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ORIGINAL ARTICLE

Kinetic Study of the Prooxidant Effect of α-Tocopherol. Hydrogen Abstraction from Lipids by α-Tocopheroxyl Radical

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Abstract A kinetic study of the prooxidant effect of α-tocopherol was performed. The rates of allylic hydrogen abstraction from various unsaturated fatty acid esters (ethyl stearate **1**, ethyl oleate **2**, ethyl linoleate **3**, ethyl linolenate **4**, and ethyl arachidonate **5**) by α-tocopheroxyl radical in toluene were determined, using a double-mixing stopped-flow spectrophotometer. The second-order rate constants (k_p) obtained are $<1 \times 10^{-2}$ M^{-1} s^{-1} for **1**, 1.90×10^{-2} M^{-1} s^{-1} for **2**, 8.33×10^{-2} M^{-1} s^{-1} for **3**, 1.92×10^{-1} M^{-1} s^{-1} for **4**, and 2.43×10^{-1} M^{-1} s^{-1} for **5** at 25.0 °C. Fatty acid esters **3**, **4**, and **5** contain two, four, and six $–CH_2–$ hydrogen atoms activated by two π-electron systems (–C=C–CH_2–C=C–). On the other hand, fatty acid ester **2** has four $–CH_2–$ hydrogen atoms activated by a single π-electron system ($–CH_2–C=C–CH_2–$). Thus, the rate constants, k_{abstr}/H, given on an available hydrogen basis are $k_p/4 = 4.75 \times 10^{-3}$ M^{-1} s^{-1} for **2**, $k_p/2 = 4.16 \times 10^{-2}$ M^{-1} s^{-1} for **3**, $k_p/4 = 4.79 \times 10^{-2}$ M^{-1} s^{-1} for **4**, and $k_p/6 = 4.05 \times 10^{-2}$ M^{-1} s^{-1} for **5**. The k_{abstr}/H values obtained for **3**, **4**, and **5** are similar to each other, and are by about one order of magnitude higher than that for **2**. From these results, it is suggested that the prooxidant effect of α-tocopherol in edible oils, fats, and low-density lipoproteins may be induced by the above hydrogen abstraction reaction.

Keywords α-Tocopherol · α-Tocopheroxyl radical · Prooxidant effect · Kinetic study · Reaction rate constant · Stopped-flow spectrophotometer · Unsaturated lipids · Fatty acids · Vitamin E

Abbreviations

ArOH	2,6-Di-*tert*-butyl-4(4′-methoxyphenyl)phenol
ArO·	2,6-Di-*tert*-butyl-4(4′-methoxyphenyl)phenoxyl (aroxyl)
AsH^-	Ascorbate mono anion
$As·^-$	Ascorbate mono anion radical
5,7-Di-iPr-Toc·	5,7-Di-isopropyl-tocopheroxyl
ESR	Electron spin resonance
LDL	Low-density lipoprotein
LH	Lipid (or fatty acid ethyl ester)
LOOH	Lipid hydroperoxide (or methyl linoleate hydroperoxide)
LOO·	Lipid peroxyl radical
LO·	Lipid alkoxyl radical
NRP	Non-radical products
α-TocH	α-Tocopherol
α-Toc·	α-Tocopheroxyl

Introduction

It is well known that vitamin E (α-tocopherol, α-TocH) is localized in biomembranes and functions as an antioxidant

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