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Minireview

Phycobiliproteins and phycobilisomes: the early observations

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Abstract

The purpose of this minireview is to highlight the early observations that led to the discovery of the physicochemical properties of the phycobiliproteins, their structure and function, and to their architectural organization in supramolecular complexes, the phycobilisomes. Generally attached on the stromal surface of the thylakoid membranes in both prokaryotic (cyanobacteria) and eukaryotic cells (cyanelles, red algae and cryptomonads), these complexes represent the most abundant soluble proteins and the major light-harvesting antennae for photosynthesis. This review mainly focuses on the years prior to the development of the molecular biology of cyanobacteria that flourished in the 1980s. We refer the reader to the comprehensive and excellent review by Sidler (1994) for more recent discoveries and more detailed literature on this topic.

'It would be difficult to find another series of colouring matters of greater beauty or with such remarkable and instructive chemical and physical peculiarities.'
– H. Sorby, 1877

Introduction

As early as 1836, Nees Esenbeck described a brilliantly blue-colored, red-fluorescent, photo-labile and water-soluble pigment released by the cyanobacterium *Oscillatoria* sp., which he designated 'saprocyanin'.[1] A few years later, Kützing (1843) renamed this pigment 'phykokyan'[1] – *a name more appropriate to its beautiful blue color* – and he isolated a water-soluble red pigment, the 'phykoerythrin,'[1] from a number of red algae (Figure 1). In 1854, Sir G.G. Stokes performed the first spectroscopic analyses – *important bases for the development of the concept of the Stokes shift* – and noted the intense orange fluorescence of this red pigment. This observation was confirmed by Sorby (1877) who reported on the strong orange and red fluorescence of phycoerythrin and phycocyanin, respectively, from groups of red algae and the cyanobacterium *Oscillatoria nigra*. Sorby (1877) also provided the first evidence for allophycocyanin based on thermal denaturation studies of 'purple and pink phycocyan' solutions containing 'clean white lump (of) sugar'! In 1888, Schütt (1888) showed that wavelengths of light between 486 – 600nm had the power of exciting fluorescence of phycoerythrin in solution, the maximum emission being situated between 560 and 590 nm. Hanson (1909) later proposed that blue light caused the orange fluorescence of phycoerythrin which assisted light assimilation by 'degrading' it to yellow and red wavelengths corres-

Figure 1. Purified phycobiliproteins. allophycocyanin (left), phycocyanin (center) and phycoerythrin (right). Adapted from Tandeau de Marsac, Biofutur, no. 121, 1993. For a color version of this figure, see color section in the front of the issue.

ponding to those absorbed by chlorophyll – *a kind of energy transfer from phycoerythrin to chlorophyll was thus anticipated!*

Are phycoerythrin and phycocyanin true proteins?

