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Stability of lycopene during heating and illumination in a model system

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Abstract

The stability of lycopene during heating and illumination was studied. Lycopene standard was heated at 50, 100 and 150 °C or illuminated at 25 °C for varied lengths of time. Lycopene and its *cis* isomers were analysed by HPLC with photodiode array detection. The degradation of total amount of lycopene (all-*trans* plus *cis* forms) during heating or illumination was found to fit a first-order model. At 50 °C, the isomerization dominated in the first 9 h; however, degradation was favoured afterwards. At 100 and 150°, the degradation proceeded faster than the isomerization while, during illumination, the isomerization was the main reaction. The degradation rate constant (min^{-1}) of lycopene rose with increasing temperature, and the activation energy was calculated to be 61.0 kJ/mol.

Keywords: Lycopene; HPLC; Heating; Illumination

1. Introduction

Lycopene, an important carotenoid, has received great attention in recent years because of its beneficial effect in the treatment of diseases such as skin cancer (Ribayo-Mercado, Garmyn, Gilchrest, & Russell, 1995) and prostate cancer (Steven & Clinton, 1998). However, because of the presence of a long chain of conjugated carbon–carbon double bonds, lycopene is susceptible to chemical changes when exposed to light and heat, and the formation of *cis* isomers of lycopene may decrease its biological activity (Nguyen & Schwartz, 1999). Thus, it is important to learn about the stability of lycopene and its *cis* isomers, as affected by processing treatments.

Theoretically a large number (2048) of lycopene isomers is possible because lycopene contains 11 conjugated double bonds. However, because of steric hindrance effects, only 72 may exist in nature (Zechmeister, 1962). Several studies have indicated that all-*trans*-lycopene and its mono-*cis* isomers, such as 5-*cis*-, 9-*cis*-, 13-*cis*- and 15-*cis*-lycopene, are present in tomato products and human serum (Schierle et al., 1997; Stahl, Sundquist, Hanush, Schwarz, & Sies, 1993; Yeum et al., 1996). As lycopene is present naturally in the *trans* form in food products, the formation of *cis* forms of lycopene is probably due to processing or storage (Nguyen & Schwartz, 1999). Bošković (1979) proposed a reaction pathway showing the fate of lycopene during processing and storage of tomato powder. No *trans–cis* isomerization is observed during freeze-drying; however, the isomerization occurs during dehydration or storage of tomato powder.

The stability of lycopene during heating and illumination has been controversial. Pesek and Warthesen (1987) reported that the degradation rate of lycopene was lower than β-carotene when a vegetable juice containing lycopene was exposed to light at 4 °C for 8 days. In contrast, Henry, Catignani, and Schwartz (1998) found that the degradation rate of lycopene was higher than β-carotene when safflower oil was heated at 75, 85 or 95 °C. Obviously the stability of lycopene may be variable in different food systems because of the complex nature of food components. The objectives of this report were to study the degradation and isomerization of lycopene in a model system during heating and illumination.

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2. Materials & Methods

2.1. Materials

All-*trans*-lycopene standard was purchased from Extrasynthese Co. (France) and was used without further purification. The HPLC-grade solvents, including hexane, acetonitrile, methylene chloride and 1-butanol, were obtained from Mallinckrodt Co. (Paris, Ky, USA). Deionized water was made from a Milli-Q water purification system (Millipore Co., Bedford, MA, USA). A polymeric C_{30} column (250×4.6 mm i.d.), containing 5 μm particles, was from YMC Co (Wilmington, NC, USA).

2.2. Instrumentation

The HPLC system is composed of a DG-440 degassing system (Phenomenex Co., Torrance, CA, USA), a Rheodyne Model 7161 injector (Rheodyne Co., CA, USA), a Jasco PU-980 pump (Jasco Co., Tokyo, Japan), a Jasco UV-970 UV–vis detector, and a Jasco MD-915 photodiode-array detector. The low-temperature incubator (Model TL 520R) was from Seng-Long Co. (Taipei, Taiwan). The light meter (Model TES-1330) was from Tai-Se Electronic Co (Taipei, Taiwan).

2.3. Illumination of lycopene standard

Ten mg of lycopene was dissolved in 50 ml hexane and the mixture was poured into 250 2 ml vials, separately, so that each contained 40 μg of lycopene. The solution of each vial was evaporated to dryness with nitrogen and a thin film was formed on the surface of the bottom. The vials were placed in a closed incubator and illuminated at 25 °C for 6 days. Four 20 W fluorescent tubes, with a length of 55 cm each, were placed above the vials with a distance of 30 cm and the illumination intensity was ranged 2000–3000 lux. Samples were collected at intervals, following illumination times of 1, 2, 4, 8, 12, 16, 24, 32, 40, 48, 56, 64, 72, 96, 120 and 144 h. A total of 51 vials including three controls were used. Each sample was dissolved in 200 μl hexane and filtered through a 0.2 μm membrane filter, of which 20 μl was collected for HPLC analysis.

