

# Photolysis of carotenoids in chloroform: enhanced yields of carotenoid radical cations in the presence of a tryptophan ester

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## Abstract

The presence of an acetyl tryptophan ester gives rise to enhanced yields of carotenoid radical cations in chloroform following 355 nm laser excitation of the carotenoid, even though the tryptophan does not absorb at this wavelength. The increase is attributed to positive charge transfer from semi-oxidized tryptophan itself generated by light absorbed by the carotenoid. The mechanism of these radical processes has been elucidated by pulse radiolysis studies.

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*Keywords:* Carotenoids; Tryptophan; Positive charge transfer; Radical cations

## 1. Introduction

There is considerable recent interest in the chemistry underpinning carotenoid/radical reactions. Several dietary carotenoids are believed to act as radical scavengers *in vivo* and hence possibly may be linked to disease prevention. Many epidemiological studies have suggested a link between carotenoid-rich diets and a lower incidence of several serious diseases including cancer, atherosclerosis, age-related blindness and even ageing itself (Blot *et al.*, 1993; Gaziano *et al.*, 1994; Mares-Perlman *et al.*, 1995). However, the situation has become somewhat confused by intervention trials which have shown no health benefits from dietary supplementation with  $\beta$ -carotene, and even a possible deleterious effect in some sub-populations, such as heavy smokers (Study Group, 1994; Omenn *et al.*, 1996). These sub-groups are often deficient in other anti-oxidants such as ascorbic

acid, and this has led to an interest in the interactions between carotenoids and such anti-oxidants. Indeed, we have shown synergistic protection of human lymphocytes from damage by the nitrogen dioxide radical and the peroxynitrite anion by combinations of carotenoids with such anti-oxidants (Böhm *et al.*, 1998). The interaction between  $\beta$ -carotene and the nitrogen dioxide radical has also been discussed by Khopde *et al.* (1998). The structures of the carotenoids and those of the amino acid derivatives studied in this work are given in Fig. 1.

Pulsed laser irradiation (355 nm) of carotenoids in chloroform generates the radical cation of the carotenoids and another species, whose structure is not fully established, but which decays to generate additional radical cation (Mortensen and Skibsted, 1997). An increase in the yield of carotenoid radicals is obtained following light irradiation of mixtures of carotenoid and *N*-acetyl tryptophan ester (TrpHE) even when the irradiation is at wavelengths not absorbed by the amino acid. Pulse radiolysis was used to elucidate the radical mechanisms associated with these observations. A

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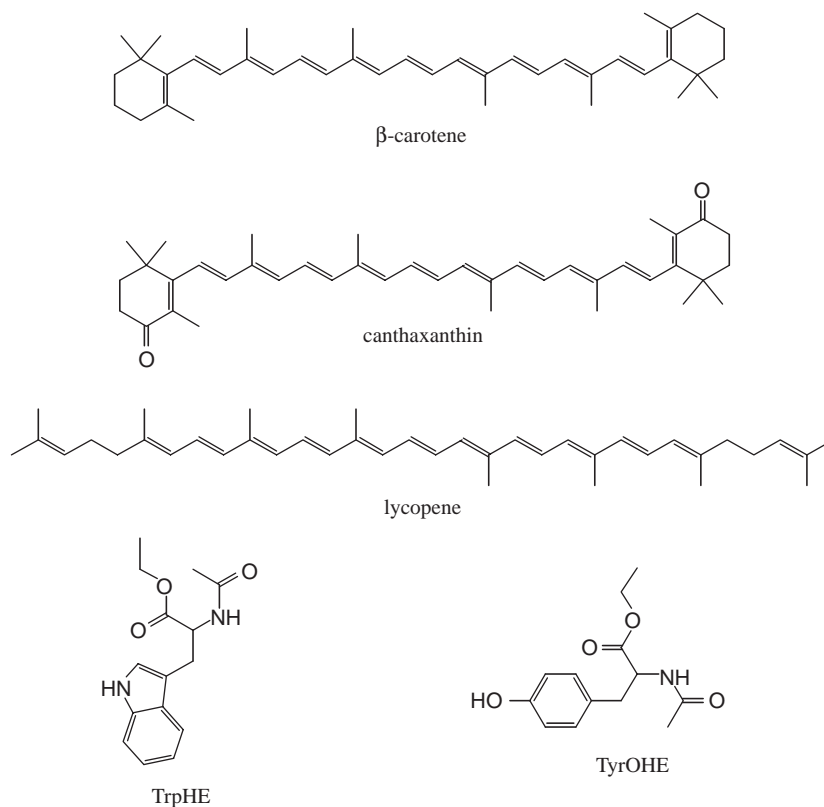


Fig. 1. Structures of the carotenoids and amino acid derivatives used in this study.

previous pulse radiolysis study of positive charge transfer between carotenoids and tryptophan radical cations in aqueous micellar environments led to estimates being gained of the one-electron reduction potentials of the radical cations of five dietary carotenoids in the range 980–1060 mV (Burke et al., 2001).

## 2. Experimental

All carotenoids were supplied by Hoffmann-la Roche (Basle) and used as supplied. TrpHE and *N*-acetyl tyrosine ethyl ester (TyrOHE) were obtained from Sigma and both were recrystallised from ethanol before use. A long wavelength ‘tail’ in the absorption spectrum of TrpHE showed evidence of slight impurities that were removed by recrystallisation. Chloroform was HPLC grade from Rathburn (pulse radiolysis) or BDH (laser flash photolysis).

Laser flash photolysis studies were undertaken using a system similar to that described previously (Tinkler et al., 1996), using 355 nm radiation where direct excitation of the carotenoid in chloroform has been shown by Mortensen and Skibsted (1997) to generate carotenoid radical cations. Pulse radiolysis measure-

ments were made using a 9–12 MeV Vickers linear accelerator as described previously (Keene, 1964; Butler et al., 1989) with pulses of 10–100 ns duration and doses between 1 and 10 Gy. Quartz flow-through cells were used with a monitoring optical path length of 2.5 cm. Absorption spectra were recorded using a Perkin-Elmer Lambda-2 UV/Vis spectrophotometer. All solutions were air-saturated unless otherwise stated.

## 3. Results and discussion

Laser excitation (355 nm) of canthaxanthin, β-carotene and lycopene (all 200 μM) in air-saturated chloroform leads to the previously reported transient infrared absorptions assigned to the carotenoid radical cation and a less well-defined precursor a peroxy radical-carotenoid adduct/ion pair with an absorption maximum at somewhat shorter wavelengths than the corresponding carotenoid radical cation (Hill et al., 1995; Mortensen and Skibsted, 1997; Edge et al., 1998). In the presence of TrpHE (up to 10 mM) we observe a marked increase in the yield of the carotenoid radical for all three carotenoids even though TrpHE has no absorption at 355 nm. This is illustrated in Fig. 2,

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