.4 ± 0.0
Pizza sauce	Ripe tomato pizza sauce	Kagome	66.6 ± 2.8	33.4 ± 2.8	14.2 ± 1.0	2.2 ± 0.1	5.2 ± 1.5	2.2 ± 0.3	9.6 ± 0.0
Tomato soup	Vege grano	Kagome	67.4 ± 2.1	32.6 ± 2.1	11.3 ± 0.5	3.9 ± 0.7	6.2 ± 0.5	2.6 ± 0.9	8.6 ± 0.5
	Ripe tomato minestrone	Meiji	72.7 ± 1.5	27.3 ± 1.5	9.4 ± 1.7	2.5 ± 0.4	6.5 ± 0.1	2.0 ± 0.5	7.0 ± 0.3
Tomato supplement	Lycopene VE	Kagome	87.2 ± 0.4	12.8 ± 0.4	4.6 ± 0.4	1.5 ± 0.4	2.5 ± 0.6	1.4 ± 0.4	2.8 ± 0.2
	Lycopene	DHC	85.4 ± 1.1	14.6 ± 1.1	4.0 ± 0.0	2.4 ± 0.8	4.9 ± 1.9	2.4 ± 1.4	0.9 ± 0.3

[a]Percentage content of *E*/*Z*-isomers of lycopene relative to the total amount of lycopene isomers. Results are presented as means ± standard error (n = 2). ND, not detected substantially.
[b]Total content of *Z*-isomers of lycopene.
[c]Sum of *Z*-isomer of lycopene other than 5*Z*-, 9*Z*-, 13*Z*- and 15*Z*-forms.
[d]Chromatograms are shown in Fig. 2.

Table 3. Effect of the types of oils on thermal *E*/*Z*-isomerization of lycopene contained in tomato puree[a]

