Destabilization as an Advantage

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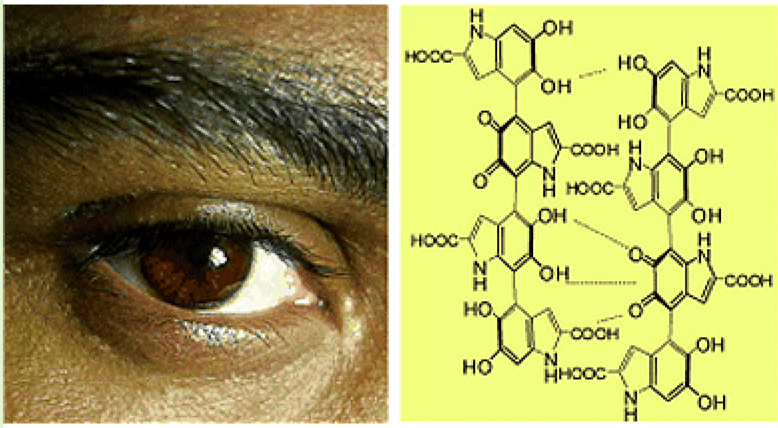

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Skin Pigments with Technological Potential

A black and insoluble biopolymer called eumelanin and other types of melanin together determine skin and hair color, particularly for dark phenotypes. Eumelanin is also a soft, biocompatible nanomaterial with technological potential. However, previous studies of this substance have primarily been carried out with synthetic samples. In the journal *Angewandte Chemie*, Italian researchers have now revealed why natural eumelanin is significantly superior to the synthetic version as a radical scavenger, antioxidant, and photoprotectant.

Thanks to its unusual optoelectronic, dielectric, metal-binding, and radical-scavenging properties, eumelanin could be useful for a variety of technical applications, including organic electronic components or antioxidants for plastics. However, it was recently discovered that the properties of synthetic eumelanin are significantly different from those of the natural product.

Within pigment cells, eumelanin is produced enzymatically from tyrosine or DOPA. An important intermediate step in this process is the isomerization of dopachrome to 5,6-dihydroxyindole-2-carboxylic acid (DHICA). In contrast to the natural process, the laboratory synthesis does not use enzymes. In this case, a carboxylic acid group spontaneously splits off to give 5,6-dihydroxyindole (DHI). While natural eumelanins contain over 50 % DHICA-derived components, synthetic versions primarily consist of building blocks derived from DHI.

Natural Eumelanin versus Synthetic Eumelanin

A team at the University of Naples and the National Research Council of Italy, Pozzuoli, Italy, has now produced melanins based on DHI and DHICA, and compared them. The results demonstrated that the molecular structures and morphologies, as well as the optoelectronic and paramagnetic properties of the two variants are very different. Whereas the DHI-based polymers exist as small, spherical aggregates, the DHICA-based versions form micrometer-long rods from elongated aggregates. The DHICA polymer is a considerably stronger proton donor and radical scavenger than the DHI polymer.

The researchers, headed by Marco d'Ischia, determined that the cause of this difference is the different way in which the building blocks of the two types of melanin are attached to each other. In the DHI biopolymer, the electrons from double bonds can move freely throughout the entire molecule (conjugated double bonds). This has a stabilizing effect and results in flat molecules that aggregate into compact stacks. In the DHICA-based melanins, this conjugation between the building blocks is hindered, which has a destabilizing effect and leads to monomer-like behavior and less aggregation.

Paradoxically it is precisely this destabilization that gives the DHICA melanins their unusually efficient antioxidant, redox, and photoprotectant properties– making them excellent protective skin pigments.

The researchers are optimistic that the outstanding radical-scavenging powers of the DHICA-based melanins will also prove to be superior to previously tested DHI polymers in technical applications.