Two forms of crystals of 'rhodospermin,' obtained by Cramer (1862) from a red alga, were thirty-two years later recognized by Mölisch (1894) to be phycoerythrin. Mölisch (1895) obtained the first crystals of phycocyanin. According to Hanson (1909), phycoerythrin was '... probably a colloidal nitrogenous substance, related to protein, but not a true protein ....' Kylin (1910, 1912) succeeded in separating phycoerythrin and phycocyanin in a pure state from a red alga, analyzed their spectral characteristics and concluded from the properties of the crystals that both phycobiliproteins resembled hemoglobin in being made up of two components, one proteinaceous, as proposed by Mölisch (1895) and one pigment. The name 'phycochromoproteid,' originally proposed by Kylin, was replaced by 'phycobilin' following the work of Lemberg (1928, 1930, 1930), who found that the chromophoric groups of phycoerythrin and phycocyanin were both related to animal bile pigments. The chromophores being strongly bound to their protein counterpart, several attempts to isolate the prosthetic groups of phycocyanin and phycoerythrin generated artifacts due to degradation (for a discussion on that topic, see O'hEocha 1965). Thanks to C. O'hEocha (1958), and to many other researchers, who modified the extraction procedures and used various analytical-chemical methods, the spectral properties and structure of the chromophores, and their mode of linkage to the proteins began to be elucidated in the 1960s (for reviews, see O'hEocha 1962, 1965; Siegelman et al. 1968; Rüdiger 1970,1975; O'Carra 1970; Scheer 1981). At present, four main types of chromophores-phycoerythrobilin, phycocyanobilin, phycourobilin and phycobiliviolin-covalently bound by thioether linkages to their cognate proteins, have been characterized from red algae and cyanobacteria, and five additional ones from cryptomonads (for a review, see Sidler 1994). Three major phycobiliprotein families – the phycoerythrins, phycocyanins and allophycocyanins – are present in red algae and cyanobacteria, but only the first two are present in cryptomonads. Prefixes to phycobiliprotein classes were initially proposed by Svedberg and Katsurai (1929) to be used for distinguishing their taxonomic origin (R- for red algae, C- for cyanobacteria). However, after the discovery of two spectrally slightly different phycoerythrins in primitive red algae of the order Bangiales, B-phycoerythrin (Airth and Blinks 1956) and b-phycoerythrin (Gantt and Lipschultz 1974), the nomenclature of 'R' for red algae was no longer valid. Consequently, these prefixes no more refer to the type of source organisms but denote their specific spectral characteristics.

Structural units of the phycobiliproteins

Although generally obtained as high molecular mass complexes ranging from approximately 100,000 to 208,000 daltons, T. Svedberg and co-workers (Svedberg and Lewis 1928; Svedberg and Katsurai 1929; Svedberg and Eriksson 1932) found the minimum assembly unit of phycocyanins and phycoerythrins to be about 34,700 daltons at alkaline pH. In the 1970s, smaller and more precise values emerged from further studies of the physico-chemical properties of these phycobiliproteins. In their native forms, they were shown to consist of two dissimilar subunits, α (M_r 10 000–19 000) and β (M_r 14 000–21 000), in a 1:1 molar ratio (Bennett and Bogorad 1971; Glazer and Cohen-Bazire 1971; O'Carra and Killilea 1971; Gysi and Zuber 1974). An additional subunit of a larger molecular mass (M_r 30 000) was found in B-phycoerythrin, but not in b-phycoerythrin in the red alga *Porphyridium cruentum* (Gantt and Lipschultz 1974).

The aggregation states for red algal and cyanobacterial phycobiliproteins in solution depend on the purification protocol and the source (i.e., the organism).

However, with the exception of the subunit structure of B-phycoerythrin determined to be $(\alpha\beta)_6\gamma$ (Glazer and Hixson 1977), the most frequently found aggregation states were hexamers $(\alpha\beta)_6$or trimers$(\alpha\beta)_3$(Berns and Edwards 1965; Craig and Carr 1968; Neufeld and Riggs 1969; MacColl et al. 1971; Cohen-Bazire et al. 1977). The structure of the phycocyanin hexamers examined by electron microscopy revealed a round, disc-like structure of 120–130 Å in diameter and 60 Å in height. Moreover, with fresh extracts of cyanobacterial cells, short rods of stacks of disc-shaped hexamers were also observed (Berns and Edwards 1965; Kessel et al. 1973)). X-ray diffraction studies by Dobler and co-workers (1972) indicated the crystal units of phycocyanin from *Mastigocladus laminosus* to consist of two trimers and served as a basis for the determination of the crystal structure of this phycobiliprotein at high resolution by T. Schirmer and co-workers in the mid 1980s (for a review, see Sidler 1994).