2.4. Heating of lycopene standard

Lycopene samples were prepared in the same way, as described earlier, and a thin film was formed on the surface of the bottom of each vial. The vials were placed into an oil bath and heated at 50, 100 and 150 °C for varied lengths of time. At 50 °C, the heating times were 20, 40, 60, 80 and 100 h, while, at 100°C, they were 20, 40, 60, 80, 100 and 120 min. The heating time was shortened to 2, 4, 6, 8 and 10 min for 150 °C because of the susceptibility of lycopene to heat loss at high temperature. In total, 51 vials were used. After heating, samples were collected at intervals and dissolved in 200 μl hexane. After filtration through a 0.2 μm membrane filter, 20 μl samples were collected for HPLC analysis.

2.5. Analysis of lycopene and its cis isomers

A mobile phase of 1-butanol–acetonitrile–methylene chloride (30:70:10, v/v/v) with a flow rate of 2.0 ml/min and detection at 476 nm was used to separate lycopene and its *cis* isomers using a C_{30} column (Lee & Chen, in press). The sensitivity was 0.005 AUFS. All-*trans*-lycopene was identified by comparison of retention time of unknown peak with reference standard and cochromatography with added standard. The tentative identification of *cis* isomers of lycopene was carried out, based on spectral characteristics and Q ratios, as reported in a previous study (Lee & Chen, 2001). The quantification of lycopene and its *cis* isomers was achieved using an internal standard of β-carotene and calibration curves. Ten all-*trans*-lycopene concentrations, 25, 50, 75, 100, 125, 150, 175, 200, 225 and 250 μg/ml were prepared and β-carotene (50 μg/ml) was added. The solution was subjected to HPLC analysis and the calibration curve was obtained by plotting concentration ratio against area ratio. As all-*trans*-lycopene standard was found to contain several *cis* isomers (Lee & Chen, in press), the calibration curve of each *cis* isomer was prepared following the same procedure. For all-*trans*-lycopene and its *cis* isomers, the correlation coefficient (r^2), ranging 0.9856–0.9944, was obtained for all the standard curves.

The quantitation limits (QL) and detection limits (DL) of all-*trans*-lycopene and its *cis* isomers were determined based on a method described by the International Conference on Harmonization (1996). Three concentrations (10, 25 and 50 μg/ml) were prepared and each was analysed three times. Both DL and QL were calculated, based on a previous report by Lin and Chen (2001). The DL of all-*trans*-, 5-*cis*-, 9-*cis*-, 13-*cis*- and 15-*cis*-lycopene were found to be 2.55, 0.11, 0.07, 0.12 and 0.03μg/g, respectively, while the QL were 7.73, 0.32, 0.20, 0.38 and 0.11 μg/g.

2.6. Statistical analysis

Triplicate analyses were conducted for each heating and illumination treatment. Each sample was injected three times and the mean value was obtained. All the data were subjected to analysis of variance and Duncan's multiple range test, using a SAS system (SAS/STAT, 1985). The degradation rate constant of total amount of lycopene (all-*trans* plus *cis* forms) were calculated using the following formula:

$$k = -1\mathrm{n}(\mathrm{CA}/\mathrm{CA}_0)/t$$

where CA: the total amount of lycopene after heating; CA_0: the initial amount of lycopene; t: heating time.

3. Results and discussion

3.1. HPLC analysis of lycopene and its cis isomers

A mobile phase of *n*-butanal–acetonitrile–methylene chloride (30:70:10, v/v/v) and a C_{30} column were found to provide adequate resolution of lycopene and its nine *cis* isomers with a flow rate at 2.0 ml/min and a detection wavelength at 476 nm within 35 min (Lee & Chen, 2001). The lycopene standard used in this study was found to contain various *cis* isomers of lycopene, including 5-*cis*-, 9-*cis*, 13-*cis*-, 15-*cis*-lycopene, and possibly one more mono-*cis* and four di-*cis* isomers. These *cis*-isomers of lycopene were tentatively identified, based on spectral characteristics and Q ratios, as reported in a previous study (Lee & Chen, 2001).

