No. 0818

Analysis of Degradation of Chlorophylls in Marine Photosynthetic Prokaryotes

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Summary

Chlorophylls in marine photosynthetic prokaryotes play important roles in photosynthetic activity in the ocean. In contrast, degradation products of chlorophylls such as pheophorbide and pyropheophorbide were reported to have photo-toxicity. We should pay attention to photo-toxic chlorophyll degradation products in foods from the ocean. Therefore, elucidation of chlorophyll degradation in marine photosynthetic prokaryotes and biochemical properties of their degradation products will be useful in the research area of biological chemistry as well as food science. In this project, we study demetalation of chlorophylls *d* and *a*, which is one of the important steps in chlorophyll degradation pathway. In addition, we synthesize and characterize degradation products and their derivatives of chlorophylls *d* and *a*.

Demetalation kinetics of chlorophyll *d* from a cyanobacterium *Acaryochloris marina* under weakly acidic conditions, and is compared with those of chlorophylls *a* and *b*. Demetalation rate constants of chlorophyll *d* possessing a formyl group at the 3-position were smaller than those of chlorophyll *a*, which had no formyl group, but larger than those of chlorophyll *b* possessing a formyl group at the 7-position. In order to the effects of formyl groups on demetalation properties, demetalation kinetics and NMR measurements of bacteriochlorophylls *c* and *e* from green sulfur photosynthetic bacteria were examined. Demetalation rate constants of bacteriochlorophyll *e* possessing a formyl group at the 7-position were significantly smaller than those of bacteriochlorophyll *c*, which had a methyl group at this position. ^{15}N-NMR spectra of ^{15}N-labeled bacteriochlorophyll *c* and *e* isomers, which were purified from green sulfur bacteria grown in a medium containing $^{15}NH_4Cl$, were measured. These spectra suggest that the electron-withdrawing formyl groups of chlorophyll molecules affect electronic states of the chlorophyll π-system and caused chlorophylls possessing a formyl group to be tolerant for demetalation.

Degradation products of chlorophyll *a* and chlorophyll *d* and their derivatives were successfully synthesized from naturally occurring chlorophyll *a* from a cyanobacterium *Spirulin*a, and their chemical and biochemical properties were characterized.