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Oxidation and Isomerization of Lycopene under Thermal Treatment and Light Irradiation in Food Processing

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Abstract

Lycopene as a natural antioxidant may provide protection against a broad range of epithelial cancers and chronic diseases. Lycopene concentrate extracted from tomatoes can be used as functional food. Lycopene would undergo degradation via isomerization and oxidation under different processing conditions, which impact its bioactivity and reduce the functionality for health benefits. Heat and light induce lycopene oxidation and isomerization of all-*trans* form to *cis* form. The effects of thermal treatment and light irradiation on the stability of lycopene were determined. Results have shown that lycopene stability depends on the extent of oxidation and isomerization. *Cis*-isomers are less stable than *trans*-isomers. The level of *cis*-isomers increased as treatment time increased but only for a short period during the beginning of the treatment. The major effect of thermal treatment and light irradiation was a significant decrease in the total lycopene content. A true assessment of health benefits of lycopene concentrate depends on the lycopene content and the composition of all *trans*-isomers and *cis*-isomers.

Key words: degradation, heat, isomerization, light, lycopene, oxidation, tomato

INTRODUCTION

Recently there has been growing interest in the ability of lycopene to act as a cancer-preventative agent. Lycopene appears to provide protection against a broad range of epithelial cancers at sites such as the digestive tract, pancreas and bladder (1-3). The number of servings of lycopene-rich food, such as tomatoes, tomato sauce, and pizza, significantly correlated with a low risk for prostate cancer (4). Lycopene is able to function as an antioxidant and to quench singlet oxygen *in vitro*. The quenching constant of lycopene was found to be more than double that of β-carotene and 10 times more than that of α-tocopherol, which makes its presence in the diet of considerable interest (5,6). Levy et al. (2) studied the inhibitory effect of lycopene, comparing it with that of α-and β-carotene on the growth of several human cancer cells, and found lycopene to be the most potent inhibitor.

Lycopene is known to exist in a variety of isomeric forms, including the all-*trans*, mono-*cis*, and poly-*cis* forms. The all-*trans* isomer of lycopene is the predominant geometrical isomer in fresh tomatoes. All-*trans*- isomer lycopene ($C_{40}H_{56}$) is an acyclic, open chain polyene hydrocarbon with 13 double bonds, of which 11 are conjugated in a linear array (Fig. 1). But 7 bonds can isomerize from the *trans*-form to the mono or poly-*cis* (Fig. 2) form under the influence of heat, light, and certain chemical reactions. Lycopene undergoes degradation via isomerization and oxidation.

It is generally accepted that the all-*trans*- isomers have the highest bioactivity stability and the *cis*-isomers have the lowest bioactivity stability. Bioactivity potency is dependent on the extent of isomerization and oxidation. A true assessment of the nutritional quality of tomato products depends not only on the total lycopene content but on the distribution of lycopene isomerization. The characterization and quantification of isomers would be desirable to more accurately assess the bioactivity than relying on only the total lycopene content with no knowledge of its isomeric composition. The objective of this study was to investigate the oxidation and isomerization of lycopene under different intensities of thermal treatment and light irradiation.

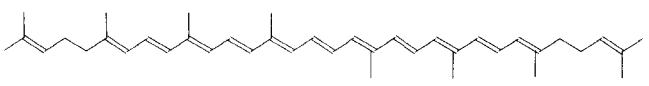

Fig. 1. Structure of lycopene.