3.2. Stability of lycopene during illumination

Fig. 1 shows the HPLC chromatogram of lycopene and its *cis* isomers during illumination for 32 h. A new pigment, which was tentatively identified as the di-*cis* isomer of lycopene, based on spectrum characteristics, was formed. The concentration of this pigment followed an increased order and reached a plateau in the first 120 h, and then declined afterwards. The formation of di-*cis*-lycopene was probably due to conversion of mono-*cis*-lycopene. This phenomenon has been shown for formation of di-*cis*-β-carotene during illumination or heating (Chen, Chen, & Chien, 1994; Zechmeister, 1944). The concentration changes of lycopene and its *cis* isomers during illumination are shown in Table 1. The content of all-*trans*-lycopene was found to decrease with increasing illumination time, and the residual concentration was 12.4 μg/g after 144 h exposure to light, which amounted to a 94% loss. All the mono-*cis* isomers of lycopene showed an inconsistent change. For instance, the level of 5-*cis*-lycopene was found to increase in the beginning and then decreased after illumination time reached 2 h. Likewise, a similar trend was observed for 9-*cis*-, 13-*cis*-, and 15-*cis*-lycopene. This result indicated that isomerization and degradation of lycopene and its *cis* isomers, during illumination, may proceed simultaneously. The increased level of mono-*cis*-lycopene is probably due to conversion of all-*trans*-lycopene, after which a decrease could occur for mono-*cis*-lycopene because it might be further converted to another *cis* form of lycopene through intermediate all-*trans*-lycopene or undergo degradation. Compared with concentration, the percentage changes of all-*trans*-lycopene and its *cis* isomers showed a different trend when the total amount of lycopene was taken into account. Prior to illumination, the total amount of lycopene was found to contain 96.4% all-*trans*-lycopene, 0.99% 5-*cis*-lycopene, 0.71% 9-*cis*-lycopene, 0.60% 13-*cis*-lycopene and 0.27% 15-*cis*-lycopene. After light storage for 144 h, a loss (13.1%) of lycopene occurred for all-*trans*-lycopene, while an increase of 1.47, 0.92, 5.28 and 0.44% was found for 5-*cis*-, 9-*cis*-, 13-*cis*- and 15-*cis*-lycopene, respectively. Di-*cis*-lycopene also rose by 3.04%. The small percentage loss of all-*trans*-lycopene during light storage revealed that all-*trans*-lycopene

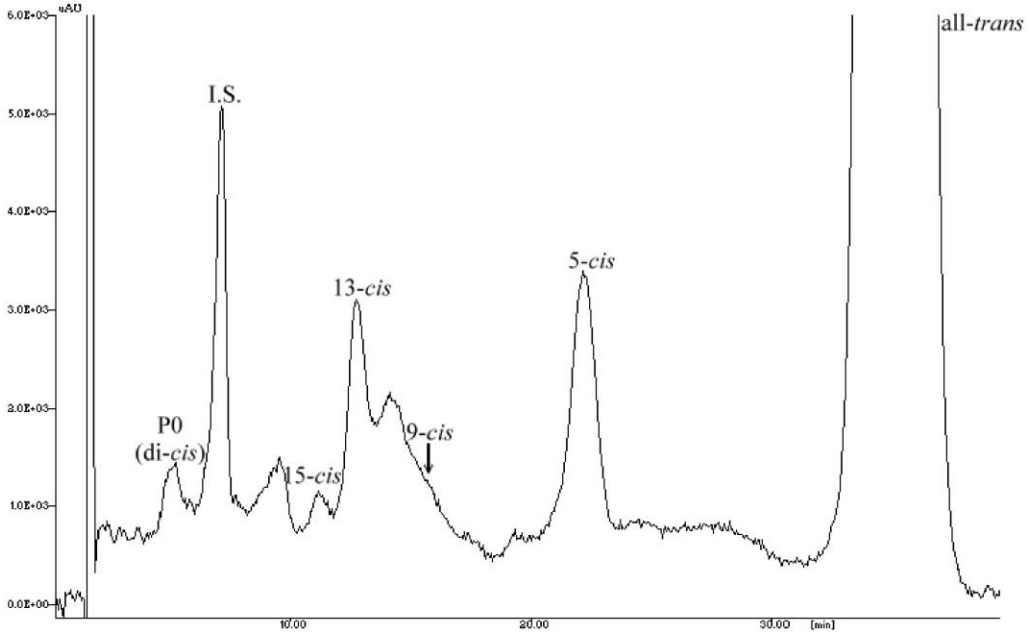

Fig. 1. HPLC chromatogram of lycopene and its *cis* isomers after illumination for 32 h. Chromatographic conditions described in text.

Table 1
Concentration (μg/g) and percentage (%) changes of lycopene and its *cis* isomers during illumination at 25 °C

