

Melanin Pigments of Medicinal Mushrooms

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Black or dark brown polyphenolic pigments (melanins) play an important role in the survival of fungi. Melanins are not essential for normal growth and development and seem to function in the protection of organisms against environmental stress. Interest in melanin pigments is increasing worldwide because the pigments display pronounced antimutagenic, anticarcinogenic, antioxidant, photoprotective, radioprotective, and antibacterial activity. Melanin pigments synthesized by mycelial fungi may be a readily available and cost-efficient feedstock for the pharmaceutical industry.

An investigation of melanin production by known medicinal mushrooms belonging to the genera *Phellinus*, *Inonotus*, *Bjerkandera*, *Lentinus*, and their physicochemical properties was carried out. Dark brown pigments from the xylotrophic basidiomycetes mycelia studied showed typical properties of melanins. They were insoluble in chloroform, isoamyl alcohol, butanol, ether, and ethyl acetate; dissolved only in alkali at pH > 10 and in precipitates at pH < 3; and were bleached in H₂O₂.

Melanins of the macromycetes were derived from catechol (GDHB) and contained peptide units. A study of the elementary composition of the melanins showed that they contained 35–40% C, 5–6% H, and trace amounts of N. The pigments possessed various functional groups: carboxyl, carbonyl, methoxyl, phenolic, and alcoholic hydroxyls. It was revealed that heavy metal ions, especially copper ions in some concentrations, were able to induce or accelerate synthesis

of melanin by the mushrooms investigated. Monocyclic compounds (pyrocatechol a.o.) exerted a great stimulating effect on melagenesis. In a surface culture melanin synthesis was more stable than in a submerged one. *Phellinus robustus* P. Karst. grown on solid media contained up to 32% melanin in biomass.

Pigmented mycelia of the mushrooms studied were remarkable for high heavy metal ion biosorption activity. *Ph. robustus* had the highest sorption capacity among the investigated mushrooms. Metal ion sorption was most frequently of the order: melanin–chitin complex > melanin > dark mycelium > light mycelium. However, it depended on the mushroom species and type of metal. It was found that alkali treatment of pigmented mycelia improved their activity for metals ion binding. According to IR spectra of H and Cu forms of melanins, carboxyl groups were the main copper binding sites. An electron spin resonance (ESR) study showed that copper–polyphenol interactions in all examined melanins were mostly ionic and involved oxygen atoms. In addition, on the basis of ESR spectra it was supposed that nitrogen-containing groups can take part in heavy metal ion binding.

Experiments on the effects of *Phellinus robustus* and *Inonotus obliquus* (Pers.) Pil. melanins on peroxidase-mediated oxidation of aminobiphenyls indicated their considerable antioxidant and gene-protecting activity *in vitro*. These diversified melanin properties are promising for elaboration of new medicinal preparations.