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Antioxidant activities of annatto and palm tocotrienol-rich fractions in fish oil and structured lipid-based infant formula emulsion

Long Zou, Casimir C. Akoh *

Department of Food Science and Technology, The University of Georgia, Athens, GA 30602, USA

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ABSTRACT

The abilities of annatto and palm tocotrienol-rich fractions (TRFs), as natural antioxidants, to inhibit lipid oxidation in menhaden fish oil and structured lipid-based infant formula emulsion, were evaluated and compared. The peroxide and anisidine values of the bulk oil and oil-in-water emulsion samples stored at 37 °C were measured over a 28-day period. The results showed that annatto TRF was a more effective antioxidant than palm TRF and α-tocopherol in both food systems at 0.02% and 0.05%. Factors, including structural differences in chromanol head and isoprenoid tail, polarity, concentration, oxidation time, and the method used to monitor lipid oxidation, were responsible for the different behaviours of tocopherols and tocotrienols. In contrast to the reported findings *in vivo*, addition of α-tocopherol (0–75%) did not interfere with the antioxidant activity of tocopherol-free annatto TRF in foods. Our findings may lead to the development of new natural antioxidant products for food applications.

1. Introduction

Lipid oxidation in foods has become a major concern with the increased use of polyunsaturated vegetable, fish, or microbial oils for health benefits. It not only produces undesirable off-flavours, but also decreases the nutritional quality and safety of food products (McClements & Decker, 2000), which are unacceptable to consumers. Among the methods employed to retard or inhibit oxidation of lipids, addition of antioxidants can be an effective solution (Shahidi & Zhong, 2010; Waraho, McClements, & Decker, 2011). Due to the safety concerns about potentially toxic effects of synthetic additives, there is a worldwide trend toward the use of natural antioxidants (Waraho et al., 2011). Moreover, many natural antioxidants possess additional health-promoting benefits *in vivo*.

Vitamin E compounds (tocopherols and tocotrienols) are considered to be a major group of natural fat-soluble chain-breaking antioxidants to prevent lipid oxidation in foods and biological systems (Eitenmiller & Lee, 2004). Structurally, they are characterized by a chromanol head with two rings (one phenolic and one heterocyclic) and a lipophilic isoprenoid tail (Fig. 1). The tocopherols have a saturated phytyl tail, whereas their corresponding tocotrienols have a shorter unsaturated farnesyl tail with three isolated double bonds. The position and number of methyl groups on the chromanol head determine the specific type of tocopherol or tocotrienol homologues, named α, β, γ, or δ. It is widely accepted that the antioxidant activity of tocopherols and tocotrienols is mainly due to their ability to donate phenolic hydrogen to lipid free radicals, with less contribution from singlet oxygen quenching (Eitenmiller & Lee, 2004). The more methyl substituents at the ortho- and/or para-position to the hydroxyl group, the more easily can the O–H bond be cleaved (Kamal-Eldin & Appelqvist, 1996; Wright, Johnson, & DiLabio, 2001). Thus, the relative antioxidant effectiveness of different isomers is originally believed to be in the order of $\alpha > \beta > \gamma > \delta$ on the basis of hydrogen-donating power (Kamal-Eldin & Appelqvist, 1996). The corresponding tocopherols and tocotrienols are also expected to exert similar antioxidant potential due to the presence of the same chromanol group. However, there is considerable conflicting evidence regarding their antioxidant activities *in vivo, in vitro*, in model systems, and in specific food matrices (Eitenmiller & Lee, 2004; Kamal-Eldin & Appelqvist, 1996; Seppanen, Song, & Csallany, 2010). The reasons behind this confusion have not yet been fully understood. It is recognized that the effectiveness of an antioxidant in foods is not only determined by its structure and chemical reactivity toward lipid radicals, but also dependent on other factors, including its stability, polarity, molecular size, concentration, environmental conditions (e.g., pH and temperature), physical distribution and mobility in

* Corresponding author. Tel.: +1 706 542 1067; fax: +1 706 542 1050.
E-mail address: cakoh@uga.edu (C.C. Akoh).