Illuminating time (h)	Lycopene											
	P0 (di-*cis*)		15-*cis*		13-*cis*		9-*cis*		5-*cis*		All-*trans*	
	Conc.	%	Conc.	%	Conc.	%	Conc.	%	Conc.	%	Conc.	%
0	nd	–	0.61ab	0.27b	1.37abcd	0.60b	1.64b	0.71b	2.28bc	0.99b	222a	96.4a
1	nd	–	0.77a	0.33b	1.78a	0.76b	3.05a	1.30a	3.87a	1.65b	222a	94.8a
2	nd	–	0.24de	0.10b	1.46abc	0.64b	1.10c	0.48b	3.68a	1.60b	222a	96.4a
4	nd	–	0.42bcd	0.19b	1.11bcde	0.51b	0.16gh	0.07b	2.62b	1.20b	214b	97.4a
8	nd	–	0.40bcd	0.19b	1.18bcd	0.55b	0.31fgh	0.15b	2.67b	1.25b	207bc	97.0a
12	nd	–	0.28de	0.13b	0.86cde	0.42b	0.11h	0.05b	2.24bcd	1.09b	201bc	97.5a
16	nd	–	0.34cd	0.16b	1.09bcde	0.51b	0.15gh	0.07b	2.69b	1.27b	206bc	97.2a
24	nd	–	0.54bc	0.30b	1.67ab	0.92b	0.29fgh	0.16b	2.25bcd	1.25b	174cd	96.2a
32	0.25b	0.16b	0.45bcd	0.29b	1.27abcd	0.82b	0.26fgh	0.17b	1.87cd	1.21b	148de	95.7a
40	0.65a	0.45b	0.38bcd	0.26b	1.04cde	0.71b	0.38fgh	0.26b	1.72cd	1.18b	140def	95.8a
48	0.63a	0.46b	0.46bcd	0.34b	1.10bcde	0.81b	0.57def	0.43b	1.75cd	1.29b	129efg	95.3a
56	0.71a	0.62b	0.41bcd	0.36b	1.06cde	0.92b	0.46efg	0.40b	1.66cd	1.45b	108fgh	94.7a
64	0.71a	0.80b	0.39bcd	0.44b	1.19bcd	1.34b	0.42fgh	0.47b	1.62cd	1.83b	82.8h	93.1a
72	0.85a	0.79b	0.46bcd	0.43b	1.44abc	1.34b	0.54def	0.50b	1.59d	1.48b	100gh	93.3a
96	0.89a	1.73b	0.28de	0.55b	0.82de	1.60b	0.81cd	1.59a	0.84e	1.64b	45.8i	89.7a
120	0.79a	2.55b	0.22de	0.71a	0.55e	1.78b	0.75de	2.43a	0.66e	2.13b	26.8i	86.9a
144	0.45b	3.04a	0.11e	0.71a	0.88cde	5.88a	0.24fgh	1.63a	0.37e	2.46a	12.4i	83.3b

Values of means bearing different letters in the same column are significantly different ($P < 0.05$). nd, not detected.

might be isomerized to form mono-*cis*- or di-*cis*-lycopene. This result may account for the percentage increase of all the mono-*cis* and di-*cis* forms of lycopene during illumination. It has been reported that the activation energy required for isomerization of β-carotene in the central double bond was lower than the other position (Zechmeister, 1944). This phenomenon could be applied to lycopene and a larger percentage increase was thus found for 13-*cis*-lycopene, followed by 5-*cis*-, 9-*cis*- and 15-*cis*-lycopene. Theoretically 15-*cis*-lycopene should be formed in the greatest amount; however, because of a possible steric hindrance effect, it would be difficult to form, and once it was formed, it could be converted to other *cis* forms of lycopene (Chen et al., 1994; Chen & Huang, 1998). Fig. 2 shows the first-order plot for the degradation of total amount of lycopene during illumination at 25 °C for 144 h. A linear correlation ($r^2 = 0.9609$) was found for the plot of the logarithum of the concentrations of lycopene versus time and the degradation rate constant (h^{-1})was found to be 0.0176. Similar results were reported by Pesek and Warthesen (1987), who studied the stability of lycopene during illumination.

3.3. Stability of lycopene during heating

The concentration change of lycopene and its *cis* isomers during heating is shown in Table 2. Two new peaks, which were tentatively identified as di-*cis* isomers of lycopene, were formed after a 3 h heating at 50 °C, and the concentrations followed an increasing trend afterwards. No significant change of all-*trans*-lycopene was found within the first 12 h; however, the content began to decline thereafter. Interestingly, the levels of all the mono-*cis* forms of lycopene were found to decrease with increasing heating time. This result indicated that the degradation rates of 5-*cis*-, 9-*cis*-, 13-*cis*- or 15-*cis*-lycopene might be greater than the formation rate. Similar to β-carotene, it is also possible that the mono-*cis* forms of lycopene could be converted to di-*cis* forms of lycopene (Chen et al., 1994). The total amount of lycopene was found to contain 93.1% all-*trans*-lycopene, 2.50% 5-*cis*-lycopene, 1.20% 9-*cis*-lycopene, 1.24% 13-*cis*-lycopene and 0.45% 15-*cis*-lycopene. Only a slight variation was found for the percentage change of all-*trans*-lycopene. The degradation of all-*trans*-lycopene was not pronounced, probably because of mild heating condition. Nevertheless, a decreasing trend occurred for all the mono-*cis* forms of lycopene. This phenomenon was the same as the concentration change and might be explained by a further conversion to di-*cis*-lycopene from mono-*cis*-lycopene, or a fast degradation of mono-*cis*-lycopene. Unlike all the mono-*cis* forms of lycopene, the percentage change of two di-*cis* isomers showed increasing trends, which were probably due to conversion of mono-*cis*-lycopene. Fig. 3 shows the first-order plot for the degradation of total amount of lycopene during heating. The concentration change in the first 9 h was not taken into account because no significant change occurred. After 9 h of heating, a linear correlation ($r^2 = 0.98$) was found for the plot of the logarithm of the total concentration of lycopene versus time and the degradation rate constant was found to be 0.0075 (min^{-1}). This result revealed that the isomerization

