FLAVIN PHOTOSENSITIZED OXIDATION OF LONG-CHAIN OMEGA-3 AND OMEGA-6 FATTY ACID METHYL ESTERS

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Methyl esters of arachidonic acid (AA), eicosapentaenoic acid (EPA), and docosahexaenoic acid (DHA) quench triplet-excited state of riboflavin in efficient bimolecular reactions with rate constants of $(6.2 \pm 0.3 \cdot 10^6) \text{ l} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$, $(7.9 \pm 1.0 \cdot 10^6) \text{ l} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$, and $(1.2 \pm 0.5 \cdot 10^7) \text{ l} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$, respectively, as determined by laser flash photolysis for acetonitrile/water (8:2 v/v) solutions at $25.0 \pm 0.5 \degree C$. This reductive deactivation of triplet-excited riboflavin as photosensitizer of importance for skin and eye health by fatty acid esters with 4, 5 or 6 double bonds is faster than for the methyl esters of linoleic and linolenic acids, and the rate constant, are shown to depend linearly on the number of bis-allylic hydrogen atoms and assigned as an entropy effect leading to a maximal second order rate constant of $1.1 \pm 0.3 \cdot 10^8 \text{ l} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ for any fatty acid for bimolecular hydrogen abstraction by triplet excited flavins. Density functional theory (DFT) calculations for formal hydrogen atom abstraction indicate not only the expected large difference between the allylic and the bis-allylic methylene groups, but also a significant decrease for the outmost and the innermost allylic methylene groups in the marine fatty acid esters in agreement with higher sensitivity to photooxidation compared to plant fatty acids.