From fluorescence polarization analyses of purified phycobiliproteins, Dale and Teale (1970) and Teale and Dale (1970) concluded that phycoerythrin and phycocyanin contain two types of chromophores, a sensitizing ('s') and a fluorescing ('f') ones. According to Alexander Glazer and co-workers (Glazer and Fang 1973a; Glazer et al. 1973), the β and α phycocyanin subunits carried two s-type and one f-type chromophores, respectively, with the energy absorbed by the β subunit being transferred, *via* the α subunit, to the next acceptor. Such a process could indeed provide an efficient directional flow of energy to the chlorophyll (Chl) *a* located in the thylakoid membrane (for reviews, see Glazer 1976, 1989). Figure 2 shows Alexander Glazer and several other scientists involved in phycobilisome research. [See Brody (2002) and Mimuro (2002) for early energy transfer measurements.] Glazer and co-workers (Glazer et al. 1973; Glazer and Fang 1973b) were the first to perform *in vitro* reconstitution of a phycocyanin indistinguishable from the native protein. Importantly, these experiments demonstrated that the formation of the phycocyanin monomer $\alpha\beta$ was not accompanied by major changes in the spectra of the chromophores (Glazer 1976).

Acclimation to the light intensity or to the spectral light quality?

At the end of the 19th century, Engelmann (1883, 1884) attributed the vertical distribution of seaweeds to their ability to synthesize pigments complementary to the spectral quality of the incident light. This observation was in disagreement with Oltmanns (1892) who proposed vertical distribution to be determined by the light intensity rather that the light quality. However, the acclimation process, called by Engelmann (1902) 'complementary chromatic adaptation' (CCA), was confirmed by further detailed studies. Gaidukov (1902, 1903a,b, 1923) showed that the cyanobacterium *Oscillaria sancta* became red when grown under green light and blue green after growth under orange light. Moreover, Boresch (1919, 1921) described that the change in color corresponded to a change in the proportion of phycoerythrin and phycocyanin, and that CCA occurred only in some cyanobacterial strains that contained phycoerythrin.

The divergent views of Engelmann and Oltmans were reconciled by Harder (1923), who proposed that pigment adaptation of seaweeds depended on both the color and intensity of the light available at different water depths, a proposal later confirmed by several groups on various algae (Brody and Emerson 1959; Jones and Myers 1965; Ghosh and Govindjee 1966; Ramus et al. 1976a,b). In these cases, however, the acclimation to the light spectral quality led to a change in the ratio of the accessory pigments to Chl *a*, a phenomenon called inverse chromatic adaptation that occurs in all photosynthetic organisms and differs from CCA in which Hattori and Fujita (1959a) and Fujita and Hattori (1960) showed that *Tolypothrix tenuis* cells specifically synthesize pigments with the highest absorbance for the incident wavelengths, i.e., phycocyanin under red light and phycoerythrin under green light. Thanks to a collection of pure cyanobacterial strains, established on R. Y. Stanier's initiative in the 1960s, a large survey by Tandeau de Marsac and Cohen-Bazire (1977) demonstrated that among chromatic adapters two groups could be distinguished. In the first group, cells modulated the synthesis of phycocyanin under red light and phycoerythrin under green light, while in the second one only the synthesis of the latter pigment was regulated.

The pioneering work of Y. Fujita and A. Hattori (Hattori and Fujita 1959a, 1959b; Fujita and Hattori 1962, 1963) revealed that CCA was controlled by a photoreversible pigment responding to green and red

Figure 2. Alexander N. Glazer and Marcel Lefort-Tran (top left), Nicole Tandeau de Marsac (top right) Donald Bryant (middle left) and Germaine Cohen-Bazire (middle center) at the IVth International Symposium on Photosynthetic Prokaryotes in Bombannes, France, in 1982. Elisabeth Gantt (middle right) and Herbert Zuber (bottom right) at the Japan-US symposium on Phycobiliproteins in Okazaki, Japan, in 1982. Lawrence Bogorad (bottom left) in his office in 1975. Yoshihiko Fujita (bottom center) when he visited Elisabeth Gantt's laboratory in 1995.

