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Spectral characterisation of *Z*-isomers of lycopene formed during heat treatment and solvent effects on the *E*/*Z* isomerisation process

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ABSTRACT

The geometric isomerisation of (all-*E*)-lycopene, purified from tomato paste, was investigated in various organic solvents. Isomerisation ratios to the *Z*-isomers of lycopene in CH_2Cl_2 and $CHCl_3$ over 24 h were calculated to be 19.7% and 11.4% at 4 °C and 77.8% and 48.4% at 50 °C, respectively. In CH_2Br_2, more than 60% was attained in the first several hours, independent of temperature. The predominant *Z*-isomers obtained thermally, (9*Z*)-lycopene and (13*Z*)-lycopene, were purified and their absorption maxima and molar extinction coefficients in hexane were determined for the first time. Absorption values at 460 nm were also measured for both *Z*-isomers along with (all-*E*)-lycopene to accurately evaluate their concentrations by HPLC analysis. This approach successfully revealed that (13*Z*)-lycopene formed predominantly in benzene or $CHCl_3$ at 50 °C; in contrast, the 5*Z*-isomer was preferentially obtained in CH_2Cl_2 or CH_2Br_2.

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1. Introduction

Lycopene is an acyclic carotenoid ($C_{40}H_{56}$) found in great abundance in vegetables and fruits with bright-red colouring, as exemplified by tomatoes. Lycopene has strong antioxidant properties and is known to be effective in the prevention of cancer and arteriosclerosis (Cantrell, McGarvey, Truscott, Rancan, & Böhm, 2003; Dahan, Fennal, & Kumar, 2008; Di Mascio, Kaiser, & Sies, 1989; Stahl & Sies, 2003). (All-*E*)-lycopene is the most predominant geometric isomer in raw tomatoes, with a concentration of around 94–96%. Reports have shown that the concentration of *Z*-isomers (Fig. 1) increases when (all-*E*)-lycopene is dissolved in oil, organic solvents, or supercritical CO_2 and is subsequently heated (Hackett, Lee, Francis, & Schwartz, 2004; Takehara et al., 2014; Wang & Chen, 2006). These *Z*-isomers are also quite common in thermally processed tomato products; for example, a spaghetti sauce sample was reported to contain 27% of (5*Z*)-lycopene, 14% of (9*Z*)-lycopene, and 25% of other *Z*-isomers (Schierle et al., 1997). In contrast, the *Z*-isomers of lycopene are mainly found within living animals, for instance, in sera and cellular tissues of humans over 50% of the total lycopene exists in the *Z*-form (Clinton et al., 1996; Stahl, Schwarz, Sundquist, & Sies, 1992). Because of their abundance in the human body, the *Z*-isomers of lycopene may have a greater potential for bioavailability than (all-*E*)-lycopene, and the intake of processed foods that are rich in the *Z*-isomers of lycopene may offer benefits to human health (Unlu et al., 2007). In fact, tests using cultured cells of the small intestine as well as with animal experimentation using ferrets have strongly supported this suggestion (Boileau, Merchen, Wasson, Atkinson, & Erdman, 1999; Failla, Chitchumroonchokchai, & Ishida, 2008). The *Z*-isomers of lycopene are also expected to show a higher antioxidant capacity than that of the (all-*E*)-lycopene (Böhm, Puspitasari-Nienaber, Ferruzzi, & Schwartz, 2002; Müller et al., 2011); therefore, it is important to gain a better understanding of the isomerisation of (all-*E*)-lycopene to the *Z*-isomers and to develop a facile method for this reaction.

The *E*/*Z* isomerisation of carotenoids upon heating has been demonstrated for some representative compounds, including β-carotene, lutein, and zeaxanthin (Aman, Schieber, & Carle, 2005; Knockaert et al., 2012; Subagio, Morita, & Sawada, 1998; Updike & Schwartz, 2003). It has also been reported that astaxanthin was isomerised by heating in organic solvents, and a higher rate of isomerisation was achieved in alkyl halides such as dichloromethane (CH_2Cl_2) and chloroform ($CHCl_3$) (Yuan & Chen, 1999, 2001). However, there are few reports discussing the effect of solvents on the *E*/*Z* isomerisation of lycopene; consequently, the present investigation was conducted to characterise the isomerisation of lycopene in various organic solvents. Based on the study

