Synthesis and Physical Properties of ^{18}O-Labelled Chlorophyll Derivatives

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Chlorophylls are naturally occurring magnesium complexes of cyclic tetrapyrroles and are characterized by an exo-five-membered ring possessing a keto carbonyl group. Naturally photoactive chlorophylls possess a C=O group at the 13-position. Some chlorophylls have a C-OH or C=O group at the 3-position such as chlorophyll-d and bacteriochlorophylls-*a, b, c, d, e.* These oxygen functional groups play various important roles to organize and modify photochemical function in photosynthetic apparatus by specific non-covalent interactions. My attention has thus been focused on such 3^{1}- and 13^{1}-oxygen atoms and facile, efficient and regioselective ^{18}O-labelling of chlorophyll derivatives by organic synthesis, not by biosynthesis.

Two procedures for ^{18}O-labelling chlorophyll derivatives were established; (i) acidic hydrolysis of ethylene ketal (acetal) by treatment with TFA and H$_2^{18}$O(ca. 95% ^{18}O), (ii) exchange of proton attacked carbonyl oxygen atoms with H$_2^{18}$O-oxygen (ca. 95% ^{18}O) atoms. About 92% and 86% ^{18}O-labelling degrees were obtained by procedures (i) and (ii), respectively. Little or no loss of labelled chlorophyllous ^{18}O was obtained during almost organic modification except for using high acidic and moisture conditions, which led to other various ^{18}O-labelled chlorophyll derivatives. Furthermore, preparation of regioselectively 7^{1}-^{18}O-labelled bacteriochlorophyll-*e* (naturally occurring pigment) was achieved by using the procedure of (ii).

^{18}O-Labelled carbonyl stretching vibrational modes moved to an about 30-cm^{-1} smaller wavenumber and ^{18}O-bonding ^{13}C-resonance signals were shifted to high-field by about 0.02-0.05 ppm in the chemical shift. These results indicated that ^{18}O-labelled chlorophyll derivatives were selectively detectable by using IR, Resonance Raman and ^{13}C-NMR measurements. Therefore, obtained ^{18}O-labelled compounds are useful for elucidating supramolecular structure of naturally occurring and artificial photosynthetic apparatuses containing chlorophyll pigments by means of vibrational and NMR spectroscopic techniques.