Infancy and evolution of the phenolic metabolism

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Evolution of the phenolic metabolism is usually assumed to be associated with plant transition from water to land and occurrence of lignified vasculature for water transport. The accuracy of this assumption was investigated using as reporters P450 enzymes of the CYP98 family, which catalyze the second phenolic ring hydroxylation and first irreversible step committed to lignin synthesis in vascular plants. Our investigation reveals that the ancestral phenolic metabolism in moss, which is devoid of lignin and vasculature, is unexpectedly required for the formation of the cuticle polymer and essential to ensure surface impermeability[1]. The pleiotropic moss CYP98 enzyme that forms precursors of this polymer seems to use a substrate that is different from the substrate used by seed plants. This assumption seems further confirmed by the characterization of a BAHD acyl transferase expected to generate the substrate of the moss CYP98. A transition of CYP98 substrate preference to shikimate/quinate esters of *p*-coumaric acid is observed only in highly lignified seed plants, in particular in angiosperms, most likely to prevent a depletion in aromatic amino acids for protein synthesis. In angiosperms, *CYP98* gene duplications allow for further functional evolution and emergence of novel pathways, as exemplified by the evolution of a phenolamide pathway to form pollen precursors in Brassicaceae[2] or of a pathway supporting phenolic conjugates-based defense in poplar. Taken together, CYP98-focused phylogenomics, molecular evolution, and functional data provide an unprecedented example of how evolution of a versatile P450 enzyme over 500 million years can alternatively lead to specialization in a high flux pathway under purifying selection, or, when gene duplication relaxes selection, to functional diversification with various outcomes in different species. They also provide a background knowledge required for man-made engineering of the plant phenolic metabolism.