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Phytochemistry 67 (2006) 743–753
PHYTOCHEMISTRY
www.elsevier.com/locate/phytochem

Modeling suberization with peroxidase-catalyzed polymerization of hydroxycinnamic acids: Cross-coupling and dimerization reactions

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Received 8 July 2005; received in revised form 29 December 2005
Available online 9 March 2006

Abstract

An anionic potato peroxidase (EC 1.11.1.7, APP) thought to be involved in suberization after wounding was isolated from slices of *Solanum tuberosum* in order to elucidate the first steps of dehydrogenative polymerization between pairs of different hydroxycinnamic acids (FA, CafA, CA and SA) present in wound-healing plant tissues. Use of a commercial horseradish peroxidase (HRP) – H_2O_2 catalytic system gave the identical major products in these coupling reactions, providing sufficient quantities for purification and structural elucidation. Using an equimolar mixture of pairs of hydroxycinnamic acid suberin precursors, only caffeic acid is coupled to ferulic acid and sinapic acid in separate cross-coupling reactions. For the other systems, HRP and APP reacted as follows: (1) preferentially with ferulic acid in a reaction mixture that contained *p*-coumaric and ferulic acids; (2) with sinapic acid in a mixture of *p*-coumaric and sinapic acids; (3) with sinapic acid in a mixture of ferulic and sinapic acids; (4) with caffeic acid in a reaction mixture of *p*-coumaric and caffeic acids. The resulting products, isolated and identified by NMR and MS analysis, had predominantly β-β-γ-lactone and β-5 benzofuran molecular frameworks. Five cross-coupling products are described for the first time, whereas the β-O-4 dehydrodimers identified from the caffeic acid and sinapic acid cross-coupling reaction are known materials that are highly abundant in plants. These reactivity trends lead to testable hypotheses regarding the molecular architecture of intractable suberin protective plant materials, complementing prior analysis of monomeric constituents by GC–MS and polymer functional group identification from solid-state NMR, respectively.
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Keywords: Anionic potato peroxidase; Horseradish peroxidase; Hydroxycinnamic acids; Dehydrodimers; Radical cross-coupling reaction; Suberin

1. Introduction

Suberin is a complex, intractable biopolymer found in specialized plant cell walls (e.g., mature roots, tubers, stolons, rhizomes, bark), thought to be comprised of a phenolic domain attached to the cell wall and aliphatic components that are probably attached to the phenolic domain (Kolattukudy, 1978, 1980). Its chemical constituents include long-chain fatty acids as the aliphatic component (Kolattukudy, 1980, 1984) and phenolic derivatives as the aromatic component (Cottle and Kolattukudy, 1982; Bernards and Razem, 2001; Bernards, 2002). Whereas the nature of the phenolic matrix is incompletely defined, the evidence to date shows that in potato (*Solanum tuberosum* L.) tubers it is comprised primarily of hydroxycinnamic acids and their derivatives, hydroxycinnamoyl alcohols, and glycerol (Moire et al., 1999). Solid-state ^{13}C NMR of the intact material has provided detailed information on the composition of suberized potato cell wall (Garbow et al., 1989) and, in particular, clear-cut evidence for the occurrence of hydroxycinnamic acid and alcohol structural moieties (Bernards et al., 1995; Yan and Stark, 2000). The isolation of specific peroxidases (Espelie and Kolattukudy, 1985; Bernards et al., 1999; Quiroga et al., 2000) has prompted the suggestion that polymerization of these phenolic acids to form the suberin aromatic network occurs via a peroxidase/H_2O_2-mediated free radical coupling process

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0031-9422/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.phytochem.2006.01.026

(Razem and Bernards, 2002) analogous to lignification (Kolattukudy, 1980). In spite of these advances, neither the identity of the inter-unit bonds nor the molecular structure of suberin's phenolic core is currently known.

Model systems designed to elucidate the role of peroxidase enzymes (EC 1.11.1.7) in lignin biosynthetic pathways have often used horseradish peroxidase (Syrjänen and Brunow, 1998, 2000), generating dehydrogenative polymers of hydroxycinnamoyl alcohols, hydroxycinnamoyl aldehydes and hydroxycinnamic acids. The type of product is influenced by the rate at which substrates (phenolic compounds and H_2O_2) are added to the enzyme, and the proportion of dimers as compared with polymeric products depends on pH (Syrjänen and Brunow, 2000; Larsen et al., 2001). The ferulic acid dimers in particular have been compared with the structures deduced from solid-state ^{13}C NMR of suberized potato tissues (Bernards et al., 1995; Yan and Stark, 2000).