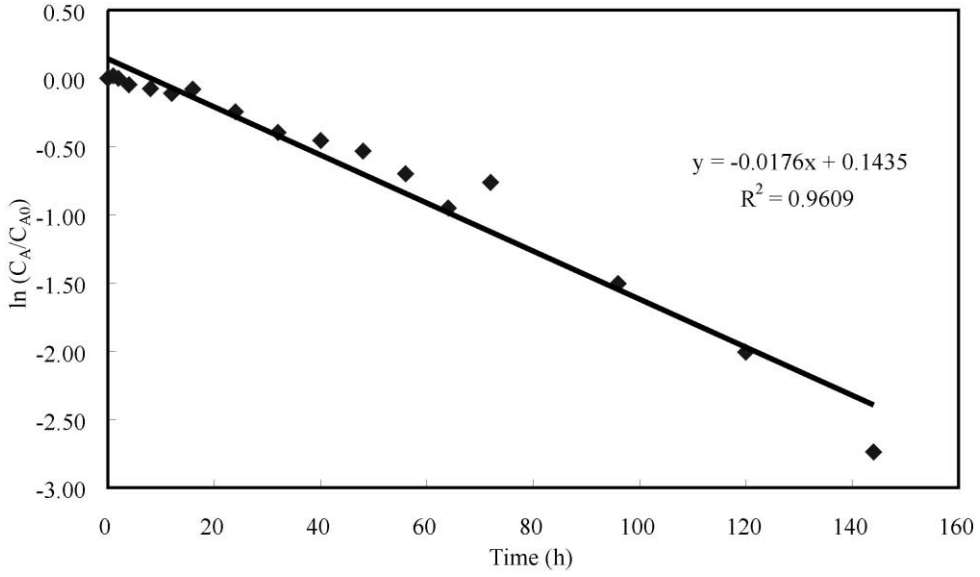

Fig. 2. First-order plot for the degradation of total amount of lycopene during illumination at 25 °C for 144 h.

Table 2
Concentration (μg/g) and percentage (%) changes of lycopene and its *cis* isomers during heating at 50 °C

Heating time (h)	Lycopene													
	P0–1 (di-*cis*)		P0–2 (di-*cis*)		15-*cis*		13-*cis*		9-*cis*		5-*cis*		All-*trans*	
	Conc.	%	Conc.	%	Conc.	%	Conc.	%	Conc.	%	Conc.	%	Conc.	%
0	nd	–	nd	–	0.83a	0.45ab	2.27a	1.24a	2.21b	1.20b	4.59a	2.50a	171a	93.1d
3	0.13c	0.08d	0.54b	0.33b	0.80ab	0.48a	2.08a	1.25a	2.89a	1.74a	2.74cd	1.65cd	155b	93.0d
6	0.16bc	0.09cd	0.48b	0.29b	0.68c	0.41bc	1.52b	0.91b	2.61a	1.57a	3.00bc	1.80bc	156ab	93.7c
9	0.20bc	0.11cd	0.63ab	0.35b	0.70bc	0.39c	1.54b	0.86b	2.04b	1.14b	3.42b	1.91b	169ab	94.1c
12	0.28ab	0.18bc	0.67ab	0.42b	0.36d	0.23d	0.88c	0.55c	0.49c	0.30c	2.38de	1.48de	155ab	96.4ab
15	0.27ab	0.19b	0.67ab	0.47b	0.31d	0.22d	0.67c	0.47c	0.20c	0.14c	2.01ef	1.41e	137bc	96.6a
18	0.38a	0.32a	0.93a	0.78a	0.28d	0.24d	0.63c	0.53c	0.20c	0.17c	1.76f	1.48de	114c	95.8b

Values of means bearing different letters in the same column are significantly different ($P<0.05$). nd, not detected.

