

Marine Biomolecules

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The diversity of marine ecosystem and the overall dimension of this part of our planet are very impressive. Oceans include the greatest extremes of pressure, temperature and light and habitats can range from tropical waters to ocean trenches, several kilometers below sea level at high pressure. However with its 70% of the surface of our planet, marine ecosystems and related organisms still remains largely unexplored, understudied and underexploited in comparison with terrestrial counterparts.

Comparing the amount of scientific hits (articles, reviews, patents, etc.) containing the three concepts of “marine enzymes”, “marine natural products” and “biocatalysis”, during last decades (1961-2009) the well known exploit for biocatalysis related articles, starting around 1980, cannot be recognized for the concepts “marine natural products” or “marine enzymes” both showing indeed a similar slow-increasing trend over the whole half century (1961-2009). Even considering cautiously the above examination it can be derived that marine enzymes have been mostly neglected by organic chemists’ practicing biocatalysis, otherwise a major number of articles should be found for the concept “marine enzymes” descending by biocatalysis exploit. A few words on the complexity of marine environments could reveal the reasons for this forgetfulness. The complexity ranges from symbiotic relationships to biology and chemistry of defence mechanisms and from chemoeology of marine invasions up to the strategies found in prokaryotes to adapt to extreme environments. Today the interdisciplinary study of this complexity will enable researchers to find an arsenal of enzymes and pathways greatly demanded in biotechnological applications. In particular the adaptation of marine organisms to a wide range of environmental conditions in the specific environment (temperature, salinity, tides, pressure, radiation, light, etc.) made them an enormous reservoir of interesting biological material for both basic research and biotechnological improvements. As a consequence marine ecosystem can be valued as a source of enzymes and other biomolecules exhibiting new functions and activities to fulfill human needs. Indeed, in recent years it has been recognised as an untapped source of novel enzymes and metabolites even though, with regard to the assignment of precise biological functions to genes, proteins and enzymes, it is still considered as the least developed. As far as marine enzymes are concerned they may carry novel chemical and stereochemical properties, thus biocatalytically oriented studies (testing of suitable substrates, appropriate checking of reaction conditions, study of stereochemical asset of catalysis) should be performed to appropriately reveal this “chemical biodiversity” which increases interest for these enzymes. Using metagenomics to recover genetic material directly from environmental samples, this biogenetic diversification can be accessed but despite recent contributions from metagenomic technologies the new field requires major improvements.

As shown in the present literature [1-8], novel chemical and stereochemical properties found in examples of marine biocatalysts should be appended to the list of habitat related characteristics possessed by marine enzymes. Important examples have been found among oxidoreductases where enzymes with different stereoselectivity are observed with respect to terrestrial counterparts adding value to the often observed usual resistance to high salt concentration and/or organic solvent resistance of marine enzymes. In the realm of enzymes

used by marine organisms to face environmental pollution, very interesting examples are noticed which are characterized by a potent chemical action on non-activated carbon atoms difficult to manage by pure chemical routes. Also in these cases substrate preferences and positions of functionalization could differ from known examples. Among enzymes acting on carbohydrates, potency of catalytic activity, in terms of both large number of enzymes and particular catalytic characteristics, can be outlined. Among others the tendency about polyglycosylation is an interesting common quality of enzymes originating from *Aplysia* and other enzymes of marine origin although this aspect deserves in-depth examination. Important in this realm are polysaccharidases from marine micro- and macroorganisms. The case of fucoidan, an important polymer possessing diverse biological activities, including anti-tumor, immunomodulatory, antibacterial, antiviral, anti-inflammatory, anticoagulant and antithrombotic effects show us the importance of fucoidanase acting hydrolytically on it for the preparation of low molecular weight oligosaccharides for structure-activity relationship studies. From the digestive fluid of *Aplysia kurodai* a mannan-degrading activity has been recognized as an important enzyme to produce manno-oligosaccharides. Mannan and related degradation products, i.e., manno-oligosaccharides, have been attracting research and industrial attention in the food and pharmaceutical domains for various beneficial effects on human health that these molecules possess. As far as lipid active hydrolases are concerned, interesting unusual characteristics are also found among enzymes acting on wax esters coupled to cold adaptivity. Other hydrolytic activities specific for different substrates (proteins, phosphate esters, etc.) include very interesting examples. Generally speaking, there is a large technological interest in hydrolytic enzymes in the processing of organic material for exploitation as food or animal feed. Marine enzymes are recognized as advantageous in the hydrolysis of organic waste coming from seafood farming. Great advantage from marine enzymes has been demonstrated also by studies on epoxide hydrolase with the possibility of setting up an enantioconvergent application for the production of interesting diol with specific stereochemistry.

The importance of all examples reported and the many patents found concerning use and applications of marine catalysts in various technological fields remind us of the marine environment. The potential of this habitat should be thoroughly known and possibly the way for access to a useful biocatalysts should avoid destructive large-scale collections of marine biomass for enzyme production. These two aspects are day by day becoming of interest and a future increase

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Received October 26, 2013; **Accepted** October 28, 2013; **Published** October 30, 2013

Citation: Trincone A (2013) Marine Biomolecules. Oceanography 1: e104. doi:[10.4172/2332-2632.1000e104](https://doi.org/10.4172/2332-2632.1000e104)

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in the use of marine enzymes in biocatalysis should be expected. As demonstrated here, the enormous pool of biodiversity found in marine ecosystems is an excellent source for collecting an inventory of diverse biocatalysts.

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