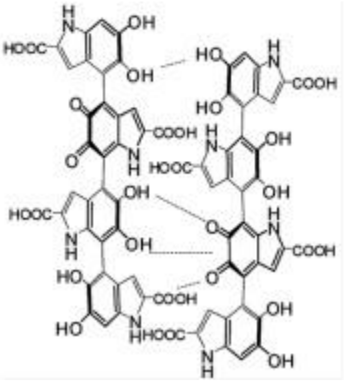
- Atypical Structural and π-Electron Features of a Melanin Polymer that Lead to Superior Free-Radical-Scavenging Properties,
  Lucia Panzella, Gennaro Gentile, Gerardino D'Errico, Nicola F. Della Vecchia, Maria E. Errico, Alessandra Napolitano, Cosimo Carfagna, Marco d'Ischia,
  Angew. Chem. Int. Ed. **2013**.
  DOI: 10.1002/anie.201305747

Ultraviolet protection: Natural and synthetic

http://www.spectroscopynow.com/details/ezine/141fed5f375/Ultraviolet-protection-Natural-and-synthetic.html

- **Published:** Nov 1, 2013
- **Author:** David Bradley
- **Channels:** UV/Vis Spectroscopy

Solving the insoluble



The insoluble black biopolymer, eumelanin, together with other related melanin compounds determine skin and hair colour, particularly for people with a dark phenotypes. Synthetic eumelanin itself has also been investigated recently as a biocompatible nanomaterial that could have many technological applications.

Now, Italian researchers describe in the journal *Angewandte Chemie* how it is possible to engineer in the laboratory a synthetic mimic of natural eumelanin with atypical structural characteristics. This material has much better radical-scavenging properties than commonly reported synthetic counterparts, the team reports. The synthetic mimic might also have a more significant role as a photoprotectant against ultraviolet damage and oxidative stress.

Eumelanin has intriguing optoelectronic, paramagnetic, metal-binding and radical-scavenging properties and as such has been mooted as a component in organic electronic components or as an antioxidant for plastics.

Within human pigment cells, eumelanin is generated enzymatically from tyrosine or 3,4-dihydroxyphenylalanine (DOPA) via an important intermediate step in which dopachrome is isomerized to 5,6-dihydroxyindole-2-carboxylic acid (DHICA). By contrast, the laboratory synthesis is non-enzymatic and involves the splitting off of a carboxylic acid group spontaneously to give 5,6-dihydroxyindole (DHI). More than half of the substance of natural eumelanins is derived from DHICA, whereas the synthetic versions consist primarily of material derived from DHI building blocks.

Skin deep science

A team at the University of Naples and the National Research Council of Italy in Pozzuoli has made melanins based on DHI and DHICA, and compared the chemical and physical properties. The results demonstrated that the molecular structures and morphologies, as well as the optoelectronic and paramagnetic properties of the two different forms are dissimilar. Whereas the DHI-based polymers exist as small, spherical aggregates, the DHICA-based versions form micrometre-long rods from elongated aggregates. The DHICA polymer is a much stronger proton donor and radical scavenger than the DHI polymer, the team reports.

Research leader Marco d'Ischia and colleagues demonstrated that what underpins this difference is the mechanism by which the building blocks of the two types of melanin are linked together. In the DHI biopolymer, there is a conjugated double bond system, which has a stabilizing effect and results in flat molecules that aggregate into compact stacks. On the other hand, the DHICA-based melanins have hindered conjugation, which destabilizes the structure so that monomer-like behaviour predominates inducing less aggregation. Of course, it is this destabilization that endows the DHICA melanins with their potent antioxidant and photoprotectant properties. The researchers are optimistic that the outstanding radical-scavenging powers of the DHICA-based melanins will also prove to be superior to previously tested DHI polymers in technical applications.

Plausible photoprotection

The team suggests that their work offers a plausible chemical explanation as to why DHICA-based molecules evolved as the photoprotective components of skin pigments. The researchers concede, however that their suggested model is yet to be confirmed fully but hope that their results will stimulate additional work into melanin from a biological and technological perspective.

"Ongoing work is directed to explore possible applications of DHICA-based melanins, in collaboration with teams belonging to the European Network for Melanin Research (EuMelaNet)," d'Ischia told SpectroscopyNOW. "Taking lessons from nature, new melanin-based functional materials will be developed and tailored for possible applications in polymer science, organic electronics and nanomedicine," he adds.

Related Links

Angew Chem 2013, online: Atypical Structural and p-Electron Features of a Melanin Polymer That Lead to Superior Free-Radical-Scavenging Properties"

Article by David Bradley