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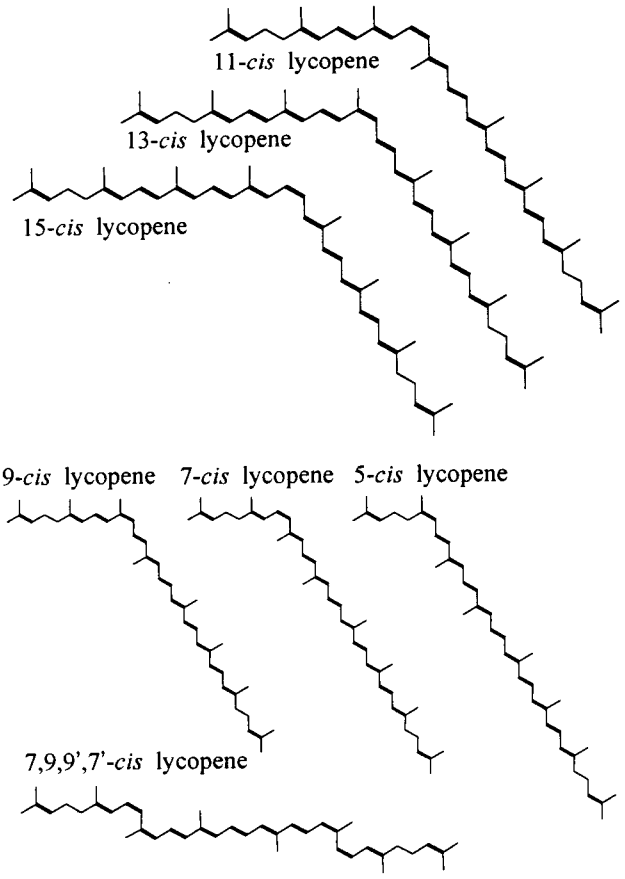


Fig. 2. Molecular structures of some *cis*-isomers.

MATERIAL AND METHODS

Material

Lycopene concentrate was separated from tomatoes by a supercritical CO_2 fluid extraction process. All-*trans*-lycopene standard was purchased from Sigma Chemical Co. (St. Louis, MO). Canola oil was purchased from a local supermarket. All chemical solvents and reagents were of HPLC grade from Fisher Chemicals Co. (Nepean, Ontario, Canada).

One milligram of all-*trans*-lycopene standard was dissolved in 50 mL hexane-isooctane solution (1:1). The lycopene concentrate was dissolved in canola oil at the ratio of 1:11. The lycopene-oil mixture (4 mL) was transferred to a vial and was flushed with N_2, and capped. Isooctane was the control solvent to compare the results with the oil. Triplicate samples of each treatment were taken at each time point for HPLC analysis.

Thermal treatment

Thermal treatment of lycopene extract was carried out in an oven (Isotemp, Model 285A, Fisher Scientific, USA) at atmospheric pressure. 10 mL of sample were placed in a test tube. The tube was wrapped with aluminum foil to protect the sample from light. In order to exclude oxygen in the headspace, as much air as possible was excluded from the tubes by leaving minimum headspace and purging with N_2. The samples were heated at 25, 100 and 180°C for 30, 60 and 90 min, respectively, to promote isomerization and oxidation of lycopene. The treatment at 25°C was a control. Samples were rapidly cooled under dim light, transferred into vials and stored at -30°C until analysed within 7 days. To limit photo-oxidative degradation of the samples during storage, the vials were wrapped in aluminum foil.

Light irradiation treatment

Samples were exposed to visible light of different intensities in a controlled environmental chamber at 25± 1°C. The lycopene concentrates (10 mL) were subjected to irradiation of 2010 (outdoor), 900, 650 and 140 (indoor) μmol m^{-2} s^{-1} for 1 to 6 days. For the light treatment, sample preparation procedures were the same as for thermal treatment, except that no aluminum foil was wrapped around the vials. Samples were taken daily and stored at -30°C prior to HPLC analysis. Measurements of light intensity were taken with a LI-COR Photometer, model LI-210SA, equipped with a LI-190SA Quantum Sensor (LI-COR, Lincoln, NE). Quantum sensors measured photosynthetically active radiation (PAR) in units of μmol m^{-2} s^{-1}.