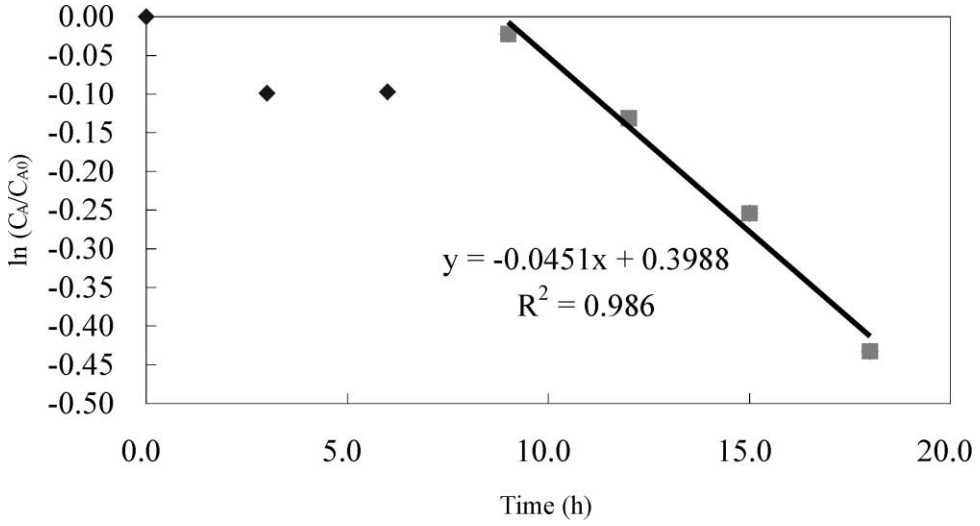

Fig. 3. First-order plot for the degradation of total amount of lycopene during heating at 50 °C.

was the main reaction to proceed during heating in the first 9 h, after which the degradation reaction dominated. A similar result was observed for the concentration change of all-*trans*-lycopene and its *cis* isomers during heating at 100 °C (Table 3). The level of all-*trans*-lycopene decreased by 134 μg/g after 120 min heating, which amounted to a 78% loss. All the mono-*cis* forms of lycopene showed a decreasing trend, probably because of conversion to di-*cis* or all-*trans* forms of lycopene. The levels of two di-*cis* isomers were found to rise in the first 60 min and then decreased, implying that di-*cis*-lycopene might be converted to mono-*cis*-lycopene or undergo degradation after prolonged heating. The total amount of lycopene was found to contain 93.1% all-*trans*-lycopene, 2.5% 5-*cis*-lycopene, 1.2% 9-*cis*-lycopene, 1.24% 13-*cis*-lycopene and 0.45% 15-*cis*-lycopene. Only a slight difference was found for the percentage changes of all the mono-*cis* forms of lycopene. On the other hand, a pronounced increase occurred for the two di-*cis* isomers, while a minor decrease was observed for all-*trans*-lycopene. As explained previously, the formation of di-*cis* isomers was probably due to conversion of mono-*cis* isomers. Fig. 4 shows the plot of logarithm of total amount of lycopene versus time during heating at 100 °C. The degradation of all-*trans* plus *cis* forms of lycopene was found to fit a first-order model because a linear correlation ($r^2 = 0.9847$) was observed, and the rate constant was calculated to be 0.0124 (min^{-1}).

The concentration change of lycopene and its *cis* isomers during heating at 150 °C is shown in Table 4. A large decrease was shown for the concentration of all-*trans*- lycopene during heating, and no lycopene was detected after 10 min. The levels of all the mono-*cis* forms of lycopene showed the same trend, implying that degradation was the main reaction to proceed at 150 °C. In the first 4 min, the levels of both di-*cis* isomers rose and then decreased afterwards. This result indicated that the isomerization reaction was favoured at the beginning, and then the degradation dominated after prolonged heating at high temperature. For the total amount of lycopene, only a slight variation was found

Table 3
Concentration (μg/g) and percentage (%) changes of lycopene and its *cis* isomers during heating at 100 °C

Heatin time (min)	Lycopene													
	P0–1 (di-*cis*)		P0–2 (di-*cis*)		15-*cis*		13-*cis*		9-*cis*		5-*cis*		All-*trans*	
	Conc.	%	Conc.	%	Conc.	%	Conc.	%	Conc.	%	Conc.	%	Conc.	%
0	nd	–	nd	–	0.83a	0.45a	2.27a	1.24ab	2.21a	1.20a	4.59a	2.50a	171a	93.1ab
20	0.19b	0.11b	0.60bc	0.36b	0.70a	0.42a	1.58b	0.96b	1.77ab	1.07a	2.97b	1.80a	155a	93.7a
40	0.28ab	0.23b	0.86abc	0.72b	0.66ab	0.55a	1.39bc	1.16ab	1.60abc	1.34a	2.32bc	1.94a	110b	91.8abc
60	0.45a	0.52a	1.18a	1.36a	0.39c	0.45a	1.03cd	1.19ab	1.42abc	1.64a	1.82cd	2.11a	78.3c	90.5abc
80	0.43a	0.55a	1.04ab	1.33a	0.44bc	0.56a	0.96d	1.23ab	1.23bc	1.58a	1.96cd	2.51a	70.2c	89.9abc
100	0.37ab	0.62a	0.86abc	1.46a	0.30c	0.50a	0.74d	1.25ab	1.03bc	1.75a	1.40de	2.37a	52.8cd	89.2bc
120	0.25ab	0.61a	0.61c	1.47a	0.25c	0.61a	0.63d	1.52a	0.76c	1.83a	0.96e	2.30a	36.9d	88.8c

Values of means bearing different letters in the same column are significantly different ($P < 0.05$). nd, not detected.

