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Review article

Unfinished story of polyamines: Role of conjugation, transport and light-related regulation in the polyamine metabolism in plants

Magda Pál *, Gabriella Szalai, Orsolya Kinga Gondor, Tibor Janda

Department of Plant Physiology, Agricultural Institute, Centre for Agricultural Research, Eötvös Loránd Research Network, Brunszvik u. 2, Martonvásár, H-2462, Hungary

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ABSTRACT

Polyamines play a fundamental role in the functioning of all cells. Their regulatory role in plant development, their function under stress conditions, and their metabolism have been well documented as regards both synthesis and catabolism in an increasing number of plant species. However, the majority of these studies concentrate on the levels of the most abundant polyamines, sometimes providing data on the enzyme activity or gene expression levels during polyamine synthesis, but generally making no mention of the fact that changes in the polyamine pool are very dynamic, and that other processes are also involved in the regulation of actual polyamine levels. Differences in the distribution of individual polyamines and their conjugation with other compounds were described some time ago, but these have been given little attention. In addition, the role of polyamine transporters in plants is only now being recognised. The present review highlights the importance of conjugated polyamines and also points out that investigations should not only deal with the polyamine metabolism itself, but should also cover other important questions, such as the relationship between light perception and the polyamine metabolism, or the involvement of polyamines in the circadian rhythm.

1. Introduction

Polyamines (PAs), which are low-molecular-weight, positively charged biogenic amines, are present in all plant cells. Besides their ability to interact with negatively charged molecules such as RNA, DNA, phospholipids or proteins, due to their cationic nature [1] they can also bind covalently to small molecules, such as hydroxycinnamic acids (coumaric, caffeic, ferulic acid, and others) [2], or to cell walls [3]. Due to these various interactions, PAs are involved in the regulation of numerous cellular, physiological and biochemical processes (transcription, translation, cell division and elongation, photosynthesis, ion transport, antioxidant system and signalling) [4]. Not surprisingly, this means that PAs have an important role in biotic and abiotic stress responses and tolerance [reviews: 5–9]. Correlations between plant production parameters (e.g. grain filling rate and yield components) and PA contents [10] have also been reported. Other authors have demonstrated that treatment with the same concentration of different PA compounds may have either positive or negative effects, depending on the PA applied (putrescine: Put, spermidine: Spd or spermine: Spm), on the mode of PA treatment, on the investigated plant species, and on the stress factor, suggesting that "the more PA the better" is not always true [11–15].

Two main routes for Put biosynthesis have been described in plants, both using arginine as precursor. In the arginine decarboxylation pathway, arginine decarboxylase (ADC) converts arginine into agmatine, which is then converted by agmatine iminohydrolase (AIH) into N-carbamoylputrescine: this is finally converted into Put by N-carbamolylputrescine amidohydrolase (CPA). In the ornithine route, which exists

Abbreviations: ABA, abscisic acid; ACT, agmatine coumaroyltransferase; ADC, arginine decarboxylase; AIH, agmatine iminohydrolase; ARGAH, arginine amidinohydrolyase; CCA1, Circadian Clock Associated 1; CDC, citrulline decarboxylase; CPA, N-carbamoylputrescine amidohydrolase; DAO, diamine oxidase; EC, "evening-complex"; ELF3 and ELF4, Early Flowering 3 and 4; ET, ethylene; HCAAs, hydroxycinnamic acid amides; LAT, L-type amino acid transporter; LUX, Lux Arrhythmo; MATE, membrane-localized multidrug and toxin extrusion transporters; MTA, 5′-methylthioadenosine; NATA, N-acetyltransferase; ODC, ornithine decarboxylase; PAO, polyamine oxidase; PAs, polyamines; PIF1, PHYTOCHROME-INTERACTING FACTOR 1; PQ, paraquat; PRR, Pseudo-Response Regulator; PUT, polyamine uptake transporter; Put, putrescine; RMV1, resistant to methyl viologen 1; SA, salicylic acid; SAM, S-adenosylmethionine; SAMDC, S-adenosylmethionine decarboxylase; Spd, spermidine; SPDS, spermidine synthase; Spm, spermine; SPMS, spermine synthase; TGase, transglutaminase; TOC1, Timing of CAB Expression 1.

