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Functional integration of β-carotenes and xanthophylls in photoprotection of PS II of thylakoid membrane: a theoretical approach

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The three major roles assigned to carotenoids in the photosystems of the thylakoid membranes of chloroplast are light harvesting, photoprotection and structural stability. It is suggested that photoprotective role of carotenoids gains precedence over the light harvesting in the course of evolution of oxygenic photosynthesis (Li *et al.* 2000). Carotenoids are present in the light harvesting protein complexes (LCH II), antenna (CP 43, CP47) as well as in the reaction center (RC II) of photosystem II (PS II). Lutein is the major constituent of LHC II b whereas only β-carotene is present in antenna and RC II. The minor LHC II (CP24, CP25, CP26 and CP29), closely associated with CP43 and CP47 contain xanthophylls (zeaxanthin, antheraxanthin and violaxanthin) in addition to lutein. Interconversion of various forms of xanthophylls, known as xanthophyll cycle, is associated with the photoprotection of PS II. The β-carotenes present in RC II complex are believed to play a major role in photoprotection by quenching the triplet state primary donor(^{3}P680) or reducing the oxidized form P680$^+$ (Telfer *et al.* 1991). Observation of relation between stability of xanthophylls with turnover of D1 protein of RC II during stress and senescence (Deo and Biswal 2001) prompts to conceive an interaction between carotenoids in LHC II and RC II. In this background we present a molecular model having a continuum of carotenoids in the protein complexes. The array may act as a channel favoring exciton migration from LHC II to RC II and draining out deleterious excess quanta of energy in the reverse direction to the xanthophyll quenching complex in the minor LHC II.

The model

Two β-carotenes are observed per RC II in higher plants (Mimuro *et al.* 1995). In the present model one 15-cis-β-carotene is proposed to reside in D2 protein of RC II in homology to the bacterial reaction center (Deisenhofer *et al.* 1995). And the other all- trans-β-carotene is positioned in D1 protein (Fig. 1). Cis-β-carotene is known to be an efficient triplet quencher (Koyama and Fujji 1999) whereas the trans-β-carotene is believed to be efficient in energy transfer due to its higher stability as compared to its cis-isomer. The RC-β-carotenes may have their one end close to the P680 and the far end protruding through the helices of D1/D2 heterodimer in homology to bacterial reaction center (Deisenhofer et al 1995). These protruding ends may be in close proximity (~15 Å) with atleast one of the antenna β-

carotenes. The antenna contains 3-5 all-trans-β-carotenes (Yamamoto and Bassi 1996, Raval and Rath 1998). The antenna β-carotenes being long straight chain molecules may form an interactive group by end to end proximity (~15Å). One of the members of this group being electronically interactive with xanthophyll is believed to reside at the interface of minor LHC II and antenna. Thus an electronically interactive array of xanthophylls, β-carotenes of antenna and RC II is possible and it may provide a channel to drain out harmful triplet energy from RC II by Dexter exchange mechanism (Rohatgi-Mukherjee 1986).

