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Review

Polyphenol oxidases in plants and fungi: Going places? A review

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Abstract

The more recent reports on polyphenol oxidase in plants and fungi are reviewed. The main aspects considered are the structure, distribution, location and properties of polyphenol oxidase (PPO) as well as newly discovered inhibitors of the enzyme. Particular stress is given to the possible function of the enzyme. The cloning and characterization of a large number of PPOs is surveyed. Although the active site of the enzyme is conserved, the amino acid sequence shows very considerable variability among species. Most plants and fungi PPO have multiple forms of PPO. Expression of the genes coding for the enzyme is tissue specific and also developmentally controlled. Many inhibitors of PPO have been described, which belong to very diverse chemical structures; however, their usefulness for controlling PPO activity remains in doubt. The function of PPO still remains enigmatic. In plants the positive correlation between levels of PPO and the resistance to pathogens and herbivores is frequently observed, but convincing proof of a causal relationship, in most cases, still has not been published. Evidence for the induction of PPO in plants, particularly under conditions of stress and pathogen attack is considered, including the role of jasmonate in the induction process. A clear role of PPO in a least two biosynthetic processes has been clearly demonstrated. In both cases a very high degree of substrate specificity has been found. In fungi, the function of PPO is probably different from that in plants, but there is some evidence indicating that here too PPO has a role in defense against pathogens. PPO also may be a pathogenic factor during the attack of fungi on other organisms. Although many details about structure and probably function of PPO have been revealed in the period reviewed, some of the basic questions raised over the years remain to be answered.

Keywords: Polyphenol oxidase; Structure; Genes coding; Multiplicity; Distribution; Induction; Pathogens; Herbivores; Inhibitors; Function of enzyme

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1. Introduction

Polyphenol oxidases or tyrosinases (PPO) are enzymes with a dinuclear copper centre, which are able to insert oxygen in a position *ortho*- to an existing hydroxyl group in an aromatic ring, followed by the oxidation of the diphenol to the corresponding quinone. Molecular oxygen is used in the reaction. The structure of the active site of the enzyme, in which copper is bound by six or seven histidine residues and a single cysteine residue is highly conserved. The enzyme seems to be of almost universal distribution in animals, plants, fungi and bacteria. Much is still unknown about its biological function, especially in plants, but also in fungi. Enzyme nomenclature differentiates between monophenol oxidase (tyrosinase, EC 1.14.18.1) and catechol oxidase or *o*-diphenol:oxygen oxidoreductase (EC 1.10.3.2), but in this review the general term polyphenol oxidase (PPO) will be used.

The topic of PPO has been reviewed frequently, and among the more recent general reviews is that of Steffens et al. (1994). In addition reviews of specific aspects of the biochemistry of PPO have appeared. PPO in plants has been reviewed by Yoruk and Marshall (2003), but much of their review covers ground also stressed in other surveys. The mechanism of reaction of tyrosinase has been discussed in great detail by Lerch (1995) and Sanchez-Ferrer et al. (1995), who emphasise the importance of the enzyme in melanogenesis. A survey of mushroom tyrosinase, including lists of inhibitors, the characteristics of the enzyme and its potential uses for clinical purposes has appeared (Seo et al., 2003). The browning of mushrooms, *Agaricus bisporus* is of major economic importance and the underlying mechanisms have been reviewed by Jolivet et al. (1998), with particular stress on the involvement of tyrosinase in the process. The most recent review of fungal tyrosinases and their applications in bioengineering and biotechnology is by Halalouili et al. (2006), who cover most aspects of this PPO in depth. The potential use of PPO in organic synthesis is reviewed by Burton (2003), although the emphasis in the review is on laccases rather than on PPOs. A comparative analysis of polyphenol oxidase from plants and fungal species, with particular emphasis on secondary protein structure and similarities to hemocyanin was published very recently (Marusek et al., 2006), amplifying an earlier review (van Gelder et al., 1997). Their later review emphasizes the amino acid sequence of the enzyme from different sources and especially the N- and C-terminal domains of the enzyme. The review by Marusek et al. (2006) is especially important because it deals with aspects of PPO structure not previously discussed in detail elsewhere.

Lastly it should be mentioned that the importance of PPO in browning reactions continues to occupy many researchers as indicated by an ACS Symposium (Lee and Whitaker, 1995), and very many subsequent publications describe browning reactions in a variety of species and their tissues.

Since the 1994 review hundreds of papers dealing with plant and fungal PPO have been published. The reason for this plethora of papers is probably the relative ease with which the enzyme activity can be assessed, despite the fact that there are many potential pitfalls in its assay. Many of the published papers report on correlations between levels of PPO activity and environmental factors, attacks by pathogens or changes during food processing or storage. Although useful contributions to the store of information they do not advance the basic understanding of the function of the enzyme and proof of causal relationships between observed phenomena and levels of PPO are mostly missing.

It is clear from the perusal of the literature that PPOs are quite diverse in many of their properties, distribution and cellular location. It could therefore be asked whether it is justified to review such a very diverse group. Jaenicke and Decker (2003) write "Probably there is no common tyrosinase: the enzymes found in animals, plants and fungi are different with respect to their sequences, size, glycosylation and activation". Discussing the phylogenetic tree of PPO, Wichers et al. (2003), conclude that tyrosinases (PPOs) cluster in groups for higher plants, vertebrate animals, fungi and bacteria. "Homologies within such clusters are considerably higher than between them". However, the PPOs have at least one thing in common, they all have at their active site a dinuclear copper centre, in which type 3 copper is bound to histidine residues, and this structure is highly conserved. Despite the huge variability of PPO it still seems justified to try and provide an overview of what is happening. The intention of this review is to attempt to provide such an overview for the period from 1994 until