主　論　文　要　旨

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論文題名

Structures of Natural Chlorophyll Pigments Esterified with Isoprenoid Alcohols and Their Distribution in Photosynthetic Apparatuses

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主論文要旨

All photosynthetically active chlorophylls (Chls) in mature phototrophs are engaged in light-harvesting (LH) and reaction centers (RCs) where energy/electron -transferring processes at the antennas. Such chlorophyllous molecules have a propionate-type ester group except Chls-*c*. These esterifying substituents are not directly conjugated with the cyclic tetrapyrrole π-systems in a molecule and do not affect the electronic absorption spectra of their monomeric states. In the final stage of Chl biosynthesis, a geranylgeranyl (GG) group at the propionate residue is transformed to a phytyl group. Here, the three of the four C=C double bonds in GG was regio- and stereoselectively hydrogenated via the intermediates possessing dihydrogeranylgeranyl (DHGG) and tetrahydrogeranylgeranyl (THGG) groups. In this thesis I spotlight the esterfing chains which occupy about one third (or fourth) of chlorophyll molecules by weight.

First I report structural determination of the unique THGG group in bacteriochlorophyll(BChl)-*b* isolated from the thermophilic purple photosynthetic bacterium *Halorhodospira halochloris* and also DHGG and THGG groups in Chl-*a* biosynthetic intermediates from an oxygenic phototroph, a diatom *Chaetoceros calcitrans*. The DHGG in the Chl-*a* intermediate was structurally different from that in BChl-*a* of purple photosynthetic bacteria.

Next I report composition and localization of BChl-*a* biosynthetic intermediates in purple photosynthetic bacteria *Rhodopseudomonas palustris* species. The bacteria could use some BChl-*a* intermediates as functional molecules within the LH2/4 and RC-LH1 core. Moreover metal-free bacteriopheophytin (BPhe)-*a* having different esterifying groups was found in the RCs, where BPhe-*a* having a THGG ester group functioned as an primary electron acceptor.