Chapter 13
Antipathin

Abstract Antipatharians are characterized by an erect, rigid chitinous skeleton that create long unbranched whip-like coil or tree-like, unbranched colony. The skeleton of black corals represents a structure typical for a laminated composite. However, the detailed inorganic-organic composition can differ from one species to another. Different elements that can be found in the skeleton are carbohydrates, lipids, sterols and phenols. Bromine as well as iodine seem to be the main single elements. In the antipatharian, during the skeletal formations the dominant structural components are represented by chitin and an antipathin, some kind of halogenated scleroprotein. Antipathin appears to be related with specific material properties of skeletons of black coral. The antipatharians skeletons are less rigid and more elastic in comparison to another biomaterials used as structural components in the nature such as bone, wood, insect cuticle and mollusc shell. Simultaneously, the density of antipathin is lower than bone or shell and higher than wood, but almost similar to cuticle of arthropods.

13.1 Brief Introduction in to Antipatharia

The clonial cnidarians black corals (Antipatharia) are marine organisms existing world-wide. Within the Antipatharia order (Milne-Edwards and Haime (1857) (Cnidaria, Anthozoa) there are 235 species (Schultze 1896; Totton 1923; Brugler and France 2007; Wagner et al. 2012) belonging to 39 genera and 6 families (Opresko 1974). In the 1700s, the systematic studies regarding black corals have been performed, then at the beginning of 1900s a few monographs regarding taxonomy of black corals were published such as a ground-breaking works prepared by Brook (1889), Schultze (1896), and van Pesch (1914), most of them were based on diverse oceanographic expeditions (see for overview Delage and Hérouard 1901; Cooper 1909; Kinoshita 1910; Pasternak 1977; Warner 1981; Grigg and Opresko 1977; Echeverria 2002; Loiola 2007). Both the ecology and biology of black corals have been recently reviewed by Bo (2008), Prouty et al. (2011), Wagner et al. (2012), Brugler et al. (2013), Carreiro-Silva et al. (2013), Cardona et al. (2016), and Álvarez-Valero et al. (2017).

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All species are characterized by slow growth, low natural mortality in adulthood and, consequently, by a long life. They achieve reproductive maturity rather after 10 years, which is much later in comparison with other similar marine organisms. The output of planula (lasrvae) as well as the recovery of organism is slow. Polyps possess dimensions in the range of 0.5–5 mm (Nowak et al. 2009). The age of such deep-sea black coral as *Leiopathe*s sp. has been estimated using radiocarbon analysis of around thousands years old. The oldest known organism *Leiopathes* sp. was 4265 years old (Roark et al. 2009).

Antipatharians possess a straight, stiff, chitinous skeleton in the form of a branched colony or an extended lash-like reel (similar to wire) (Fig. 13.1). The skeleton structure of antipatharians can be consider as a laminated composite, comprised of the fibrils of chitin together with the non-fibrillar protein, but the detailed chemical composition can be different for different species. The carbohydrates, lipids sterols and phenols can also exist within the skeleton, but the bromine and iodine are the major single component (Juárez de la Rosa et al. 2007).

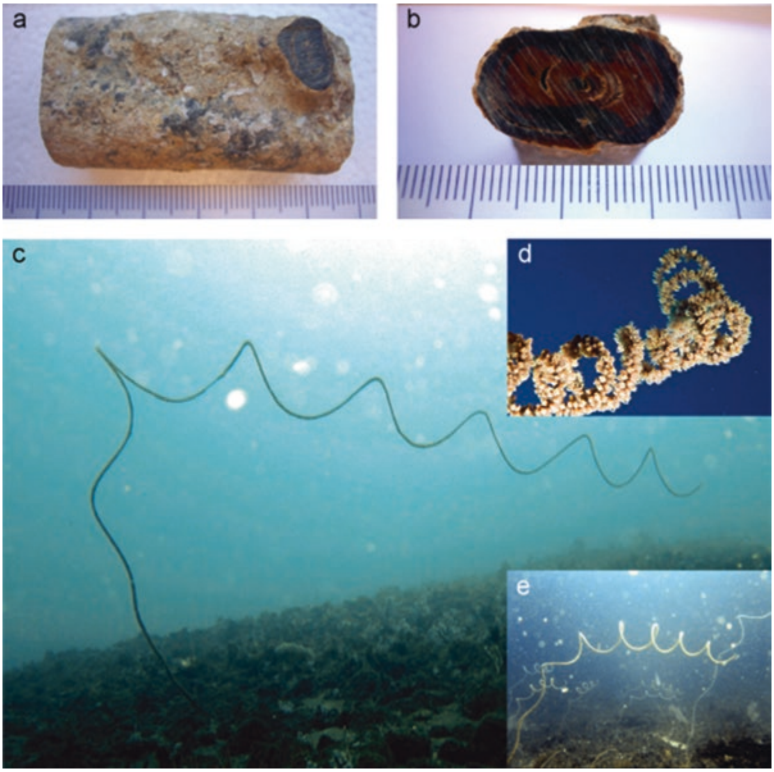

Fig. 13.1 Black corals contain gorgonin- and chitin- based very rigid skeletons (**a**, **b**) that forms a tree-like and branched colony or a huge meters-long whip-like coil that remains to be unbranched (**c**–**e**). (Images courtesy Marzia Bo, Giorgio Bavestrello and Mark Spencer)

Now, it is well recognized that the age of antipatharian corals can be estimated using the characteristic ring structures well visible on the cuts of the skeletons (Goldberg 1978). Similar to selected species of red corals, special information (e.g., on the salinity and water temperature in chronological order,) which can be potentially stored in the rings could be useful for corresponding scientific aims.