Ferulic acid (**1**) (FA), caffeic acid (**2**) (CafA), coumaric acid (**3**) (CA), and sinapic acid (**4**) (SA) are known to accumulate in potato tubers during wound healing and have been identified as monomers in the suberin structure (Kolattukudy, 1980; Bernards et al., 1995; Bernards and Lewis, 1998). A variety of regioisomeric dehydrohomodimers of these acids (Fig. 1) have been identified as products of β-β′ (**5**–**7**), 5-5′ (**8**), β-5 (**9**), 4-O-5 (**10**) and β-O-4 (**11**) radical coupling mediated by peroxidases (Ralph et al., 1994; Larsen et al., 2001). Ferulate trimers have been reported recently in maize cells, where they are believed to tighten the cell wall; higher oligomers of FA are also evident during polymerization with horseradish peroxidase (HRP) (Rouau et al., 2003). The final step in the formation of the suberin network within cell walls is thought to involve peroxidase-initiated dehydrogenative polymerization of these phenolic compounds with substituted hydroxycinnamic acids and hydroxycinnamoyl alcohols (Bernards et al., 1995; Bernards and Razem, 2001), but the polymerization itself is viewed as occurring without enzymatic control over the type or distribution of structural units. Moreover, the presence of suberin monomers other than FA raises the possibility that cross-coupling reactions mediated by a peroxidase could produce *p*-hydrophenyl, guaiacyl and syringyl subunits. Although the likelihood of cross-coupling reactions during lignin biosynthesis is supported by recent dimerization studies (Fournand et al., 2003), no analogous observations have been documented for suberin monomers.

In the current study, the anionic potato peroxidase (APP) associated with the suberization response in potato

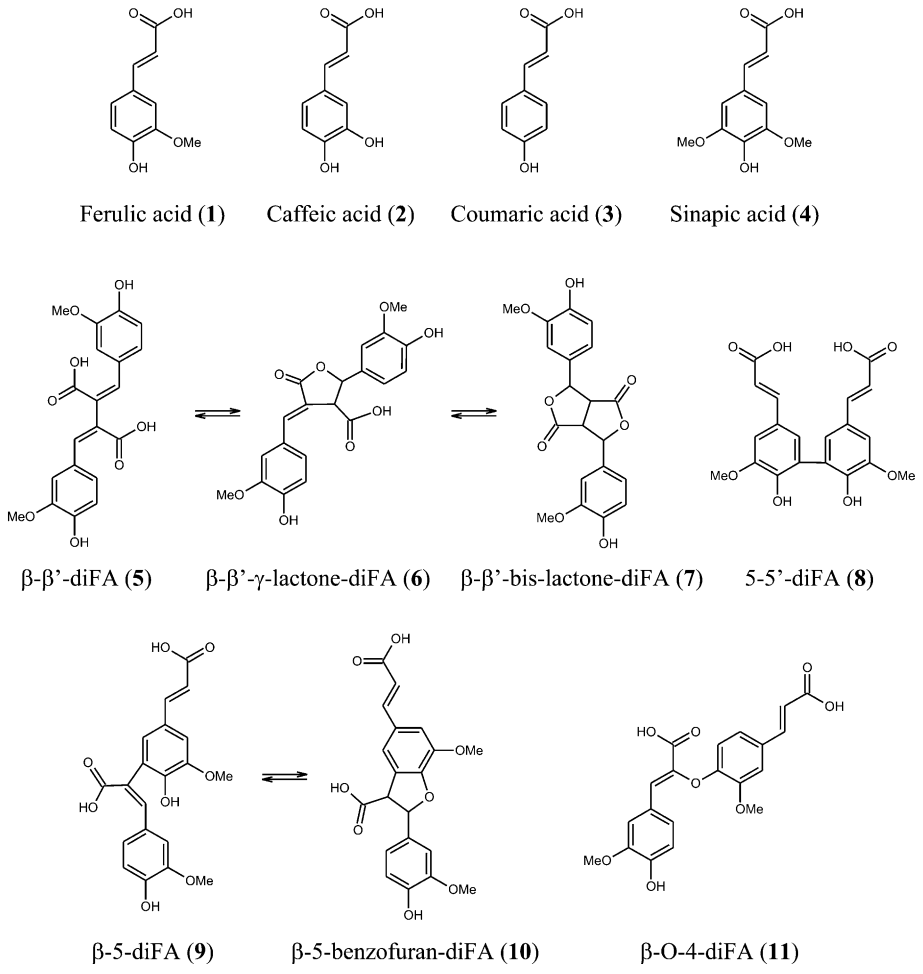

Fig. 1. Chemical structures of the major phenolic monomers and dehydrodimers isolated from plants.

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