HPLC analysis

The analysis of lycopene was performed with Agilent 1100 HPLC (Agilent Technologies, Waldbronn, Germany), with a reversed phase analytical 3-μm particle diameter, polymeric C_{30} column (4.6 mm i. d. × 250 mm, S-5) (YMC, Inc., Wilmington, NC, USA), with a UV diode array detector (model G1315B, Agilent, Waldbronn, Germany) for spectrometric peak identification at 472 nm. The mobile phase of methyl t-butyl ether / methanol / ethyl acetate (40:50:10, v/v) was used at a flow of 2 mL/min. Prior to HPLC analysis, the mobile phase was degassed by a supersonic bath and filtered through a 0.22 μ pore size filter paper. A sample volume of 20 μL was injected into the column. The column temperature and mobile phase were maintained at 25°C. Analyses were performed under dim light to prevent sample degradation by photo-oxidation. The identification of *trans*-and *cis*-isomers peaks in chromatogram is according to the method by Nguyen and Schwartz (7) and van Breemen et al. (8).

Data analysis

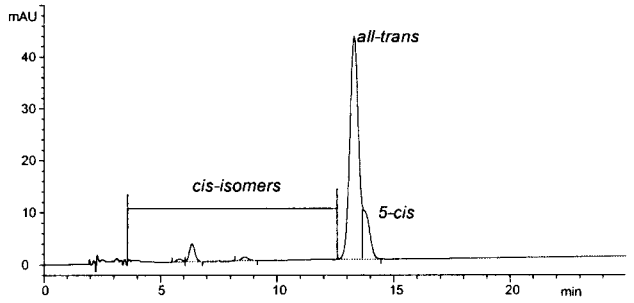
Randomized Complete Block Design was applied for this study. Different blocks were included in the experiments, each representing one kind of oil. In each block, two factors are included: temperature and light intensity. Data was processed and analyzed by the statistical meth-

ods according to the experimental design. The experiments were three times per sample for chromatographic analysis. The data were analyzed statistically using a General Linear Model and Duncan's means tests (9).

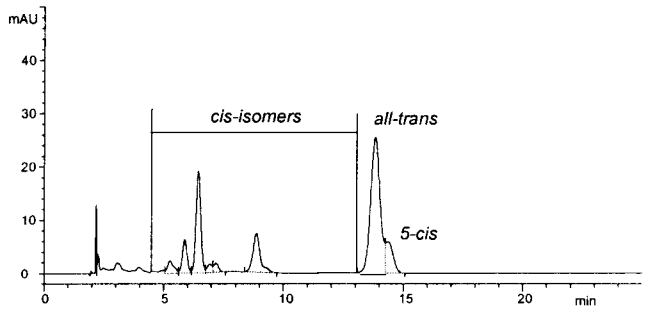
RESULTS AND DISCUSSION

Effect of thermal treatment on lycopene degradation

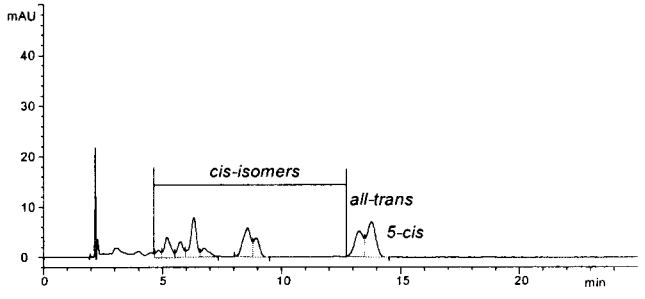
The changes in total lycopene and *cis*-isomer content in experimental samples of lycopene concentrate in oil solution during thermal treatment are shown in Fig. 3 (a, b,c). Increasing the temperature from 100 to 180°C or thermal treatment time increased the degradation of *trans*-isomer and *cis*-isomer of lycopene. It was observed that the *cis*-isomers increased with thermal treatment at 100°C, but dropped significantly with treatment at 180°C.



(a) HPLC chromatogram of lycopene in oil solution after being treated at 25°C for 90 min.