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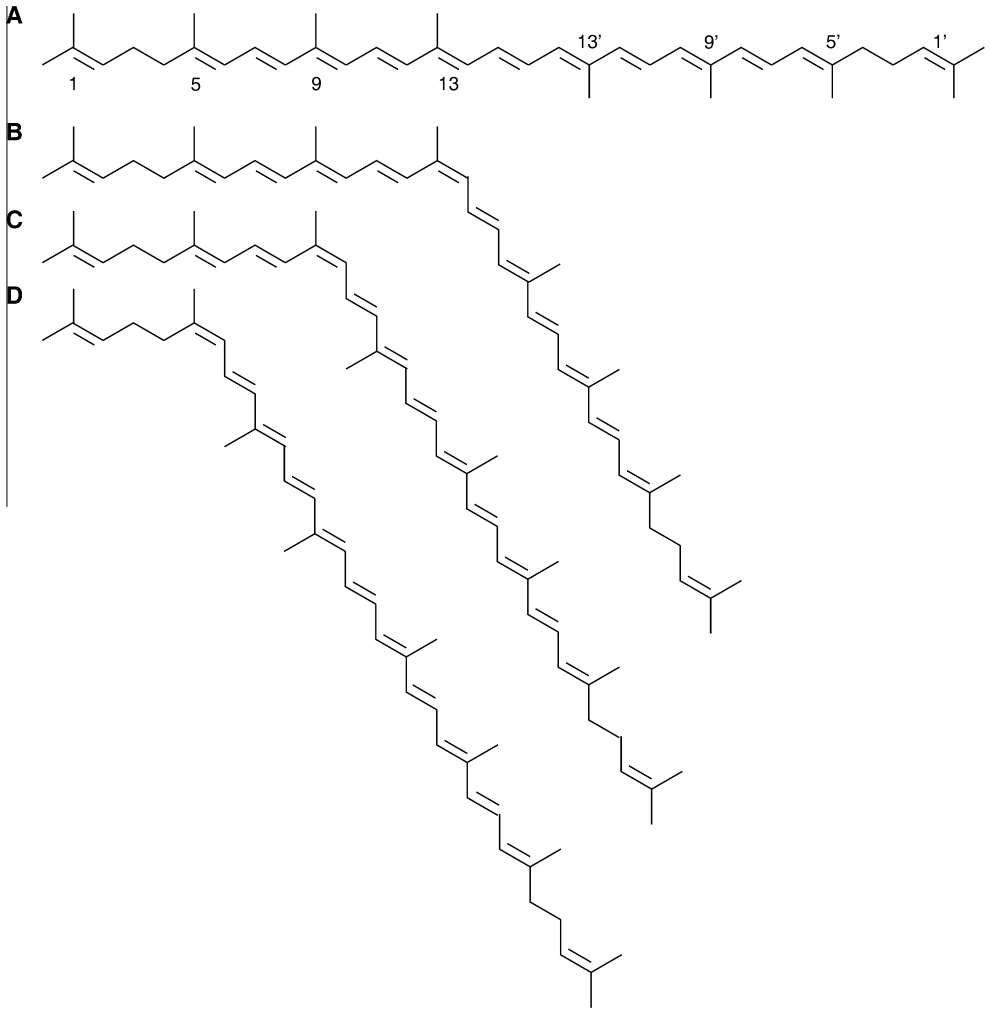

Fig. 1. Chemical structures of the predominant isomers of lycopene formed during heating: (A) (all-*E*)-lycopene; (B) (13*Z*)-lycopene; (C) (9*Z*)-lycopene; (D) (5*Z*)-lycopene.

of astaxanthin (Yuan & Chen, 1999), we focused on the solvent effects of alkyl halides including CH_2Cl_2, $CHCl_3$, carbon tetrachloride (CCl_4), and dibromomethane (CH_2Br_2), as well as acetone, hexane, and benzene, other commonly used solvents in the study of carotenoids. Furthermore, the influence of temperature on *Z*-isomerisation was investigated for each solvent.

Prior to the investigation of solvent effects on lycopene isomerisation, (9*Z*)- and (13*Z*)-lycopene, predominantly formed during the heating process, were exhaustively purified from heat-treated tomato paste and characterised by ultraviolet–visible (UV–vis) and nuclear magnetic resonance (NMR) spectroscopy, and their molar extinction coefficients were successfully determined for the first time. These fundamental spectroscopic data are essential for the investigation of the solvent effects on the *E*/*Z* isomerisation of lycopene, and will soon contribute to the characterisation of the other lycopene isomers, which are currently unidentified.

2. Materials and methods

2.1. Chemicals

High-performance liquid chromatography (HPLC)-grade acetone, hexane, benzene, CH_2Cl_2, $CHCl_3$, CCl_4, and CH_2Br_2 were obtained from Kanto Chemical Co., Inc. (Tokyo, Japan). *N*,*N*-diisopropylethylamine (DIPEA) was purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo). (All-*E*)-lycopene was obtained by a method described previously (Takehara et al., 2014) or was provided by Wako Pure Chemical Industries, Ltd. (Osaka, Japan).

2.2. Isomerisation of (all-E)-lycopene

(All-*E*)-lycopene was dissolved in the respective solvents at a concentration of 0.1 mg ml^{-1}, and the solutions were filtered through a 0.2 μm polytetrafluoroethylene (PTFE) membrane filter (Advantec Co., Ltd., Tokyo). A 5 ml sample was transferred from each of the solutions to a 10-ml screw-capped tube. The headspace was filled with nitrogen gas, and the tube was tightly capped to prevent oxygen entry through the closure. The isomerisation of (all-*E*)-lycopene was conducted at 4 °C and 50 °C in the dark. After the reaction, the solvent was removed from the reaction tube by a nitrogen gas stream, and the residue was re-dissolved in hexane. Normal-phase HPLC was used to analyse the lycopene isomers.

2.3. HPLC analysis

Normal-phase HPLC analysis was conducted according to the method described by Schierle et al. (1997) with some modifications. The sample was cooled to 5 °C using an autosampler with a cooler (L-2200, Hitachi Ltd., Tokyo) immediately before the analysis. The detection wavelength of the compound was set at 460 nm (L-2455, Hitachi Ltd.) where the differences in molar extinction coefficients among lycopene isomers are relatively

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