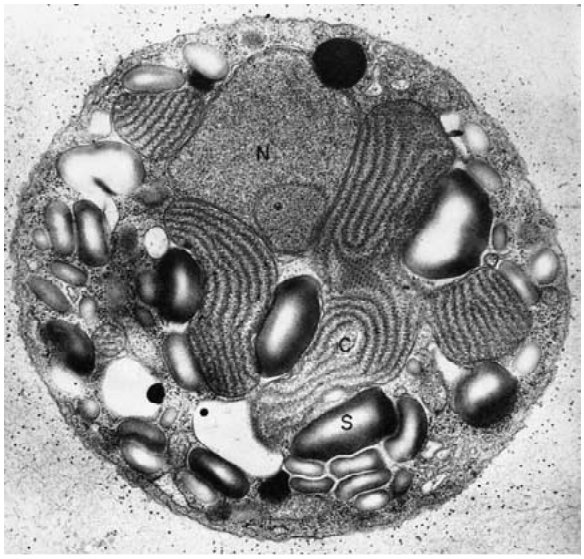

Figure 3. Electron micrograph of a section of the red alga *Porphyridium cruentum*. N – nucleus; C – chloroplast with phycobilisomes visible on the outside of the lamellae; S – starch. Reproduced from Gantt and Conti (1966).

irradiations (with maxima around 541 nm and 641 nm, respectively) in *Tolypothrix tenuis*. These results were later confirmed by radioisotopic experiments on exponentially grown cultures of *Fremyella diplosiphon* (Bennett and Bogorad 1973) and by the action spectra for phycobiliprotein synthesis performed by different groups on three cyanobacterial strains (Diakoff and Scheibe 1973; Haury and Bogorad 1977; Vogelmann and Scheibe 1978; Tandeau de Marsac et al. 1980). Although the action maxima for the cyanobacterial photoreversible pigment were different (541/641 nm) from those of the plant phytochromes (660/730 nm), both photoreceptors were suspected for a long time to belong to the same protein family. It is only very recently, however, that cyanobacterial phytochromes were found in chromatic adapters (Kehoe and Grossman 1996; Herdman et al. 2000; see Grossman, this issue) and there still remain uncertainties, since, in no case, there exists a definite proof that such molecules carry a chromophore *in vivo*, leaving open the possibility that they may act downstream in the signaling cascade rather than in the perception of the spectral light quality.

The phycobilisome: a supramolecular complex

With the introduction of electron microscopy studies in the late 1950s, new insights were put into the structure and organization of the phycobiliproteins *in vivo*. The work of William Arnold and Oppenheimer (1950) indicated that phycocyanin should be separated by no more than 40 Å from the membrane-bound Chl *a* to account for the high efficiency of the energy transfer. Jack Myers and collaborators (Myers and Kratz 1955; Myers et al. 1956) noticed that phycobiliproteins were a major constituent of red algal and cyanobacterial cells, representing up to 24% of the cell dry weight in the cyanobacterium *Anacystis nidulans* and proposed that the 22 nm granules visible between thylakoids were aggregates of these pigments. In agreement with these earlier observations, excellent ultrastructural studies by Elisabeth Gantt and coworkers (Gantt and Conti 1965, 1966a, b) on the red alga *Porphyridium cruentum* and some cyanobacteria demonstrated that phycobiliproteins were organized in alternating macromolecular structures arranged in regular rows on the stromal surfaces of the thylakoids (Figure 3). These granules of about 400 Å in diameter, twice larger than ribosomes, were given the name 'phycobilisomes' (Gantt and Conti 1966a,b). Subsequent work by Gantt and other research groups (for a review, see Gantt 1980) found a similar location and organization of the phycobiliproteins in diverse red algae and cyanobacteria.

The original method developed by Gantt and coworkers (Gantt and Conti 1966b; Gantt and Lipschultz 1972) to isolate phycobilisomes from *Porphyridium cruentum* was later adapted by the same group and many others to isolate these structures from diverse cyanobacteria and red algae (for a review, see Sidler 1994). Based on the examination of isolated phycobilisomes by electron microscopy, different morphological types were described: hemi-ellipsoidal, hemi-discoidal, block shaped and bundle shaped (for a review, see Sidler 1994). The latter type, which forms a cortical layer on the inner surface of the cytoplasmic membrane, was only found in an unusual cyanobacterium *Gloeobacter violaceus* that does not possess thylakoids (Rippka et al. 1974; Guglielmi et al. 1981).