Oil	Content (%)						
	(all-*E*)	Total *Z*[b]	(5*Z*)	(9*Z*)	(13*Z*)	(15*Z*)	Other *Z*[c]
Linseed	51.4 ± 0.4	48.6 ± 0.4	2.3 ± 0.2	7.1 ± 0.5	20.6 ± 0.7	4.7 ± 0.2	14.0 ± 0.6
	[46.7 ± 1.6]	[52.3 ± 1.6]	[2.3 ± 0.1]	[14.0 ± 0.7]	[16.8 ± 0.2]	[4.0 ± 0.1]	[16.2 ± 0.8]
Soybean	54.4 ± 0.7	45.6 ± 0.7	2.6 ± 0.1	7.4 ± 0.0	19.3 ± 0.4	4.3 ± 0.3	12.1 ± 0.9
	[48.4 ± 0.7]	[51.6 ± 0.7]	[2.6 ± 0.1]	[13.9 ± 0.9]	[15.4 ± 3.1]	[3.6 ± 0.3]	[16.1 ± 0.5]
Corn	54.7 ± 0.0	45.3 ± 0.0	2.5 ± 0.3	6.4 ± 0.0	20.2 ± 0.0	4.5 ± 0.1	11.7 ± 0.4
	[47.0 ± 0.7]	[53.0 ± 0.7]	[3.3 ± 0.5]	[12.6 ± 0.6]	[15.9 ± 0.9]	[4.0 ± 0.2]	[17.1 ± 1.6]
Sesame	49.3 ± 1.0[e]	50.7 ± 1.0[e]	3.3 ± 0.1[e]	8.1 ± 0.1	18.2 ± 0.3	4.4 ± 0.0	16.7 ± 1.2[e]
	[45.5 ± 1.4]	[54.5 ± 1.4]	[4.2 ± 0.0[e]]	[11.6 ± 0.1]	[14.4 ± 0.2]	[3.1 ± 0.1[e]]	[21.3 ± 1.3[e]]
Rapeseed	60.8 ± 3.2[e]	39.2 ± 3.2[e]	3.0 ± 0.1	7.3 ± 0.9	16.6 ± 3.1	4.0 ± 0.3	8.2 ± 0.5[e]
	[49.5 ± 1.5[e]]	[50.5 ± 1.5[e]]	[2.3 ± 0.0]	[13.3 ± 0.1]	[15.6 ± 0.0]	[4.0 ± 0.2]	[15.4 ± 1.2]
Rice bran	53.9 ± 2.6	46.1 ± 2.6	2.7 ± 0.2	7.3 ± 0.2	18.6 ± 2.0	4.1 ± 0.5	13.4 ± 0.1
	[47.4 ± 2.6]	[52.6 ± 2.6]	[2.5 ± 0.0]	[14.5 ± 1.3]	[15.3 ± 0.2]	[3.6 ± 0.0]	[16.7 ± 1.2]
Safflower seed[d]	53.1 ± 0.2	46.9 ± 0.2	2.4 ± 0.2	6.8 ± 0.1	21.2 ± 0.3[e]	4.8 ± 0.2	11.7 ± 0.6
	[45.0 ± 0.0]	[55.0 ± 0.0]	[2.6 ± 0.4]	[14.2 ± 0.5]	[17.4 ± 0.4]	[3.5 ± 0.1]	[17.4 ± 0.4]
Olive	56.5 ± 1.2	43.5 ± 1.2	2.5 ± 0.7	5.9 ± 0.1	18.8 ± 1.7	4.0 ± 0.5	12.3 ± 0.5
	[46.4 ± 0.5]	[53.6 ± 0.5]	[2.4 ± 0.3]	[11.3 ± 0.5]	[16.8 ± 0.1]	[4.5 ± 0.0]	[18.8 ± 0.8]
Sunflower seed[d]	59.0 ± 0.3	41.0 ± 0.3	2.7 ± 0.3	5.2 ± 0.0[e]	19.0 ± 0.5	4.2 ± 0.0	9.8 ± 0.1
	[48.8 ± 2.2]	[51.2 ± 2.2]	[3.1 ± 1.0]	[12.0 ± 1.5]	[17.0 ± 0.3]	[4.0 ± 0.2]	[15.0 ± 1.3]
Coconut	56.0 ± 1.7	44.0 ± 1.7	2.8 ± 0.3	6.0 ± 0.8	19.4 ± 0.3	4.3 ± 0.1	11.5 ± 0.8
	[53.4 ± 0.0]	[46.7 ± 0.0]	[2.7 ± 0.3]	[9.9 ± 1.1[e]]	[16.7 ± 1.1]	[4.0 ± 0.1]	[13.4 ± 0.3[e]]
beef tallow	53.1 ± 2.2	46.9 ± 2.2	2.8 ± 0.2	7.7 ± 0.7	18.4 ± 0.2	4.4 ± 0.2	13.7 ± 1.3
	[48.6 ± 0.6]	[51.4 ± 0.6]	[2.9 ± 0.0]	[12.6 ± 0.2]	[16.1 ± 0.1]	[3.9 ± 0.1]	[16.0 ± 0.5]
pork lard	53.5 ± 0.7	46.5 ± 0.7	2.8 ± 0.0	7.2 ± 0.5	18.9 ± 0.1	4.4 ± 0.0	13.2 ± 0.4
	[45.6 ± 3.6]	[54.4 ± 3.6]	[2.6 ± 0.1]	[13.8 ± 0.8]	[15.1 ± 0.2]	[3.7 ± 0.2]	[19.3 ± 2.7]

[a]Tomato puree added 5% of oils was heated at 120 °C for 30 min [or 1 h] in an oil bath. Percentage content of *E*/*Z*-isomers of lycopene relative to the total amount of lycopene isomers. Results are presented as means ± standard error (n = 2). ND, not detected substantially.
[b]Total content of *Z*-isomers of lycopene.
[c]Sum of *Z*-isomer of lycopene other than 5Z-, 9*Z*-, 13*Z*- and 15*Z*-forms.
[d]Oil with high oleic acid content.
[e]Statistically significant (p<0.05, Student's t-test) in each column.