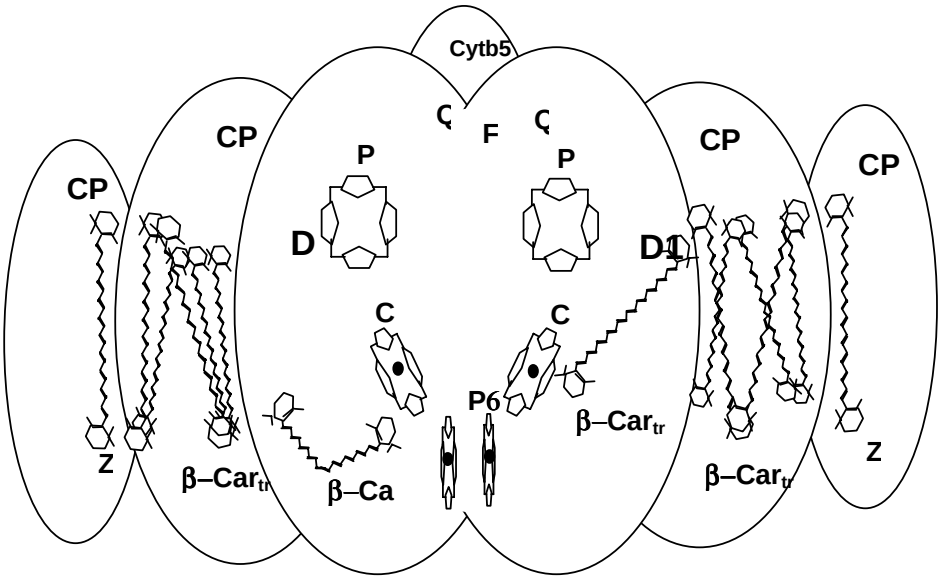

Fig.1. A schematic representation of organization of corotenoids in photosystem II protein complex. P680: primary donor; Pheo: pheophytin; Q_A, Q_B: quinone in D2 and D1 protein respectively; Chla: accessory chlorophyll *a*; b-Car: b-carotene; Zea: zeaxanthin; Cytb559: cytochrome b559.

The quenching complex

Xanthophylls, namely, zeaxanthin, are reported to dissipate excess energy through formation of a quenching complex with chlorophyll *a* and minor LHC II CP26 and CP29 (Gilmore 1997). However, the molecular structure of the complex is not yet known. We propose, in the present model, a structure and mechanism of formation of the quenching complex (Fig. 2). The Glu on lumenal side of the helix C of minor LHC II equivalent to Glu131 of LHC II b of pea (Kühlbrandt *et al.* 1994; Rath *et al.* 1997) is the proposed site for the binding of zeaxanthin. The carboxylate group of the Glu forms ligand to Mg^{2+} of the chlorophyll *a*. The negative charge on the carboxylate ion at pH >5 is delocalized over both the oxygen atoms of the group and both form ligands to Mg^{2+}. This may prevent binding of Glu to zeaxanthin. However, at pH<5 protonation of the carboxylic group may change the orientation of the group. The carbonyl oxygen may form ligand to Mg2+ while OH group may form hydrogen bond to the oxygen of alcoholic group of zeaxanthin (Fig. 2).

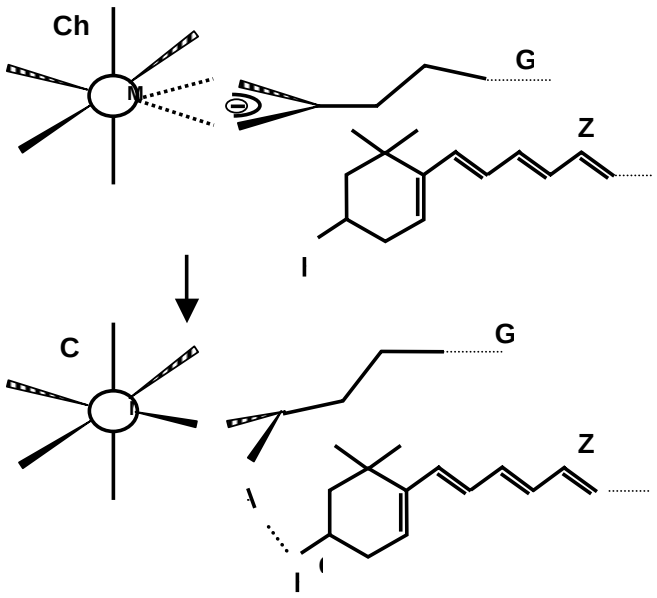

Fig.2. Proposed mechanism for formation of quenching complex. Chla: chlorophyll a; Glu: glutamic acid side chain in light harvesting proteins; Zea: zeaxanthin.

This molecular complex may act as a sink for the thermal dissipation of the triplet excitonic energy as per the following scheme.

$$RC\text{-}\beta\text{-}Car_{cis}(T_1) + CP\text{-}\beta\text{-}Car_{trans}(S_0) = RC\text{-}\beta\text{-}Car_{cis}(S_0) + CP\text{-}\beta\text{-}Car_{trans}(T_1)$$

$$CP\text{-}\beta\text{-}Car_{trans}(T_1) + Zea(S_0) = CP\text{-}\beta\text{-}Car_{trans}(S_0) + Zea(T_1)$$

$$Zea(T_1) = Zea(S_0) + Heat \quad \text{(thermal relaxation)}$$

The long-lived $RC\text{-}\beta\text{-}Car_{cis}(T_1)$ may isomerize to all trans conformation under prolonged stress condition leading to change in conformation of D1/D2 heterodimer in RC II which in turn may activate protease resulting in degradation of D1 protein.

The model defines a topology of carotenoids in PS II so as to enhance their photoprotective efficacy. The interactive array of the carotenoids adds to their efficiency performed individually and locally.

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