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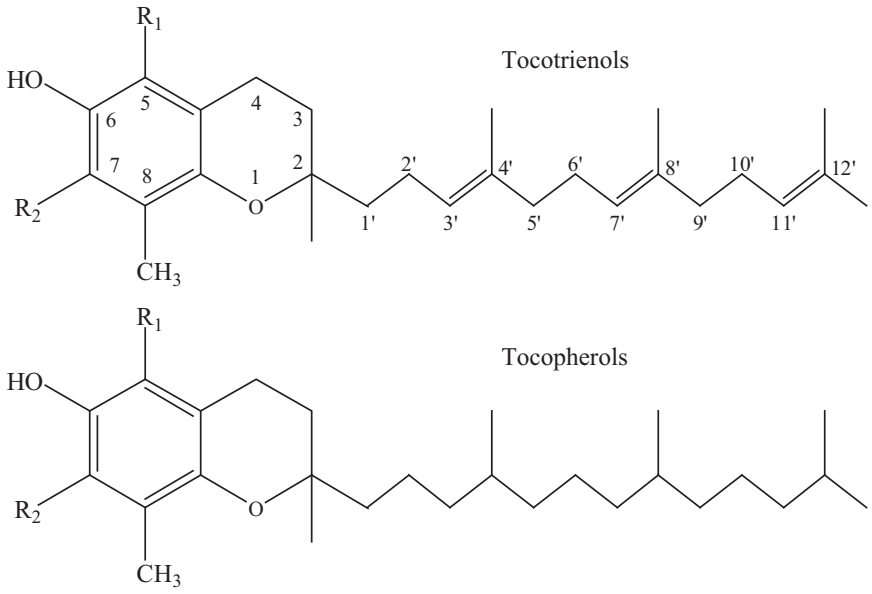

Tocotrienols or tocopherols	R_1	R_2
α (5,7,8-trimethyl)	CH_3	CH_3
β (5,8-dimethyl)	CH_3	H
γ (7,8-dimethyl)	H	CH_3
δ (8-monomethyl)	H	H

Fig. 1. Chemical structures of tocotrienols and tocopherols.

the media (e.g., bulk oil or oil-in-water emulsion), and presence of antagonists or synergists (Decker, Warner, Richards, & Shahidi, 2005; Shahidi & Zhong, 2011; Waraho et al., 2011). Huang, Frankel, and German (1994) also proposed that whether α-tocopherol acted as an antioxidant or prooxidant depended on concentration, oxidation time, the method used to determine oxidation, and physical state (bulk phase or emulsion). Although the antioxidant and biological properties of tocopherols, especially α-tocopherol, have been extensively investigated, little is known about antioxidant properties of tocotrienols in foods (Table 1),

Table 1
Summaries of research on the antioxidant activity of tocotrienols in model systems, fats, and oils.

Substrate	Concentration	Oxidation temperature (°C)	Measurement	Result	References
Model systems					
Methyl linoleate	0.02%, 0.05%	60	Weight gain	α-T_3 > α-T, γ-T_3 > γ-T[a]	Yamaoka, Tanaka, and Kato (1985)
Fats and oils					
Lard	0.02%, 0.05%	110	Refractometric method	Tocotrienols > Tocopherols, δ-T_3 > γ-T_3 > β-T_3 > α-T_3	Seher and Ivanov (1973)
Palm olein	0.02–0.2%	100	Rancimet test	γ-T_3 ⩾ δ-T_3 > α-T_3	Top, Ong, Kato, Watanabe, and Kawada (1989)
Palm olein	0.01–0.1%	110	OSI	γ-T_3 ⩾ γ-T > α-T_3 ≈ α-T	Feng (1995)
Palm olein	0.04%	110	TOTOX, CD	γ-T_3 > γ-T > α-T_3 ⩾ α-T	
Corn oil	0.04%	110	TOTOX, CD	γ-T_3 > γ-T > α-T_3 ≈ α-T	
Soybean oil	0.04%	110	TOTOX, CD	γ-T3 > γ-T > α-T_3 > α-T	
Coconut fat	0.01–0.1%	160	OSI	δ-T_3 > γ-T3 > β-T_3 > α-T_3,	Wagner, Wotruba, and Elmadfa (2001)
	0.01–0.1%	60	PV, CD	δ-T_3 > δ-T, γ-T_3 > γ-T δ-T_3 and γ-T_3 as antioxidants, α-T_3 and β-T_3 as prooxidants	
Canola oil	Unfixed	180	OSI	α-T at 432 mg/kg > α-T_3 at 138 mg/kg ≈ α-T at 155 mg/kg	Romero et al. (2007)
Lard	0.01–0.1%	55	Headspace oxygen, PV	δ-T3 > γ-T_3 > β-T_3 > α-T_3	Kim (2007)
Corn oil	0.01–0.5%	60	PV, OSI	γ-T_3 > δ-T_3 ≈ δ-T > α-T_3 ≈ α-T	Dolde and Wang (2011)

[a] *Abbreviations:* T_3, tocotrienol; T, tocopherol; OSI, oil stability index; TOTOX, total oxidation value; CD, conjugated diene; PV, peroxide value.