

Supplementary Material

On the antioxidant activity of eumelanin biopigments: a quantitative comparison between free radical scavenging and redox properties

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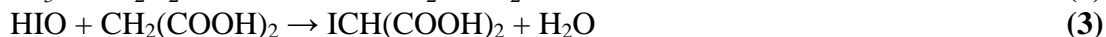
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Explanation of the chemistry involved in the Briggs Rauscher (BR) reaction (Eq.(1)):

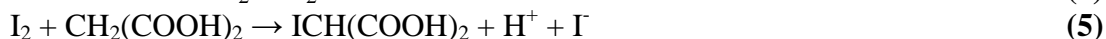


The BR reaction is accomplished through two reactions:



Eq.(2) follows a fast radical path, involving $\text{HOO}\cdot$ and the redox chemistry of the catalyst (Mn^{++}), when $[\text{I}^-]$ is low, or a non-radical path, when the $[\text{I}^-]$ is high.

Eq.(3) is a two-step reaction:



BR mixtures were prepared by mixing the appropriate amounts of stock solutions of hydrogen peroxide, iodate, perchloric acid, malonic acid and manganese sulphate using burettes in a 100-ml beaker to a total volume of 30 ml. One milliliter of starch solution was then added to the mixture.

The final composition of the BR mixture was: $[\text{malonic acid}]=0.0500 \text{ M}$, $[\text{Mn}^{2+}]=0.0067 \text{ M}$, $[\text{HClO}_4]=0.03121 \text{ M}$, $[\text{IO}_3^-]=0.0667 \text{ M}$, and $[\text{H}_2\text{O}_2]=0.8162 \text{ M}$.

Upon initial mixing of the solutions, IO_3^- reacts with H_2O_2 to produce, via a **fast, radical** path, a rapidly increasing $[\text{IO}^-]$. IO^- is partly reduced to I^- by H_2O_2 and partly reacts with I^- , producing I_2 according to Eq (4) (AMBER SOLUTION, RADICAL PATH). I_2 reacts slowly with malonic acid, thereby causing an increase in $[\text{I}^-]$ according to Eq. (5). Its high concentration triggers its reaction with IO_3^- and hence a **slow non-radical** production of IO^- (BLUE SOLUTION, NON RADICAL PATH). IO^- and I^- are consumed in the iodination of malonic acid at a faster rate compared to that of their slower production. Eventually $[\text{I}^-]$ is reduced to such a low value that the radical process takes over again. This oscillating sequence repeats until the malonic acid or IO_3^- is depleted. The oscillations can be observed in Fig.S1 below. The video represents the sonification of the potentiometer output (mV). The sound pitch is proportional to the potential. The video originally stimulates a visual-auditory synesthesia. It elicits concomitant different percepts and a crossing of sensory wiring.

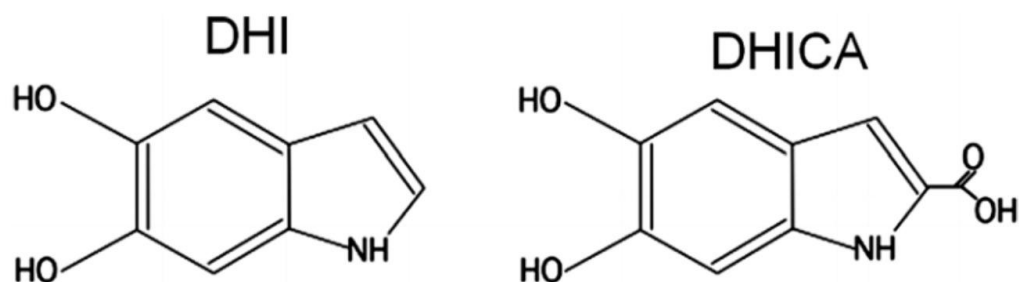


Fig. S1 Molecular structure of the melanins building blocks, namely 5,6-dihydroxyindole (DHI) and 5,6-dihydroxyindole-2-carboxylic acid (DHICA).

