Formation of Oxylipins is Catalyzed by Different Enzyme Families in Plants, Mosses, Fungi and Bacteria

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Lipid peroxidation is common to all biological systems, both appearing in developmentally and environmentally regulated processes. Products are hydroperoxy polyunsaturated fatty acids and metabolites derived there from collectively named oxylipins. They may either originate from chemical oxidation or are synthesized by the action of various enzymes. Cloning of oxylipin forming and metabolizing enzymes combined with metabolic profiling revealed insights on oxylipin formation, and first hints on enzyme mechanisms in higher eukaryotes. However, knowledge on the biosynthesis and function of oxylipins in lower eukaryotic organisms like mosses or fungi or even in prokaryotes is limited.

A still increasing amount of information on eukaryotic and prokaryotic genomes is being generated. Thus we aim to identify new enzymes that are involved in oxylipin metabolism in yet not analyzed kingdoms. In the moss *Physcomitrella patens* a novel bifunctional lipoxygenase (LOX) was identified: It produces octenols from 20:4 and as second reaction branch it initiates 18:3- and 20:4-derived formation of cyclopentenoic fatty acids. In the fungus *Aspergillus nidulans* a new linoleate dioxygenase was identified that shows homology to cyclooxygenases and synthesizes oxylipins. A related reaction is catalyzed by a LOX fusion protein from cyanobacteria. A different strategy for oxylipin synthesis is used by bacteria that are pathogenic to humans. They use LOXs and FAD-containing enzymes for oxylipin synthesis. According to these findings a new picture for oxylipin formation arises that suggests that first formation of hydroxy fatty acids may have evolved during evolution in prokaryotes and later on in eukaryotes new and additional enzymes may have been acquired that lead to formation of more complex oxylipins.