Figure legends

Figure 1. Normal-phase HPLC chromatograms of thermally generated *Z*-isomers of lycopene (50 °C for 24 h in chloroform) analyzed under different conditions: (A) three Nucleosil 300-5 columns connected in tandem; column temperature of 30 °C; mobile phase, hexane containing 0.1% DIPEA [19, 20]; (B) four Nucleosil 300-5 columns connected in tandem; column temperature of 40 °C; mobile phase, hexane containing 0.075% DIPEA. (5*Z*)-, (9*Z*)-, (13*Z*)- and (15*Z*)-Lycopene designated in the charts were identified according to the previous studies [5, 19, 29–31]. Peaks (1–15) were tentatively identified as shown in Table 1.

Figure 2. Normal-phase HPLC chromatograms of lycopene isomers present in (A) tomato juice (Ripe tomato, Ito En, Ltd.), (B) tomato ketchup (Tomato ketchup, Kagome Co., Ltd.), (C) tomato sauce (Basic tomato sauce, Fresh Del Monte Japan Co., Ltd.), and (D) pasta sauce (Olive and tomato, St.Cousair Ltd.). (5*Z*)-, (9*Z*)-, (13*Z*)- and (15*Z*)-Lycopene designated in the charts were identified according to the previous studies [5, 19, 29–31]. Peaks (1–15) were tentatively identified as shown in Table 1.

Figure. 3. Changes in the content of lycopene *Z*-isomers thermally isomerized at 120 °C for 1 h in tomato products. The examined tomato samples were as following: juice (Tomato juice; Kagome Co., Ltd.), ketchup (Tomato ketchup; H. J. Heinz Company), oleoresin (Lyc-O-Mato® 15%; LycoRed Ltd.), pizza sauce (Ripe tomato pizza sauce;

Kagome Co., Ltd.), supplement (Lycopene; DHC Co., Ltd.). Isomerization (%) is expressed as a percentage of the amount of *Z*-isomers to the total amount of lycopene isomers including (all-*E*)-lycopene.

Figure 4. Effect of the olive oil additive amount on thermal *Z*-isomerization of lycopene contained in tomato puree heating at 120 °C for 30 min or 1 h. Isomerization (%) is expressed as a percentage of the amount of *Z*-isomers to the total amount of lycopene isomers including (all-*E*)-lycopene.

Figures

Figure 1.