(b) HPLC chromatogram of lycopene in oil solution after being treated at 100°C for 90 min.



(c) HPLC chromatogram of lycopene in oil solution after being treated at 180°C for 90 min.

Fig. 3. Lycopene oxidation and isomerization during thermal treatment.

An increase in temperature from 100°C to 180°C caused a 76% decrease in total lycopene content (Fig. 4). The 90 min treatment at 180°C resulted in lycopene degradation and the greater concentration of total lycopene loss, compared to *cis*-isomer formation. The results suggest that degradation of lycopene, e.g. oxidation and isomerization of *trans*-and *cis*-isomers, was the main mechanism of lycopene loss when heated above 100°C. Comparing to treatment at 25°C, thermal treatment at 100°C resulted in an increase of *cis*-isomer content. *Cis*-isomer accumulation was greater than oxidation of *cis*-isomer. But the total lycopene content was reduced, comparing to the initial lycopene content. The changes in lycopene content and the formation of *cis*-isomers may result in a reduction in bioactivity potency (10-13).

The main cause of lycopene degradation is isomerization and oxidation. It is widely presumed that lycopene in general undergoes isomerization with thermal processing. This isomerization resulted in conversion of the all-*trans* isomers to the *cis*-isomers. The *cis*-isomers were formed in samples and increased with temperature and time during thermal treatment. A large loss of lycopene during processing would indicate a longer and more drastic thermal procedure.

Effect of light-irradiation on lycopene degradation

The effects of light irradiation on the content of total lycopene, *trans*-isomers and *cis*-isomers in lycopene samples under different light irradiation intensities of 2010 (outdoor), 900, 650 and 140 (indoor) μmol m^{-2} s^{-1} for 24 hrs are shown in Fig. 5 (a~d). The loss in total lycopene, *trans*-isomers and *cis*-isomers increased significantly as the intensity of the light irradiation increased. The small amount of *cis*-isomers formation during light irradiation indicate either less *cis*-isomers were formed, or that the oxidation reactions were predominate. It is possible that any *cis*-isomer formed was quickly degraded into oxidative by-

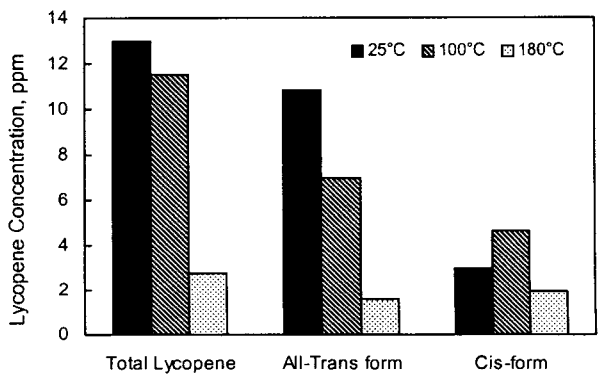
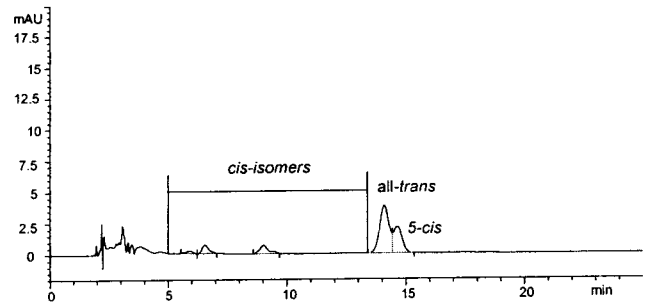
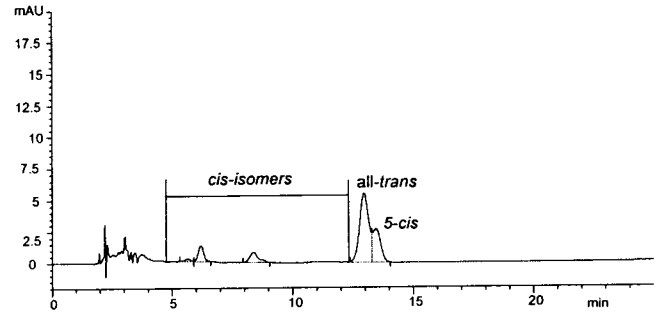