The importance of black corals for commerce and the special field of jewellery is well known since ancient times (Hickson 1924). In spite of still existing consumption of black corals in the jewellery trade, the tools of the black coral origin are listed in the Convention for the International Trade in Endangered Species (CITES) (Wood and Wells 1988).

13.2 Chemistry of Black Corals

The major structural constituents of the antipatharian skeletal formations are chitin and a halogen-containing scleroprotein known as antipathin. For instance, based on the NMR results the content of organic matter within the load bearing skeletal plate of *Antipathes fiordensis* (the New Zealand black coral) was established to be 70% protein, 15% diphenol, 10% chitin, and 5% lipid by weight (Holl et al. 1992). The *A. fiordensis* tips or younger pinnules possess not more than 3% diphenol by weight.

Hydrochloric acid treatment led to extract 3,4-dihydroxybenzaldehyde (DOBAL) and 3-(3,4-dihydroxyphenyl)-IX-alanine (DOPA) from the coral skeleton. The base of *A. fiordensis* has more DOPA the tips, additionally DOPA acts as a peptidyl component in the skeletal protein. The DOBAL and DOPA oxidation lead to obtain quinones which can be responsible for the structural proteins cross-linking to chitin or other proteins which provides mechanical stabilization of the coral skeleton (Holl et al. 1992; Kim et al. 1992).

The "antipathin" is commonly used definition to discern the "gorgonins" from these proteins. This name has been proposed for this phenol-based biological material prior to the discovery of corresponding chitin fraction (Roche and Eysseric-Lafon 1951). The highest histidine content of any known protein has been reported for antipathin (Roche and Eysseric-Lafon 1951). Additionally, iodohistidine was also detected in the skeletons of black corals (Goldberg 1976).

Antipathin, also possesses all the characteristic properties for sclerotized protein, as in the case of gorgonin (Brown 1950): proteolytic agents does not affect it, high in tyrosine, mostly dark in color, and dissoluble only in chlorine bleach. The autoclaving do not make antipathin soluble. Collagenous origin of this biomaterial has not be confirmed (Goldberg 1976). The extraordinary stability of antipathin can be explained by the existence of crosslinking between iodinate histidine and tyrosine, but the role of huge amount of histidine is still unknown. The typical stain for connective tissues such as the Mallory's, Gomori's or van Gieson's gave negative results. The only histochemically detectable polysaccharide was a sialic acid, the function of which remains to be known. Thus, the material composition, reactivity together with structure implies that it is not composed of keratin or collagen

(Goldberg 1976). Also, there is lack of any kind of scientific information in the available literature concerning the hypothetical role of antipathin in both biosilicification, or calcification.

Similar to diverse demosponges, iodine is to be found in a number of antipatharians (Roche et al. 1963; Goldberg 1976). Probably, due to high amounts of iodine in *A. salix* some kind of iodine dependent cross-linking mechanisms exists within skeletal structures of this species. It has been reported that also bromotyrosine as well as bromohistidine may also be present as in the skeletons of gorgonian corals (Roche et al. 1963). However, these compounds have yet to be isolated and identified in antipatharians.

The skeletons of all species of black corals possess significant chitin amount, which varied between 6% and 18% of the total mass of the skeleton (Nowak et al. 2009). In *Antipathia salix* the amount of chitin is equalled 14.5% of the skeletal mass (Goldberg 1976). Although, significant differences in the amount of both chitin and antipathin have been shown for diverse species of black corals. For instance, the amount of chitin in skeleton of *A. salix* estimated by NMR was two times higher that of *Antipathia fiordensis* (Holl et al. 1992). Determination of chitin content by the measuring of glucosamine content was applied by Kim et al. (1992). Authors showed that tips of *A. salix* contained about 29% more chitin than *A. fiordensis.*

Recently, the presence of morphologically distinctive multilayer hybrid structures in black corals from three different locations was reported by Nowak et al. (2009). The matrix consists of α−chitin, which content is equalled approximately 15% of its weight, supplemented by a various of carbohydrates and proteins. The chitin crystallites locations varied in different zones; the fibrils of chitin have 4 μm in width and they are located along the cells long axes in the interior zone. However, in the skeletal hydrolysates of antipathins studied previously, tyrosine is not prominent (Goldberg 1976). However, a relatively large amount of tyrosine is tightly bound with the chitin of the skeleton origin, implying an important role of covalent bonding between protein and chitin.

