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Review

Bacterial enzymes involved in lignin degradation

Gonzalo de Gonzalo[a], Dana I. Colpa[b], Mohamed H.M. Habib[b,c], Marco W. Fraaije[b,*]

[a] Departamento de Química Orgánica, Universidad de Sevilla, c/Profesor García González 1, 41012 Sevilla, Spain
[b] Molecular Enzymology, Groningen Biomolecular Sciences and Biotechnology Institute, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands
[c] Department of Microbiology and Immunology, Faculty of Pharmacy, Cairo University, 11562 Kasr El-Aini Street, Cairo, Egypt

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ABSTRACT

Lignin forms a large part of plant biomass. It is a highly heterogeneous polymer of 4-hydroxyphenylpropanoid units and is embedded within polysaccharide polymers forming lignocellulose. Lignin provides strength and rigidity to plants and is rather resilient towards degradation. To improve the (bio)processing of lignocellulosic feedstocks, more effective degradation methods of lignin are in demand. Nature has found ways to fully degrade lignin through the production of dedicated ligninolytic enzyme systems. While such enzymes have been well thoroughly studied for ligninolytic fungi, only in recent years biochemical studies on bacterial enzymes capable of lignin modification have intensified. This has revealed several types of enzymes available to bacteria that enable them to act on lignin. Two major classes of bacterial lignin-modifying enzymes are DyP-type peroxidases and laccases. Yet, recently also several other bacterial enzymes have been discovered that seem to play a role in lignin modifications. In the present review, we provide an overview of recent advances in the identification and use of bacterial enzymes acting on lignin or lignin-derived products.

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1. Introduction

Plant biomass is the most abundant renewable biomass on earth and is considered as an attractive source of bioenergy and biobased chemicals. It is mainly composed of lignin, cellulose and hemicellulose. The lignin percentage in lignocellulosic biomass is around 10–30% and is the second most abundant natural organic polymer. Lignin enables plants to generate rigid structures and provides protection against hydrolysis of cellulose and hemicellulose. The biotechnological conversion of lignocellulose into different carbohydrates, including glucose, is the basis for the production of ethanol, carbohydrates and aromatic products (Asgher et al., 2014; Ragauskas et al., 2014; Kawaguchi et al., 2016). Such plant biomass derived products can be used as fuel, polymer precursors, food and flavor compounds, and pharmaceutical building blocks. For optimizing the use of plant biomass through biorefining, lignin

* Corresponding author.
E-mail addresses: gdegonzalo@us.es (G. de Gonzalo), d.i.colpa@rug.nl (D.I. Colpa), m.habib@rug.nl (M.H.M. Habib), m.w.fraaije@rug.nl (M.W. Fraaije).

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degradation has become a key target in the last few years. Efficient and cost-effective methods for selective lignin degradation are in high demand. It is worth noting that, while the recent intensified efforts in complete valorization of plant biomass, lignin was already considered as a major industrial by-product in the first half of the previous century (Gottlieb and Pelczar, 1951).

While cellulose and hemicellulose are built from carbohydrates, lignin is a highly cross-linked polymer formed by polymerization of 4-hydroxyphenylpropanoid monomers (monolignols) through various ether and carbon–carbon bonds. The phenolic moieties of the monomeric units are *p*-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) groups and the percentage of each depends on the plant species and tissue. The formation of lignin is triggered by plant peroxidases and/or laccases. By oxidizing the phenolic monolignols into their respective phenolic radical, formation of dimers is catalyzed. Subsequent enzyme-catalyzed single electron oxidations promote polymerization. Monolignols can couple *via* various bonds with a preference of coupling through the β-carbon. The most occurring linkages involve β—β, β—*O*—4, and β—5 bonds (Vanholme et al., 2010), as shown in Fig. 1.

Due to its aromatic nature and highly branched polymer network, lignin is rather inert towards degradation (Abdel-Hamid et al., 2013). Yet, to complete global carbon cycling, nature has evolved catabolic pathways since the time that plants started to produce lignin (Nelsen et al., 2016). White-rot fungi have developed a rich collection of extracellular oxidative enzymes to attack and degrade lignin. They employ different types of heme-containing peroxidases, which include the so-called lignin peroxidases (LiP), manganese peroxidases (MnP), versatile peroxidases (VP), and dye-decolorizing peroxidases (DyP) (Lambertz et al., 2016). While some of these peroxidase are capable of attacking lignin or lignin fragments, peroxidases also attack lignin from a distance. By oxidizing mediators, small oxidizing agents are generated that can penetrate the branched lignin polymer to trigger depolymerization via radical chemistry (Nousiainen et al., 2014; Baciocchi et al., 2002; Glenn and Gold, 1999). Known mediators are lignin derived aromatic compounds (e.g. formation of veratryl alcohol cation radical) and manganese ions (Hunt et al., 2013). For effective peroxidase-based lignin degradation, also various fungal oxidases are secreted to produce the required hydrogen peroxide. Candidates for the extracellular production of hydrogen peroxide are aryl alcohol oxidases, glyoxal oxidases, and various carbohydrate oxidases. Except for peroxidases, fungi also secrete various copper-containing oxidative laccases that assist in lignin degradation. Intriguingly, it seems that the same types of enzymes used for lignin synthesis in plants (peroxidases and laccases) are used by fungi to recycle the aromatic polymer. Genome sequence analysis of ligninolytic fungi has revealed that there is not one defined set of enzymes for lignin degradation (Floudas et al., 2012). The composition of the set of oxidative enzymes being produced depends on the fungus.