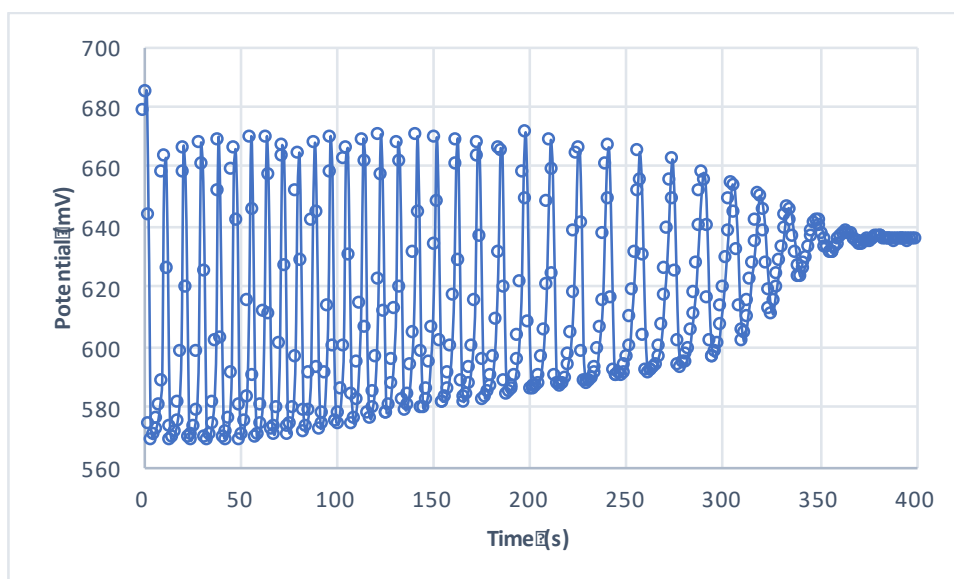


Fig. S2 Potential of a Pt electrode vs time for the active BR mixture without addition of antioxidants.

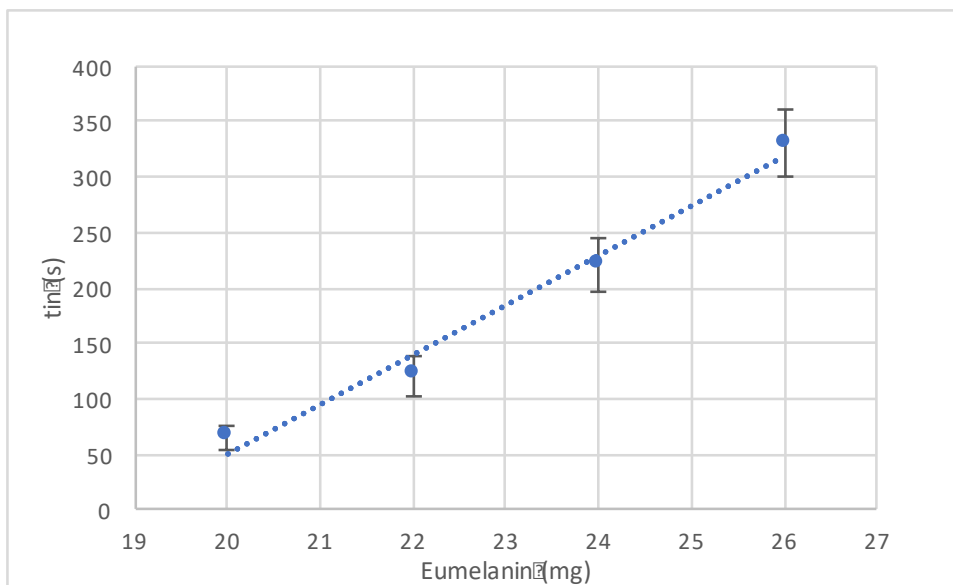


Fig. S3. Linear relationship between inhibition time (t_{in}) and mass of eumelanin added to the oscillating BR mixture. Standard deviations are obtained from *triplicate* measurements.