Gantt and Lipschultz (1974) initially reported that phycobilisomes isolated from *Porphyridium cruentum* only consisted of phycobiliproteins with 84% B- and b-phycoerythrin, 11% R-phycocyanin and 5% allophycocyanin. However, in 1977, Tandeau de Marsac and Cohen-Bazire (1977) found that cyanobacterial phycobilisomes consisted of 85% of phycobiliproteins and 15% of polypeptides which, in contrast to the pigmented phycobiliproteins, were uncolored. Although accepted with doubt by some researchers, three mo-

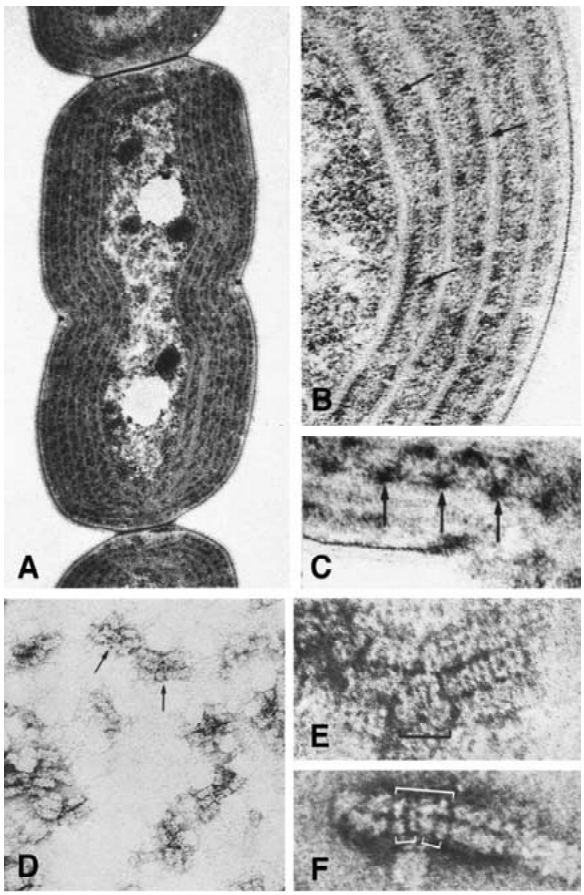

Figure 4. Electron micrographs of thin sections of cells and isolated phycobilisomes from the cyanobacterium *Pseudanabaena* sp. PCC 7409. (A) Dividing cell (18 000 ×). (B) Enlargement of a portion of a cell section perpendicular to the thylakoid surface. Rows of phycobilisomes (arrows) in longitudinal section (80 000 ×). (C) Enlargement showing rows of phycobilisomes in cross section (100 000×). (D) Isolated phycobilisomes from cells grown in red light (110 000 ×). (E) and (F). Electron micrographs of a phycobilisome isolated from cells grown in white light, in face view and base 'up,' respectively (350 000 ×). Adapted from Bryant et al. (1979).

lecular mass categories of linker polypeptides were confirmed to be unambiguously present in cyanobacterial and red algal phycobilisomes (for reviews, see Glazer 1984, 1989; Sidler 1994). Only the largest linker polypeptide, the core-membrane linker (L_{CM}), was later found by Glazer's group to carry one phycocyanobilin chromophore (Lundell et al. 1981). The discovery of the linker polypeptides was rapidly followed by the description of a three-dimensional structure of phycobilisomes from cyanobacteria by Don Bryant and co-workers who coupled biochemical and electron microscopy studies (Bryant et al. 1979) (Figure 4). This first model for cyanobacterial phycobilisomes was the basis for more detailed investigations of their structure and function by Glazer's group and other laboratories (for reviews, see Glazer 1984, 1989; Sidler 1994).