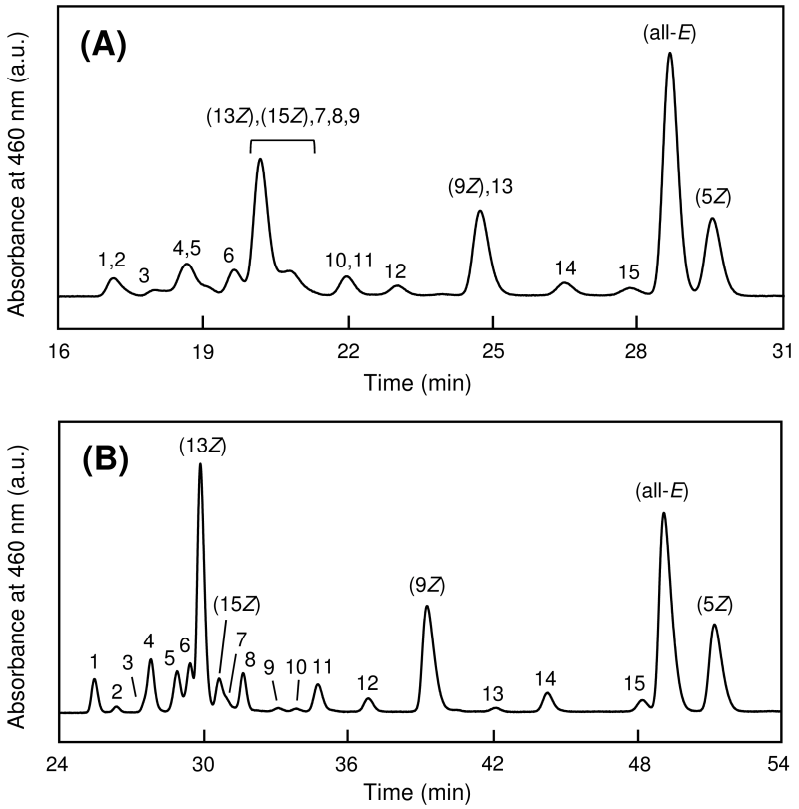


Figure 2.

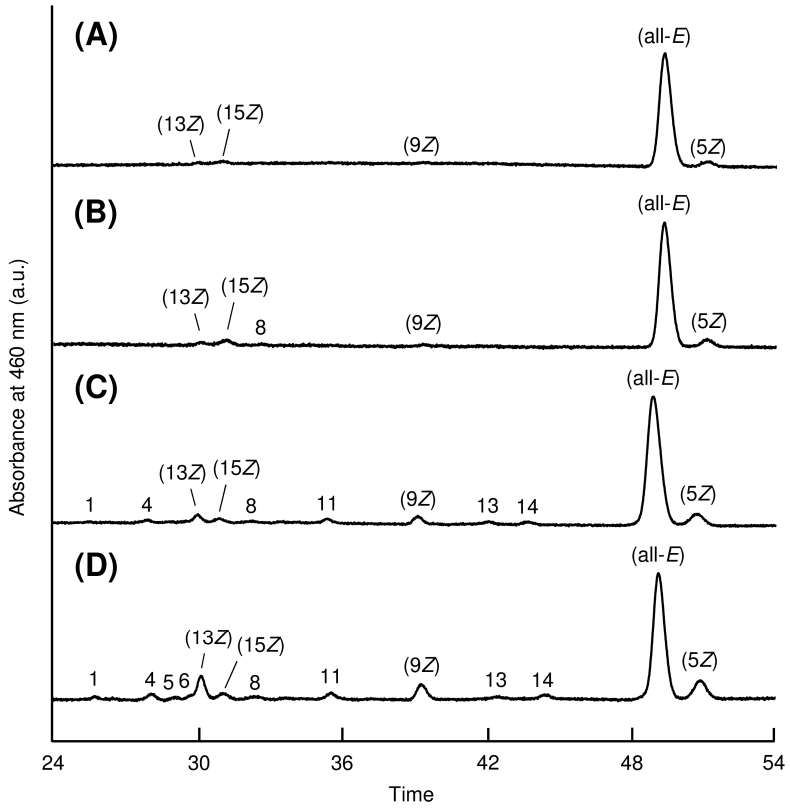

(A)
(all-E)
(13Z)
(15Z)
(9Z)
(5Z)
(B)
(all-E)
(13Z)
(15Z)
8
(9Z)
(5Z)
(C)
(all-E)
(13Z)
(15Z)
1
4
8
11
(9Z)
13
14
(5Z)
(D)
(all-E)
(13Z)
(15Z)
1
4
5
6
8
11
(9Z)
13
14
(5Z)
Absorbance at 460 nm (a.u.)
24
30
36
42
48
54
Time

Figure 3.

