

Original paper

# Carotenoid scavenging of radicals

## Effect of carotenoid structure and oxygen partial pressure on antioxidative activity

Kevin Jørgensen and Leif H. Skibsted

RVAU Centre for Food Research and Department of Dairy and Food Science, Royal Veterinary and Agricultural University, Thorvaldsensvej 40, DK-1871 Frederiksberg C, Denmark

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### Entfernung von freien Radikalen beim Carotenoid. Einfluß der Strukturen des Carotenoids und des Sauerstoffdruckes auf die antioxidative Aktivität

**Zusammenfassung.** Es wurde die Entfernung von freien Radikalen beim Carotenoid untersucht durch Peroxidation der Methylester der ungesättigten Fettsäuren unter Verwendung von Metmyoglobin in einem heterogenen Lipid/Wasser-System und azo-bis-Isobutyronitril wie ein freier Radikal-Initiator in einer homogenen Chloroform-Lösung. Für das heterogene System, unter Verwendung einer Kombination einer elektrochemischen Messung der Sauerstoffverminderung, der spektrophotometrischen Bestimmung der Lipidhydroperoxide und des Carotenoidabbaues wurde demonstriert, daß jedes der vier Carotenoide, Astaxanthin,  $\beta$ -Carotin, Canthaxanthin und Zeaxanthin, die Methylester gegen Oxidation schützt. Der antioxidative Effekt steigt mit fallendem Sauerstoffdruck ( $0,010 < p_{O_2} < 0,50$  atm); weiterhin ist er wenig abhängig von der Struktur des Carotenoids. Für das homogene System wurde der Einfluß der Struktur des Carotenoids weiterhin untersucht; und es wurde demonstriert, daß die Stabilität der vier Carotenoide in dem oxidierenden System verschieden ist, und zwar mit fallender Stabilität in der Reihe: Astaxanthin > Canthaxanthin >  $\beta$ -Carotin > Zeaxanthin. Jedes der vier Carotenoide kann die Lipidoxidation unterdrücken, der Grad der Unterdrückung der Peroxidation des Methylolats entspricht dem Unterschied in der Stabilität.

**Abstract.** Carotenoid scavenging of free radicals has been investigated in peroxidizing methyl esters of unsaturated fatty acids using (i) metmyoglobin as a water-based free-radical initiator in a heterogeneous lipid/water system, and (ii) azo-bis-isobutyronitrile as a free-radical initiator in a homogeneous chloroform solution. For the heterogeneous system, using a combination of electrochemical oxygen depletion measurements, spectrophotometric de-

termination of lipid hydroperoxides and carotenoid degradation, it was demonstrated that each of the four carotenoids astaxanthin,  $\beta$ -carotene, canthaxanthin, and zeaxanthin protects the methyl esters against oxidation. The antioxidative effect increases with increasing carotenoid concentration, increases with decreasing oxygen partial pressure ( $0.010 < p_{O_2} < 0.50$  atm), and shows little dependence on the structure of the carotenoid. For a homogeneous solution, the effect of the structure of the carotenoid was further investigated, and it was shown that the stability of the four carotenoids in the oxidizing system are different, with the order of decreasing stability being: astaxanthin > canthaxanthin >  $\beta$ -carotene > zeaxanthin. Each of the four carotenoids can suppress lipid oxidation and the degree of suppression of peroxidation of methyl linoleate corresponds to the difference in stability.

### Introduction

Oxidation of lipids has long been recognized as a major deterioration process affecting both the sensory and the nutritional quality of foods. Related oxidation processes of tissue lipids in living organisms are receiving increased attention in relation to a possible connection between lipid oxidation and aging and pathological events such as heart diseases, arteriosclerosis, and certain forms of cancer. Tocopherols are important natural lipid-soluble antioxidants both in foods and in biological systems, and the mechanism behind the action of tocopherols as a free radical scavenger in relation to inhibition of lipid oxidation has been investigated in detail [1]. Carotenoids have also been suggested to have a function as natural lipid-soluble antioxidants, and it has been documented that carotenoids are important as quenchers of singlet oxygen and sensitizing pigments in relation to harmful photooxidative processes in foods and biological systems [2–5]. However, a general function of carotenoids as scavengers of free radicals in foods and biological systems is less well

Correspondence to: L. H. Skibsted