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Melanin: a Natural Reversible Oxidation-Reduction System and Indicator.*

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The phenol-indophenol dyes induce a pallor in amphibian larvæ[1, 2] by inhibiting the enzyme tyrosinase.[3] During experiments, the results of which indicate that the enzyme tyrosinase is regulated by oxidation-reduction potentials, it was desirable to reduce certain oxidation-reduction indicator-dyes present in solutions of melanin. It was found that sodium hydrosulfite not only decolorized the dyes but also changed black melanin to a light brown or tan color. The same thing happened in melanin-solutions containing no dyes, and the pigment could be brought back to the black oxidized state by the addition of potassium ferricyanide. This was repeated in the same solution several times, so it was concluded that melanin is a natural reversible oxidation-reduction system.

The degree of color-change is indicated by the change in light-absorption determined by means of a photo-electric colorimeter. An absorption value of 0.0 was arbitrarily assigned to water. A solution of oxidized melanin absorbed 70% of the light. When reduced with sodium hydrosulfite, it absorbed only 25% of the light. On reoxidation, it again absorbed 70% of the light. Melanin produced by mealworm-tyrosinase, potato-tyrosinase, and autoöxidation of dihydroxyphenylalanine all show this same reversibility. Natural melanin appears to respond more sluggishly and to a lesser degree, but this may only be due to the necessarily low concentrations obtainable and the contaminations present in solutions of natural melanin.

The reduced form of melanin decolorizes the dyes in the series of redox indicators above and including toluylene blue. The oxidized form of melanin oxidizes the reduced indigo disulphonate, methylene blue, and thionine. Melanin must, therefore, be regarded as a natural redox system comparable to glutathione, riboflavin, and cevitamic acid. It has a relatively high potential and since it is highly colored and widely distributed, its very presence and color may become a valuable intracellular redox indicator.

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1 Lewis, M. R., *J. Exp. Zool.*, 1932, **64**, 57.

2 Figge, F. H. J., *Ibid.*, 1938, **78**, 471.

3 Figge, F. H. J., PROC. SOC. EXP. BIOL. AND MED., 1938, **39**, 569.