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Short Review

Polyamines interaction with thylakoid proteins during stress

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ABSTRACT

The involvement of polyamines in plant responses to abiotic stresses is well investigated, while there has been few reports on the specific mode of action of polyamines on the photosynthetic apparatus. The objective of this review is thus to examine the mode of interaction of polyamines with proteins of photosystem II core and LHCII, including methylamine (monoamine) as a simplified model to better understand the mode of action of polyamines. Spectroscopic methods used to determine the binding mode of amines with PSII proteins showed that amines such as spermine, putrescine and methylamine interact with protein (H-bonding) through polypeptide C═O, C—N and N—H groups with major perturbations of protein secondary structure as the concentration of amines was raised. High concentration of amines added to PSII-enriched submembrane fractions causes a significant loss of PSII activity. However, at lower concentration, polyamines, especially spermine, improve the photosynthetic functions under stress. We concluded from this review that besides the conjugation of polyamines with LHC polypeptides, polyamines are likely to interact with extrinsic proteins and the hydrophilic part of intrinsic proteins of PSII by electrostatic interaction. This could stabilize the conformation of proteins under various stresses. However, at high concentration of polyamines a strong inhibition of PSII activity is observed.

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1. Introduction

Higher plants photosystem II (PSII) is a membrane bound protein complex composed of chlorophyll and carotenoid pigments that harvest light energy to be transferred to a reaction center where charge separation takes place. This charge separation initiates the electron transport responsible for plastoquinone reduction and water oxidation with the concurrent oxygen evolution. PSII contains multiple intrinsic and extrinsic proteins. Amongst them, the extrinsic polypeptides of the luminal side with apparent masses of 17, 23 and 33 kDa are involved in maintaining the tetranuclear manganese cluster and cofactors such as Ca^{2+} and Cl^{-} in an

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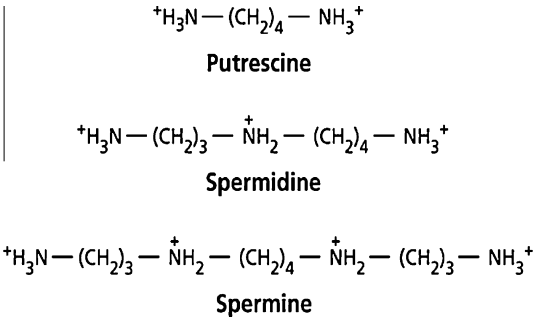

Fig. 1. Structure of endogenous polyamines.

active oxygen-evolving complex (OEC) [1]. At this site, water oxidation is performed through the so-called S-state cycle. The heterodimeric core of PSII is formed by the intrinsic proteins D1 and D2, which cross the thylakoid membrane and bind the redox-active cofactors involved in electron transfer [2]. Both subunits have been revealed to interact with the oxygen evolving site and participate in the stabilization of electron transfer reactions [3].

Polyamines (PAs) are small ubiquitous nitrogenous compounds. They are formed by aliphatic hydrocarbons substituted with two or more amino groups. Several studies have reported the interaction of PAs with proteins of PSII [4–6]. However, whereas the influence of PAs on the structural organization and functional activity of thylakoid membranes was examined in general, there is little information available regarding the site of action of PAs in PSII and about the binding modes by which PAs may affect this photosystem. PAs occur in a free form as cations at physiological pH or conjugated [7–9]. Their polycationic nature is one of the main properties believed to mediate their biological activity. In fact, membrane properties, proteins structure, and enzyme activities were shown to be strongly influenced by the interaction of PAs positive charges with the negative charges of macromolecules [8,10,11]. The purpose of this review is to summarize the available observations that indicate the electrostatic interaction of PAs or their conjugation with proteins of PSII may confer some stability of their conformational structure and function under various stresses. However, at high concentration of PAs a strong inhibition of PSII activity is observed.