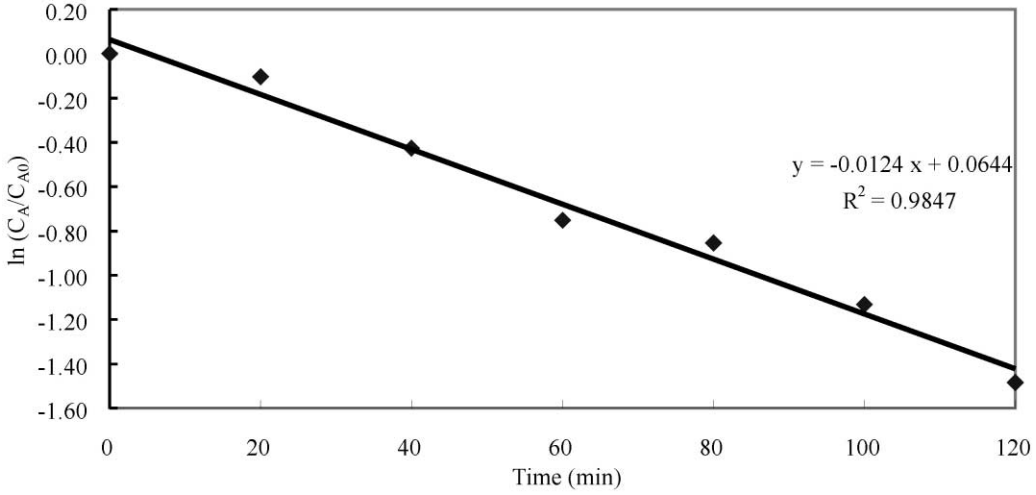

Fig. 4. First-order plot for the degradation of total amount of lycopene during heating at 100 °C.

Table 4
Concentration (μg/g) and percentage (%) changes of lycopene and its *cis* isomers during heating at 150 °C

Heating time (min)	Lycopene													
	P0–1 (di-*cis*)		P0–2 (di-*cis*)		15-*cis*		13-*cis*		9-*cis*		5-*cis*		All-*trans*	
	Conc.	%	Conc.	%	Conc.	%	Conc.	%	Conc.	%	Conc.	%	Conc.	%
0	nd[1]	–	nd	–	0.83a	0.45a	2.27a	1.24a	2.21a	1.20a	4.59a	2.50a	171a	93.1a
2	nd	–	0.72ab	0.51c	0.93a	0.66a	1.86a	1.31a	2.39a	1.69a	2.74b	1.94a	130ab	92.0a
4	0.27a	0.26a	0.83a	0.80c	0.69ab	0.67a	1.79ab	1.73a	2.03ab	1.97a	2.21bc	2.14a	93.3bc	90.5a
6	nd	–	0.81a	1.29b	0.44bc	0.70a	1.06bc	1.70a	1.43bc	2.28a	1.23c	1.98a	55.9c	89.5a
8	0.18a	0.33a	0.64ab	1.21b	0.26c	0.49a	0.95c	1.80a	0.83c	1.57a	0.98c	1.85a	48.1c	91.0a
10	nd	–	0.30b	1.98a	<QL[2]	–	<QL	–	0.53c	3.52a	<QL	–	<QL	–

Values of means bearing different letters in the same column are significantly different ($P<0.05$). nd, not detected; QL, quantitation limit.

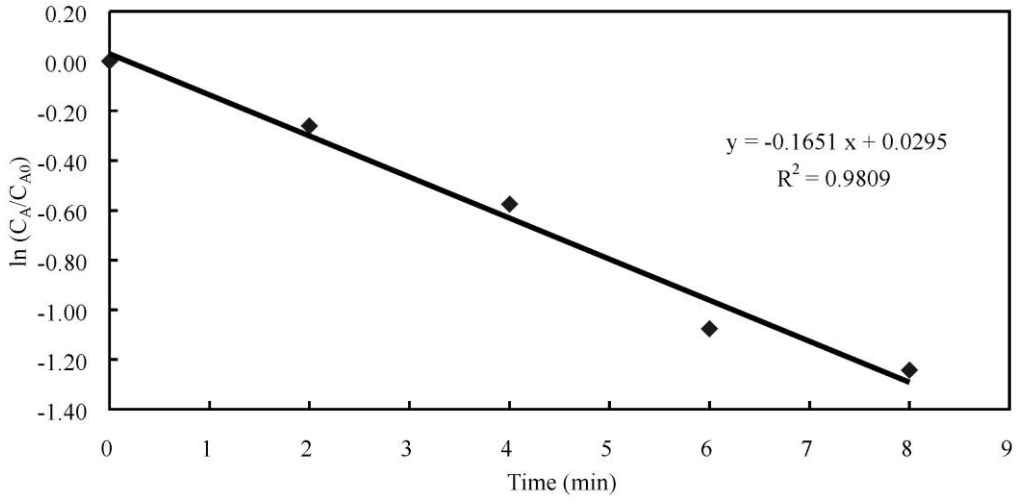

Fig. 5. First-order plot for the degradation of total amount of lycopene during heating at 150 °C.

for the percentage changes of all-*trans* and all the *cis* forms of lycopene. This result revealed that both isomerization and degradation may proceed simultaneously and a final equilibrium state may be reached during heating at high temperature. Fig. 5 shows the plot of logarithm of total amount of lycopene versus time during heating at 150 °C. A high linear correlation ($r^2=0.9809$) was observed and the degradation of lycopene was found to fit a first-order model with a rate constant of 0.1651 (min^{-1}).