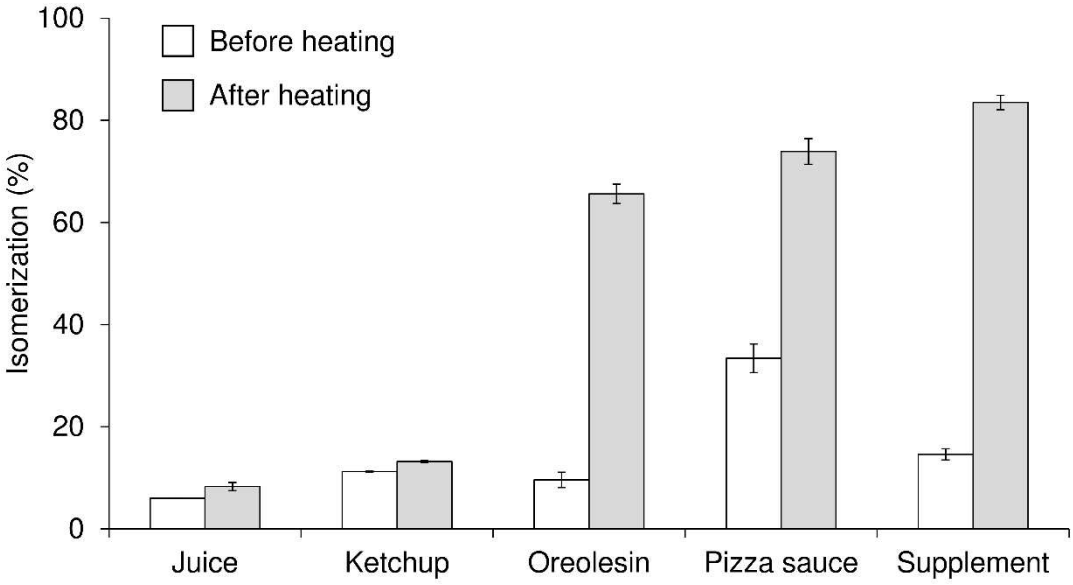
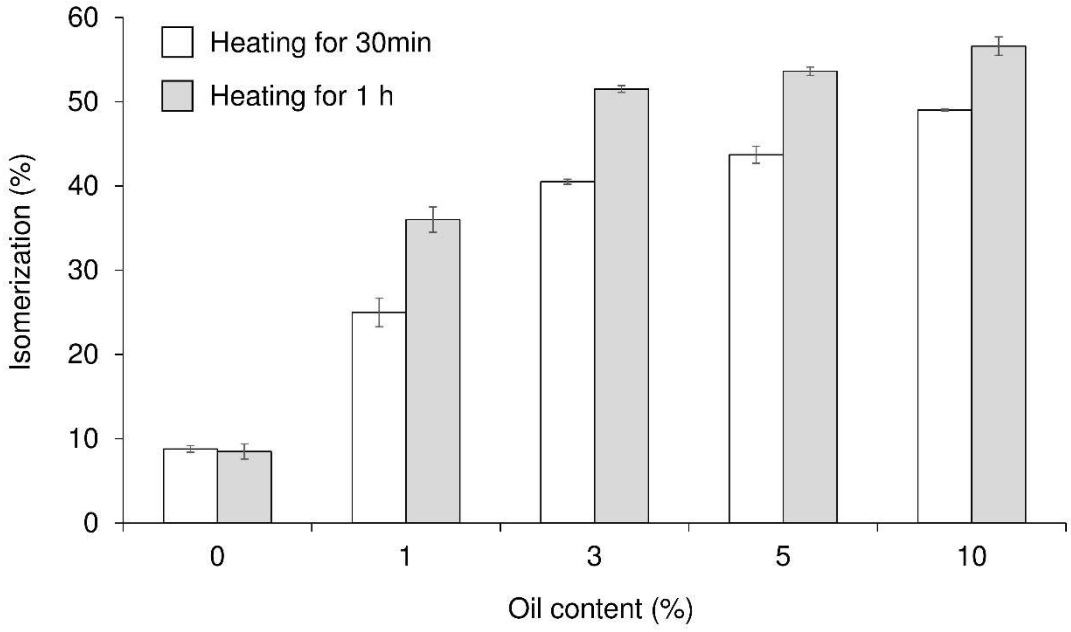

100
80
60
40
20
0
Isomerization (%)
Before heating
After heating
Juice
Ketchup
Oreolesin
Pizza sauce
Supplement

Figure 4.


Heating for 30min
Heating for 1 h
Isomerization (%)
60
50
40
30
20
10
0
0
1
3
5
10
Oil content (%)

Graphical abstract