2. Polyamine metabolism and photosynthesis

The common PAs are putrescine (PUT), spermidine (SPD) and spermine (SPM) (Fig. 1). The pathways of biosynthesis of PAs have been established in plants. Two pathways lead to PUT formation. In the first one, PUT (diamine) is synthesized by the decarboxylation of arginine by arginine decarboxylase (ADC) for the synthesis of agmatine and then PUT. The other pathway involves the decarboxylation of ornithine by the enzyme ornithine decarboxylase (ODC). PUT is converted into SPD (triamine), and then into SPM (tetraamine) by successive addition of aminopropyl groups from decarboxylated S-adenosylmethionine. The aminopropyl groups are generated from S-adenosylmethionine (SAM) by SAM decarboxylase (SAMDC). The transfer of the aminopropyl groups is catalyzed by SPD and SPM synthase, respectively [12–15]. Some of the genes involved in PA biosynthesis are found in the chloroplast [16], showing their possible relation with photosynthetic processes. The induction or inhibition of PAs biosynthesis is regulated by light and correlated with the ATP levels [17,18]. As example, ODC activity increases under illumination. In contrast, in dark-adapted materials the reduced ATP level decreases protein biosynthesis, which especially reduces ODC activity [17]. Thus light may have an important function in PAs biosynthesis.

The PAs transport across cell membranes (uptake and efflux) constitutes an important mean of regulating the intracellular PAs content [19]. The specific mechanism of this transport remains unclear. However, from cell culture studies, it was suggested that the entry of PAs into the cells is driven by the transmembrane electrical gradient, with a possible antiport mechanism between external and internal PAs [20]. Such mechanism could also intervene for the translocation of polyamines across the chloroplasts membranes.

In plant cells, PA content depends not only on their biosynthesis and transport but also on their degradation and conjugation reactions. PAs are oxidatively deaminated in reactions catalyzed by amine oxidases, in particular diamine oxidases (DAO), a copper containing enzyme, and flavin-containing PA oxidases (PAO). DAOs display high affinity for PUT, while PAOs oxidize secondary amine groups from SPD and SPM. On the other hand, PAs may occur as conjugates to small molecules like phenolic acids and also to various macromolecules such as DNA, RNA and proteins. This interaction can modulate the cell function of these compounds [21–23]. In chloroplasts, the conjugation of PAs is catalyzed by an enzyme named transglutaminase (TGase) [24]. This enzyme catalyses the incorporation of PAs into thylakoid and stromal proteins such as the light harvesting complex (LHC) and the large subunit of Rubisco [25–28]. The TGase activity is up-regulated by Ca^{2+} and light [29].

3. Polyamines and stress responses

The physiological significance of PA accumulation and their regulatory function in plant cells have attracted considerable attention [30]. PAs are involved in various physiological events such as cell division, DNA replication, development, and senescence. Moreover, it has been suggested that PAs are associated with plant responses under stress conditions [30–32,14,33–35]. Indeed, it has been observed that plants significantly accumulate PAs under environmental stresses. This accumulation constitutes a mechanism that may confer adaptive and protective functions under abiotic stresses [8,30–32]. Hence, the increase of endogenous PAs content was suggested to reverse the damaging effects and enhance the tolerance of plants to various stresses [36–38]. Stress-tolerant plants generally have a large capacity to enhance PA biosynthesis in response to abiotic stresses compare to intolerant plants. For example, ozone-tolerant tobacco and wild type of *Arabidopsis thaliana* enhanced PA accumulation in their tissues, while, the sensitive species did not increase the PA content [39,40]. Also, the enhancement of the endogenous PAs level through transgenic approaches increased the tolerance of sensitive plants [41,42].

It is now well accepted that the ability of plants to control stress is correlated to their ability to synthesize PAs [39,40, 43,44]. The expression of several genes involved in PA biosynthesis (*ADC2, SPMS, SAMDC2*) is up-regulated in the presence of one or more abiotic stresses [12,45]. The activity of ADC, a major PA biosynthetic enzyme, increased under stress conditions, leading to enhancement of PA levels [8,46,47]. These adaptation mechanisms are also pertinent to the photosynthetic apparatus. In fact, variation of thylakoid-associated PAs have been observed during plant response to various external stresses such as salinity, UV-B radiation, ozone, heavy metal, water stress, or chilling [12,32,39,43,48–50]. It was also observed that high CO_2 concentrations increased the thylakoid bound PUT [51]. However, UV-B radiations increased the thylakoid-associated SPM [32]. Some reports have shown that PUT, exogenously added during salt stress, enhances the level of the photochemical efficiency of PSII [52]. Moreover, the application of PAs during stress induced senescence, prevented chlorophyll loss, and preserved the thylakoid membranes structure [53,54].