By comparison of the results shown earlier, the largest degradation rate constant was found at 150 °C, followed by at 100 °C and 50 °C. Apparently the higher the temperature, the faster the degradation. Sharma and Maguer (1996) reported that the degradation rate constant of lycopene was 0.0023 (min^{-1}) during heating of tomato pulp at 100 °C, which was much smaller than the result (0.0124 min^{-1}) shown in this study. Obviously the presence of some macromolecules in tomato pulp (such as pectin) may offer protection for lycopene. Fig. 6 shows the plot of $\ln(k)$ versus $(1/T)$ for degradation of total amount of lycopene during heating. A high correlation coefficient ($r^2=0.9809$) with a slope -7.3×10^{-3} was obtained. According to the Arrhenius equation:

$$\ln(k) = -\frac{Ea}{R}\left(\frac{1}{T}\right) + \ln(A)$$

where Ea is activation energy (J/mol) and R is the ideal gas constant (8.3148 J/k mol). The activation energy was calculated to be 61.0 kJ/mol. This result seemed to be different from a report by Sharma and Maguer (1996), who found that the activation energy for lycopene degradation in tomato pulp ranged from 19.9 ± 6.38 to 27.7 ± 2.76 kJ/mol at −20.5 and 25 °C, respectively. The lower activation energy was probably because oven-heating was used for extraction of lycopene and a decreased stability might occur. In a later study, Henry et al. (1998) studied the lycopene degradation at 75, 85 and 95 °C, and the activation energy was calculated to be 104 ± 20.482 kJ/mol, which was larger than the result in this study and could be due to the different heating temperature used. In addition, the authors (Henry et al., 1998) immersed lycopene in sunflower oil prior to heating, which might enhance the

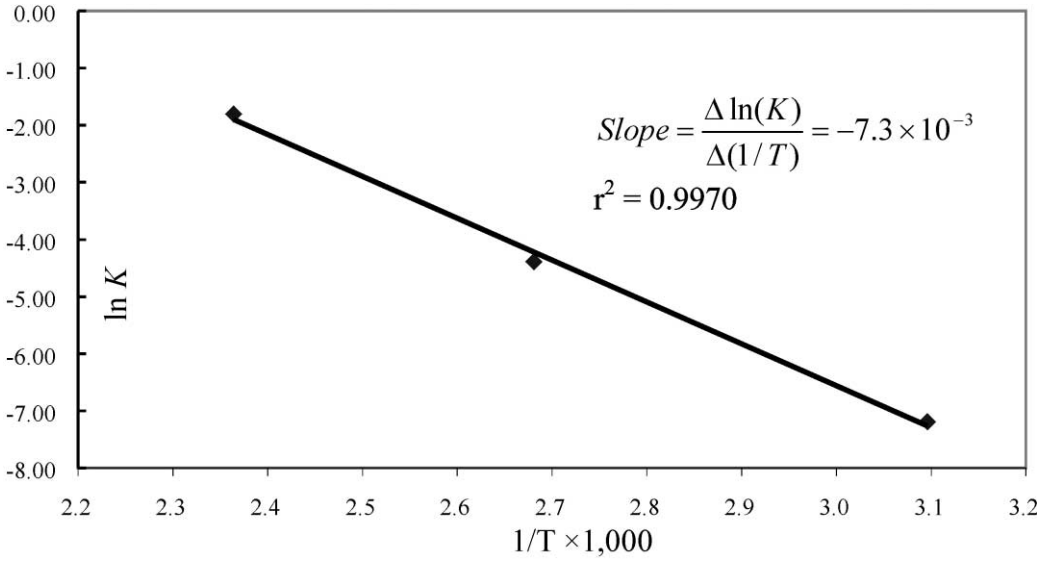

Fig. 6. Plot of ln (k) versus ($1/T$) for lycopene degradation during heating.

stability of lycopene because of the presence of antioxidants in the oil. Just like β-carotene, it has been well established that both the isomerzation and degradation of lycopene may proceed simultaneously, and which reaction dominates should depend on heating temperature, illumination intensity and presence of catalyst (Chen et al., 1994; Pesek & Warthesen, 1990). Finally, it is noteworthy that the results shown in this study may not be identical to that in a real food system because of the presence of complex components of the latter. In conclusion, with increasing temperature and heating time, the degradation was dominated over isomerization. During illumination or heating, the degradation of total amount of lycopene fits a first-order model. Further research is necessary to study the conversion mechanism between all-*trans*-lycopene and its *cis* isomers in real food systems.

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