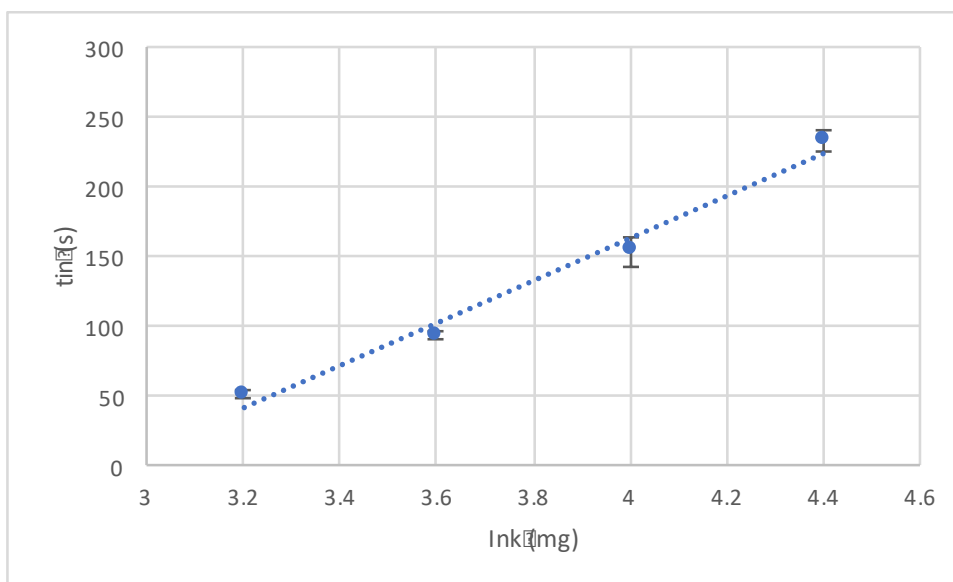


Fig. S4. Linear relationship between inhibition time (t_{in}) and mass of ink added to the oscillating BR mixture. Standard deviations are obtained from *triplicate* measurements.

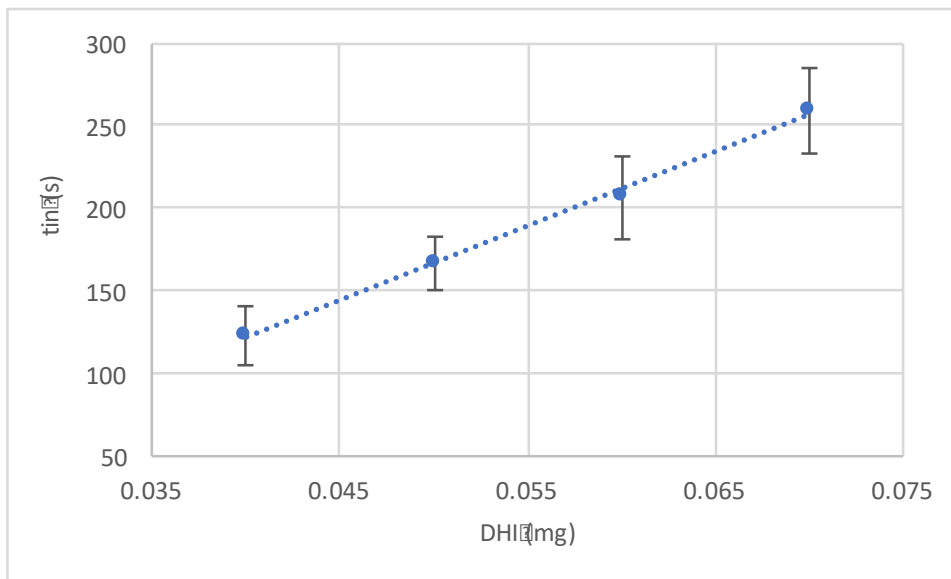


Fig. S5. Linear relationship between inhibition time (t_{in}) and mass of DHI added to the oscillating BR mixture. Standard deviations are obtained from *triplicata* measurements.

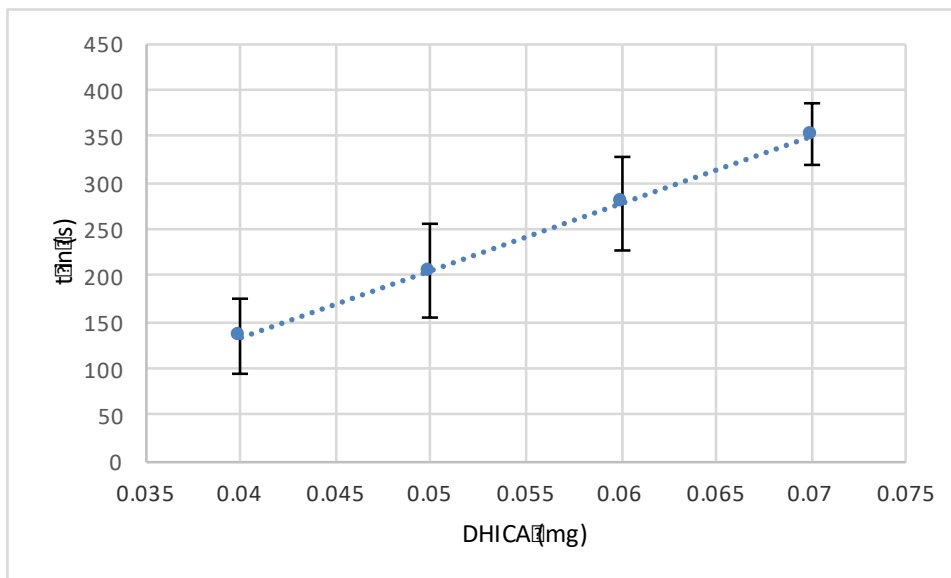


Fig. S6. Linear relationship between inhibition time (t_{in}) and mass of DHICA added to the oscillating BR mixture. Standard deviations are obtained from *triplicata* measurements.