Phycobilisomes transfer light energy for photosynthesis

The pioneering work of Engelmann (1881, 1882, 1883, 1884) on the participation of chlorophyll, carotenoids and phycobiliproteins in photosynthesis led to the demonstration that phycocyanin and phycoerythrin, but not Chl *a* and carotenoids, were used to drive photosynthetic oxygen production in these particular systems. To quantify the oxygen produced by the algae exposed to light, Engelmann had the wonderful idea of using the property of aerotactic bacteria to accumulate in the area with the highest concentration of oxygen – the first 'Mikrospectrum' for photosynthesis was realized! Although perfectly correct in his conclusions, Engelmann's work was vigorously criticized by several opponents to his theories and long neglected. About 60 years later, however, the major role of the different phycobiliproteins from red algae and cyanobacteria in light-harvesting for photosynthesis was largely confirmed and quantitatively established by several groups (Emerson and Lewis 1942; Haxo and Blinks 1950; Blinks 1954; Brody and Emerson 1959; Lemasson et al. 1973). By performing high-precision action spectra, C. Lemasson and collaborators (1973) demonstrated that allophycocyanin was more efficient than phycoerythrin or phycocyanin in cyanobacteria and that Chl *a* could become the major light-harvesting pigment under nitrogen starvation. Volk and Bishop (1968) reached similar conclusions from studies of a phycocyanin-deficient mutant of a red alga.

As noted earlier, Arnold and Oppenheimer (1950) established that the migration of light energy proceeds from phycocyanin to Chl *a* by resonance energy transfer, a mechanism described by Förster two years earlier (Förster 1948). Subsequent studies by other investigators suggested that phycocyanin was an intermediate in the light energy transfer from phycoerythrin to Chl *a* (Duysens 1951,1952; French and Young 1952). This energy transfer was shown to occur down to liquid helium temperature (4 K) and the temperature dependence was consistent with the Förster theory (Cho and Govindjee 1970). In the 1970s, it became clear that light energy collected by the phycobili-

proteins within the phycobilisomes was transferred mainly to photosystem II, with allophycocyanin acting as a link between phycocyanin and the membrane-bound Chl *a* (Halldal 1970; Gantt and Lipschultz 1973; Lemasson et al. 1973). However, the detailed description of the energy transfer process within phycobilisomes awaited the work of Glazer and collaborators about 10 years later (for reviews, see Glazer 1989; Sidler 1994).

In 1925, Kitasato determined the first amino acid composition of phycoerythrin followed by others from different phycobiliprotein classes. At the dawn of the molecular biology era, a number of N-terminal sequences and the complete sequence of both subunits of phycocyanin from *Mastigocladus laminosus* were available (Frank et al. 1978). Their comparison, as well as physico-chemical and immunological evidence, led Glazer (for a review, see Glazer 1976) to postulate that allophycocyanin was the evolutionary ancestor of phycocyanin, which in turn preceded phycoerythrin. More recently, in the light of the comparison of complete amino acid sequences of a great number of phycobiliproteins from different spectral classes, these conclusions were revisited. A divergent phylogenetic development of the α- and β-subunit families from a single-subunit ancestor molecule, that gave rise to these subunit families by a gene duplication event, was assumed to reflect the evolutionary changes of the phycobiliproteins over years (for a review, see Sidler 1994).

Conclusion

For more than 150 years, phycobiliproteins and phycobilisomes were extensively studied and revealed a lot of their mystery hidden behind their glowing colors. Their remarkable physico-chemical properties, and their wonderful structure, so precisely fitted to harvest and transfer light energy to the photosynthetic reaction centers, still fascinate researchers and will certainly continue for a long time to hold captivating interest for mankind.

Acknowledgments

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Note

[1]From the Greek: 'sapros,' rotten; 'kyanos,' blue; 'phykos,' seaweed; 'erythros,' red. Phykokyan is nowadays called phycocyanin and phykoerythrin spelt phycoerythrin.

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