Supporting Information for publication

Carotenoids: Experimental Ionization Energies and Capacity at Inhibiting Lipid Peroxidation in a Chemical Model of Dietary Oxidative Stress

Mathematical treatment for the inhibition of heme-induced lipid peroxidation. The reactions involved in the metmyoglobin-induced peroxidation of linoleic acid in the presence of a carotenoid are summed up in Scheme 1 ($MbFe^{III}$: metmyoglobin, $MbFe^{IV}$: hypervalent form, LH: PUFA, LOOH: PUFA hydroperoxide, Car: carotenoid):

The peroxidation rate can be written as: $R_p = d(LOOH)/dt = k_p(LOO^\bullet)(LH) + k_{ip}(LOO^\bullet)(Car) - k_{i1}(LOOH)(MbFe^{III}) - k_{i2}(LOOH)(MbFe^{IV}) = R_p + R_{ip} - R_{i1} - R_{i2}$

The rate of lipid consumption is: $-d(LH)/dt = R_p$

The rate of antioxidant consumption is: $R_{ip} = -d(Car)/dt$

Assuming a steady-state for the lipid peroxyl radicals, we may write:

$R_{i2} = k_{ip}(LOO^\bullet)(Car) + 2k_t(LOO^\bullet)^2$

Solving for ($LOO^\bullet$) gives: $(LOO^\bullet) = \dfrac{k_{ip}(Car)}{4k_t}[(1+\dfrac{8k_t R_{i2}}{k_{ip}^2(Car)^2})^{1/2} - 1]$

Hence, we deduce: $R_{a2} = k_a(Car)^2[(1+\dfrac{2R_{i2}}{k_a(Car)^2})^{1/2} - 1]$

with $k_a = k_{ip}^2/(4k_t)$

We also have: $R_p = \dfrac{R_{ip}(LH)}{AE(Car)}$ with $AE = k_{ip}/k_p$ (antioxidant efficiency).

Assuming a steady-state for $MbFe^{IV}$, we deduce: $R_{i1} = R_{i2} + k_d(MbFe^{IV})$

This relationship can be written as: $k_{i1}(LOOH)(MbFe^{III}) = [k_d + k_{i2}(LOOH)](MbFe^{IV})$

We thus deduce: $R_{i2} = \dfrac{R_{i1}}{1+\dfrac{C_d}{(LOOH)}}$ with $C_d = k_d/k_{i2}$

Finally, one has: $-d(MbFe^{III})/dt = R_{i1} - R_{i2}$

In the absence of antioxidant, taking into account a correction for metal contaminants (M, concentration C_M), we have: $R_p^0 = k_p(LOO^\bullet)(LH) - k_{i1}(LOOH)(MbFe^{III}) - k_{i2}(LOOH)(MbFe^{IV}) - k_M(LOOH)(M) = R_p - R_{i1} - R_{i2} - R_M$

with $R_{i2} = 2k_t(LOO^\bullet)^2$ and $-d(M)/dt = R_M$

We thus deduce: $R_p^0 = r_{ox}(LH)R_{i2}^{1/2} - R_{i1} - R_{i2} - R_M$

with $r_{ox} = k_p/(2k_t)^{1/2}$

Parameters k_a, r_{ox} and AE are also bound through the following relationship: $k_a = (r_{ox}AE)^2/2$

Finally, assuming that each antioxidant is able to scavenge n $LOO^\bullet$ radicals (with the same rate constant k_{ip}), its effective concentration can be written as n x total concentration.