Ecologically-Relevant Oxylin Pathways in Marine Diatoms: a Look at Chemical and Ecological Aspects

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Oxylinps have been emerging as important signal transduction molecules widely distributed in animals and plants, where they regulate a variety of events associated with physiological and pathological processes. The family embraces several different metabolites that share a common origin from the oxygenase-catalyzed oxidation of polyunsaturated fatty acids (1). Biological role of these compounds has been especially studied in mammals and higher plants, although a varied and very high concentration of these products has been reported from marine algae.

In this contribution, we will give a summary of our results concerning the chemical characterization of diatom oxylins with a special attention to the biosynthetic aspects (2-6). In addition to aldehydes, we will show that diatoms contain other enzymatic activities that lead to the generation of a plethora of fatty acid derivatives, including hydroxy, keto and epoxy alcohols. The communication will discuss key aspects of the lipid chemistry and bio-organic chemistry in diatoms from laboratory cultures and marine collections, focusing on metabolite characterization and biochemical pathways. Starting from the ecological role of toxic aldehydes in marine diatoms (7-8), we first proved that chloroplast-derived glycolipids are the main substrates of the above pathways. The processes, that are associated to formation of free fatty acids and lyso compounds from polar lipids but not triglycerides, seem to be regulated by acyl hydrolase activity instead of a PLA₂ as previously suggested. Preliminary characterization of the lipolytic enzymes reveals a protein of about 45 kDa forming in native conditions molecular aggregates (9). The biochemical process shows a simple regulation based on decompartmentation and mixing of preexisting enzymes and substrates, as formation of the oxylinps is immediate after cell disruption. The mechanism, that is similar to that described in the diatom-dominated blooms in North Adriatic Sea, validates a general model to generate toxic substances within this group of microalgae.

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