Posttranslational modifications (PTM) are one of the most important ways of regulating the biological activity of proteins and enzymes. The following three main PTM categories can be distinguished by the type of reactions: proteolytic cleavage of the polypeptide chain (removal of signal sequences, protein sequences determining its intracellular localization, autocatalytic cleavage of inteins), attachment of a non-protein chemical group (phosphorylation, glycosylation, prenylation, etc.), and formation of inter- and intramolecular bonds (disulfide bonds, ligation of exteins, etc.). PTM occur with the involvement of specialized enzymes performing polypeptide processing and due to autocatalysis. All known protein modifications are present in the RESID database (http://www.ncifcrf.gov/RESID/) [1]. Some enzymes do not need exogenous cofactors and use cofactors that are derivatives of protein structures obtained as a result of PTM [2]. The latter group includes proteins of the GFP family, the chromophore of which is synthesized autocatalytically due to posttranslational reactions that do not require exogenous cofactors except for molecular oxygen [3]. Thus, autocatalytic PTM of GFP-like proteins underlie their unique ability for self-tuning to a certain spectral range [4]. This property is used in the modern molecular and cell biology for the labeling of cell structures [5].

The first representative of the GFP family, green fluorescent protein, was found in 1961 in photocytes of the bioluminescent jellyfish _Aequorea victoria_ [6] belonging to the class Hydrozoa. In 1999, the genes of GFP-homologous proteins with fluorescence in the longer-wavelength spectral region were cloned from non-luminescent corals of the class Anthozoa [7]. In spite of a rather distant homology of primary structures (~20%), fluorescent proteins from the corals have a considerable homology of tertiary structures. Like GFP, the molecules of the homologous proteins are shaped as a cylinder with walls formed of 11 segments of β-folded structures. The α-helix containing the chromogenic sequence of -Xxx-Tyr-Gly-amino acids passes through the central axis of this cylinder. After the cylinder structure has been formed, the protein enters the phase of maturation characterized by autocatalytic reactions within the -Xxx-Tyr-Gly-sequence, which lead to chromophore synthesis and determine the fluorescent properties of the protein. These reactions result in the formation in GFP of a chromophore, i.e. 4-(p-hydroxybenzylidene)imidazolid-5-one (p-HBI), which is spatially located in the center of the cylinder (Scheme 1, structure VI). The p-HBI is also the initial compound at further synthesis of chromophores of homologous proteins from the corals. In the latter case, p-HBI undergoes additional PTM, which introduce changes into its conjugated π-electron system.

In the recent years much experimental material has accumulated promoting deeper insight into the biochem-
Mechanism of biosynthesis of the chromophore of green fluorescent protein. Two alternative schemes of ρ-HBI biosynthesis are presented, on the right and on the left.

Scheme 1