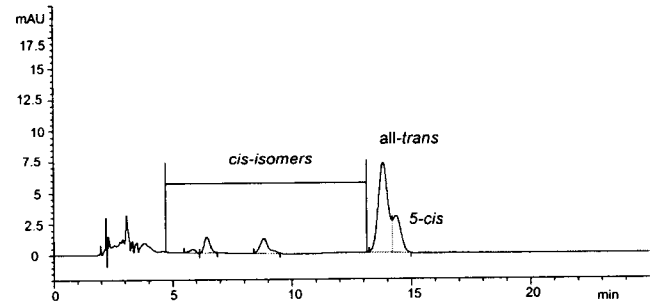
Fig. 4. Lycopene oxidation and isomerization after being heated for 90 min.



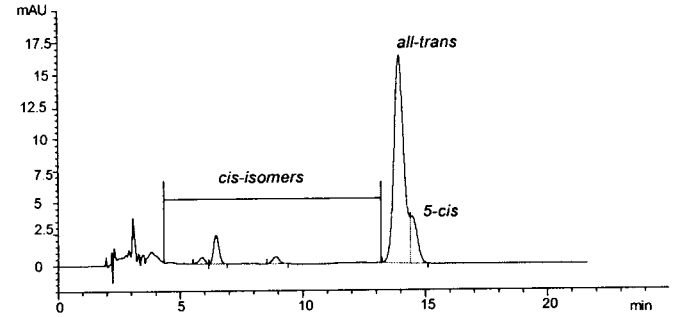
(a) HPLC chromatogram of lycopene in oil solution after irradiation by light at 2010 μmol m^{-2} s^{-1} intensity (outdoor) for 24 hrs.



(b) HPLC chromatogram of lycopene in oil solution after irradiation by light at 900 μmol m^{-2} s^{-1} intensity for 24 hrs.



(c) HPLC chromatogram of lycopene in oil solution after irradiation by light at 650 μmol m^{-2} s^{-1} intensity for 24 hrs.



(d) HPLC chromatogram of lycopene in oil solution after irradiation by 140 μmol m^{-2} s^{-1} (indoor light) for 24 hrs.

Fig. 5. Lycopene oxidation and isomerization during sun-light irradiation.

products, which indicate that the rate of *cis*-isomer oxidation during light irradiation was much greater than formation of *cis*-isomers. Comparing to treatments at 2010 μmol m^{-2} s^{-1} (outdoor) and at 140 μmol m^{-2} s^{-1} (indoor) for 24 hr, results showed 89% of total lycopene was lost. The content of total lycopene, *trans*-isomers and *cis*-isomers in lycopene concentrate decreased under all light irradiation cases, which indicate light irradiation induces lycopene oxidation.

CONCLUSION

The changes in lycopene content and the distribution of *trans-cis* isomerization will result in a reduction in biological potency, when tomato-based products and lycopene concentrate are subjected to processing (10-13). Lycopene would undergo degradation via isomerization and oxidation under different processing conditions, which impact its bioactivity and reduce the functionality for health benefits. It is the key process how to maintain high bioactive property during food processing and storage. The isomerization and oxidation of lycopene greatly depends on the treatments used since each treatment produces a different form of energy (such as heat and light, respectively). In this experiment, it was found that the light irradiation caused more losses in total lycopene than the heating treatment. In all treatments, the rate of *trans*-isomer loss was greater than the *cis*-isomer formation, which suggests that degradation through oxidation of lycopene was the predominant mechanism, as compared to isomerization of *trans*-isomer to *cis*-isomer. However, it is possible that this loss could be coupled by the conversion of *trans*- to *cis*-isomers, and followed by further direct degradation to smaller molecules of oxidized by-products which were not isomers of lycopene (14). *Cis*-isomers are unstable, while *trans*-isomers are in a stable ground state. Because lycopene is a highly unsaturated molecule, comprising many conjugated double bonds, it is very susceptible to oxidation.