While a wealth of biochemical knowledge has been obtained on fungal degradation of lignin, the ligninolytic capacity of bacteria has been less well studied. While it appears that white-rot fungi are very well equipped for lignin degradation, evidence is growing that also bacteria are capable of delignification. Already in 1930 Phillips et al. reported on a thorough study on lignin decomposition by "soil microorganisms", which presumable were bacteria (Phillips et al., 1930). While many claims of bacterial lignin degradation have been reported since then, only in the last few decades some bacterial enzymes involved in delignification have been identified. With this review we aim at providing an overview of the bacterial enzymes that have been implicated to be involved in degrading lignin or the oxidation of lignin derived degradation products.

2. Bacterial enzymes acting on lignin

2.1. DyP-type peroxidases

As described above, white-rot fungi produce several different kinds of heme-containing peroxidases to trigger lignin decomposition. However, homologs of the most common fungal ligninolytic peroxidases, LiPs MnPs and VPs, have not been encountered in biochemical studies on ligninolytic bacteria. Also when analysing sequenced genomes (Davis et al., 2013) or proteomes (Brown et al., 2011) of ligninolytic bacteria, no homologs emerge. It seems that these lignin-degrading peroxidases, belonging to the superfamily of plant peroxidase (Class II) (Welinder, 1992), are restricted to fungi. Yet, recently it has become clear that bacteria are relatively rich in another type of peroxidase, the so-called dye-decolorizing peroxidases (DyPs, EC 1.11.1.19) (Van Bloois et al., 2010). DyPs represent a newly discovered family of heme-containing peroxidases, which has recently received attention due their ability to degrade lignin and other compounds (Sugano, 2009; Colpa et al., 2014; Singh and Eltis, 2015; Yoshida and Sugano, 2015). The first discovered member of this enzyme family, DyP from *Bjerkandera adusta*, was isolated and characterized in 1999 (Kim and Shoda, 1999). Studies on the activity of this enzyme on synthetic anthraquinone and azo-dyes have served to name this family of peroxidases (Sugano et al., 2007). In recent years a large number of bacterial DyPs have been described in literature (Lambertz et al., 2016) which is in line with the observation that putative DyP-encoding genes are abundantly present in bacterial genomes (Table 1) (Van Bloois et al., 2010). In fact, already in 1988 a bacterial 'lignin peroxidase' was described from *Streptomyces viridosporus*. Unfortunately, no sequence has ever been deposited for this protein or the respective gene while several papers have appeared on cloning of the respective gene (Ramachandra et al., 1998; Wang et al., 1990; Thomas and Crawford, 1998). Yet, when analysing the recently sequenced genome of this *Streptomyces* isolate, a gene encoding a putative Tat-secreted DyP can be identified (Davis et al., 2013). This may well be the enzyme that was described long before the first fungal DyP was described.

DyPs have a protomer weight of around 40–60 kDa and various oligomeric states have been observed (Colpa et al., 2014). They belong to the peroxidase-chlorite dismutase superfamily of proteins and contain a non-covalently bound heme *b* cofactor (Zámocký et al., 2015). DyPs show a dimeric ferredoxin-like fold consisting of a four-stranded anti-parallel β-sheet surrounded by α-helices. DyP-type peroxidases contain a highly conserved GXXDG-motif and a conserved proximal histidine, which acts as the fifth ligand of the heme iron. Yet, while DyPs are structurally unrelated to the common fungal peroxidases, they exhibit similar catalytic properties with having similar redox potentials and reactivities (Liers et al., 2014). Furthermore, some of the bacterial DyPs are secreted via the Tat secretion machinery which adds to the analogy with the secreted fungal peroxidases.

Based on sequence characteristics, DyPs have been divided in four classes in the PeroxiBase database (Fawal et al., 2013). Proteins belonging to classes A–C are mainly found in bacteria, while class D DyPs are extracellular fungal representatives (Yoshida and Sugano, 2015). Class A DyPs typically have a Tat-signal sequence and are therefore secreted. In contrast, the DyP protein sequences of class B and C DyPs do not disclose any secretion signal peptides, suggesting that they are intracellular enzymes. The InterPro database currently contains 8318 DyP sequences. Approximately thirty of these enzymes have been isolated and characterized (Colpa et al., 2014; Yoshida and Sugano, 2015). DyPs are mainly active at acidic pH and show a very broad substrate profile, including several classes of synthetic dyes, monophenolic compounds, veratryl alcohol, β-carotenes, Mn^{+2} and lignin model compounds, but their physio-

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