It was proved by morphological observation that, the axial structure of antipatharians is composed of a core encased in a number of special cells (for details see Nowak et al. 2009) related to intermediate gluing layers known also as "*layers of organic cement*" (Holl et al. 1992). Corresponding clusters of periodic opaque cement can be responsible for the growth-ring pattern and lines between skeletal layers (Goldberg 1991). The variations in chemical composition of the black coral and periodicity of its structure can be related to fluctuations in environment and thus could act as a record of local environmental conditions (Holl et al. 1992; Goldberg 1978).

Guerriero et al. (1988) discovered so called leiopathic acid (hydroxydocosapenthaenoic acid) in the black coral *Leiopathes* sp. Unfortunately, there is no suggestion concerning the possible role of this fatty acid with respect to formation of some skeletal structures of antipatharians.

13.3 Material Properties of Antipathin-Based Skeletons

Skeletons of black corals can be assumed as laminated composites formed from antipathin and chitin fibrils (Bo et al. 2012). However, the layers in antipatharian skeleton remain not to be simple laminated constructs. It seems that the helically wound skeleton is fixed at multiple points due to a fact that, the spines are inserted and cemented layer upon layer (Goldberg and Taylor 1989a, b). Kim and co-workers hypothesised that "the occurrence of spines increases the surface area for cementing one skeletal layer to the other. Moreover, they could have an important role as continuous rivets, resisting delamination of shear forces produced by skeletal bending and torsion. If this statement is true, the occurrence of spines might eliminate or reduce the demand of small fibril biases between helically wound layers" (Kim et al. 1992).

The antipatharians skeletons are less rigid and more elastic than other biomaterials chosen and used in the nature as structural components such as bone, mollusc shell, wood as well as the insect cuticle. Simultaneously, the density of antipathin is lower than bone or shell higher than wood, but almost the same as cuticle of arthropods (Wainwright et al. 1976).

The specific modulus is recognized as the ratio of Young's modulus to density (E/p), and is used for evaluation of the stiffness per unit weight of corresponding materials. Low values of specific stiffness are usually considered to be inferior to high values because, these high values enable construction of lighter but stiffer structures. Although, in the case of antipatharians (Goldberg 1976; Kim et al. 1992), higher flexibility per unit of density seems to be more significant than stiffness. Consequently, black corals possess a lower specific modulus in comparison to values characteristic for insect cuticle presented by Wainwright et al. (1976).

There is an increasing amount of evidence describing a relationship between ecological function and the biomechanics of skeleton (Kim et al. 1992). Orientation to flow can reduce drag forces and increase suspension feeding efficiency in organisms with flexible skeletons (reviewed by Wainwright et al. 1976). In some gorgonian corals, acclimatization to flow can be observed in the skeleton of fan-like species as a variation in preferred orientation (Wainwright and Dillon 1969; Grigg 1972). For example, deposition of calcium carbonates within the skeleton of some branched gorgonians can lead to perpendicular reinforcement to the flow direction (Wainwright et al. 1976; Wainwright and Koehl 1976).

There are no doubts that the mechanical and structural features of the skeleton of black coral appear to be overdesigned for the hydrodynamically more docile, deeper zones where antipatharians are usually occur.

However, fitting the skeletal design to ecological function is unclear, the contradistinction between these two studied specimens has indicated that *A. salix* is harder, more hydrophobic, darker, denser, and stiffer than *A. fiordensis* (Kim et al. 1992; Holl et al. 1992). The differences in material properties of this species seem to reflect higher commercial request of *A. salix* as the subject of jewellery.

High stiffness which enables the construction of light and strong skeletons is definitively a benefit. The hardness of the skeleton of both antipatharians is hard enough to scratch calcite and is equalled 3 on the Mohs scale (Nowak et al. 2009). It seems to be bizarre that invertebrates which live in conditions which do not allow to get a lot of energy have decided to build such an energy-consuming and refined skeleton construct made of chitin instead pure mineral-based skeleton. It can be suggested that the elastic organic skeleton can obey the natural wave movements of the water currents. Additionally, the organism saves the energy, after the initial expending of material and energy on formation of the skeleton, with a "large total surplus over the scale of a life time (~40 years for colonies reaching a maximum of 1.8 m in height)" (Nowak et al. 2009).

13.4 Conclusion

Mechanical and physical properties of the skeletons of black corals are likely to imitate the nature, architecture and relative abundance of corresponding biopolymers, which stabilize their inner structure. Comprehension this high degree of variety with reference to the chemical and structural properties of antipatharians is a challenging point. The commercial harvest for jewellery purposes together with deep-fishing is a big risk for the conservation of deep-sea coral colonies including black corals. I take the liberty to agree with Brendan Roark, who recently noted that "*in light of the unusual longevity of black corals, a better understanding of deep-sea coral ecology and their interrelationships with associated benthic communities is needed to inform coherent international conservation strategies for these important deep-sea habitat-forming species*" (Roark et al. 2009).

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