Bioactivity potency depends on the content of total lycopene and the extent of isomerization (10-12,15). Thus isomerization would lead to change the bioactivity of lycopene. Characterization and quantification of lycopene isomers would provide a better understanding of the potential bioactive properties and health benefits of the lycopene-based products. Controlling isomerization and oxidation of lycopene during tomato processing and lycopene-based food preparation can be of benefit in improving product quality.

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REFERENCES

1. Micozzi MS, Beecher GR, Taylor PR, Khachik F. 1990. Carotenoid analyses of selected raw and cooked foods associated with a lower risk for cancer. *J Natl Cancer Inst* 82: 282-288.
2. Levy J, Bosin E, Feldman B, Giat Y, Minster A, Danilenko M, Sharoni Y. 1995. Lycopene is a more potent inhibitor of human cancer cell proliferation than either α-carotene or β-carotene. *Nutr Cancer* 24: 257-266.
3. Gerster H. 1997. The potential role of lycopene for human health. *J Am Coll Nutr* 16: 109-126.
4. Giovannucci E, Ascherio A, Rimm EB, Stampfer MJ, Colditz GA, Willett WC. 1995. Intake of carotenoids and retinol in relation to risk of prostate cancer. *J Natl Cancer Inst* 87: 1767-1776.
5. Di Mascio P, Murphy ME, Sies H. 1991. Antioxidant defense systems, the role of caritenoid, tocopherol and thiols. *Am J Clin Nutr Suppl* 53: 194-200.
6. Ribaya-Mercado JD, Garmyn M, Gilchrest BA, Russell RM. 1995. Skin lycopene is destroyed preferentially over β-carotene during ultraviolet irradiation in humans. *J Nutr* 125: 1854-1859.
7. Nguyen M, Schwartz S. 1999. Lycopene: chemical and biological properties. *Food Technol* 53(2): 38-45.
8. van Breemen RB, Xu X, Viana MA, Chen L, Stacewicz-Sapuntzakis M, Duncan C, Bowen P, Sgarifi R. 2002. Liquid chromatography-mass spectrometry of *cis*- and all-*trans*-lycopene in human serum and prostate tissue after dietary supplementation with tomato sauce. *J Agr Food Chem* 46-52.
9. SAS Institute Inc. 1991. SAS Users' Guide: Basics Statistical Analysis. SAS Institute, Cary, NC, USA.
10. Khachik F, Beecher GR, Goli MB, Luby WR, Smith JC. 1992. Separation and identification of carotenoids and their oxidation products in the extracts of human plasma. *Anal Chem* 64: 2111-2122.
11. Emenhiser C, Sander LC, Schwartz SJ. 1995. Capability of a polymeric C_{30} stationary phase to resolve *cis-trans* carotenoids in reversed phase liquid chromatography. *J Chromatogr A* 707: 205-216.
12. Wilberg VC, Rodriguez-Amaya BD. 1995. HPLC quantitation of major carotenoids of fresh and processed guava, mango and papaya. *Lebensm-Wiss Technol* 28: 474-480.
13. Stahl W, Sies H. 1996. Perspectives in biochemistry and biophysics– lycopene: a biological important carotenoid for human. *Arch Biochem Biophy* 336: 1-9.
14. Boskovic MA. 1979. Fate of lycopene in dehydrated tomato products: carotenoid isomerization in food system. *J Food Sci* 44: 84-86.
15. Stahl W, Sies H. 1992. Uptake of lycopene and its geometrical isomers is greater from heat-processed than from unprocessed tomato juice in humans. *J Nutr* 122: 2161-2166.

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