* Corresponding author.
E-mail address: pal.magda@atk.hu (M. Pál).

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in most plants, ornithine decarboxylase (ODC) converts ornithine directly into Put [16]. Recently, the discovery of the fact that the strongly conserved arginases (also called arginine amidinohydrolyase: ARGAH) also have arginase and agmatinase activity led to the detection of another pathway in *Arabidopsis* and soybean [17]. The strongly conserved nature of plant arginases suggests that all of these enzymes have both. Although, arginase (ARGAH2) has greater affinity for the substrate agmatine than the AIH enzyme, it can also hydrolyse arginine to form ornithine with urea as a side-product, though this reaction only appears to be import in ornithine synthesis during seed germination or in the case of biotic stresses [18,19]. This suggests that Put can be synthesised by ADC and ARGAH in plant tissues or compartments with low arginine concentration. The alternative citrulline pathway, where Put is again synthesized from arginine, but with citrulline as intermediate (catalysed by citrulline decarboxylase: CDC), has only been found to date in sesame [4]. For more details on polyamine synthesis pathways and enzymes, see the multi-species reference database PlantCyc (Plant Metabolic Network: http://www.plantcyc.org).

The ADC pathway is mainly induced under stress conditions, while the ODC pathway is responsible for plant growth and development, organ differentiation and the reproductive stage [review: 20]. In *Arabidopsis*, where the ODC gene and ODC activity are missing, ADC is encoded by *ADC1* and *ADC2*. In addition, ARGAH1 is localised in the mitochondrial matrix while ARGAH2 is present in both mitochondria and plastids in *Arabidopsis*, so the co-expression of *ADC2* and *ARGAH2* represents a second route for Put synthesis in the chloroplasts [17]. *AtADC1* expression was reported to be low during vegetative development, while *AtADC2* expression was closely associated with seed germination, root and leaf development [21]. In addition, both the expression of *AtADC2* and *ARGAH2* were strongly activated by several types of stress [17,22,23]. ADC1 is localised in the endoplasmic reticulum, and was recently reported not only to synthesize agmatine from arginine, but also to convert N^{δ}-acetylornithine to N-acetylputrescine. ADC1 co-localises with N-acetyltransferase 1 (NATA1), which produces N^{δ}-acetylornithine from ornithine and N-acetylputrescine from Put, thus also playing a role in the fine-tuning of the PA pool [24] (Fig. 1).

Higher PAs (Spd and Spm) are produced by the sequential addition of aminopropyl moieties to Put through enzymatic reactions catalysed by the spermidine and spermine synthases (SPDS and SPMS). The aminopropyl group required for the synthesis of Spd and Spm is derived from decarboxylated S-adenosylmethionine (dcSAM), which is formed by the S-adenosylmethionine decarboxylase enzyme (SAMDC) from SAM. During the transfer reactions the 5′-methylthioadenosine (MTA) released as a by-product can be recycled to methionine via the Yang cycle, leading to the production of further molecules of SAM [25]. In *Arabidopsis* SPDS activity was located in the nucleus in reproductive and vegetative tissues and in both the cytosol and nucleus in the embryo. The subcellular localization of SPMS may also depend on the presence of SPDS proteins: the presence of SPDS2 may shift the subcellular localization of SPMS from the cytosol to the nucleus [23]. The catabolism of PA by several copper-containing amine oxidases (CuAOs) and flavin-containing PA oxidases (PAOs) has been described in many plant species in connection with their terminal catabolic or back-conversion activity [26,27] (Fig. 1).

Although, PAs are found in all the organelles in plant cells, they are mostly localised in the cell wall and vacuoles, with lower concentrations in the mitochondria and chloroplasts. Furthermore, individual PAs show different localization patterns within the cells, which may also be influenced by the growth conditions [4,28]. A recent study that compared the relative subcellular distribution of the *Arabidopsis* metabolome revealed that PAs accumulation was much more pronounced in the chloroplasts and cytosol of cold-resistant genotypes than in the cold-sensitive ones. A cold-induced shift from the plastidial compartment to the vacuole was observed in the case of the Spd, while for Put the relative fraction in the chloroplasts and cytosol decreased, while the vacuolar fraction significantly increased. This

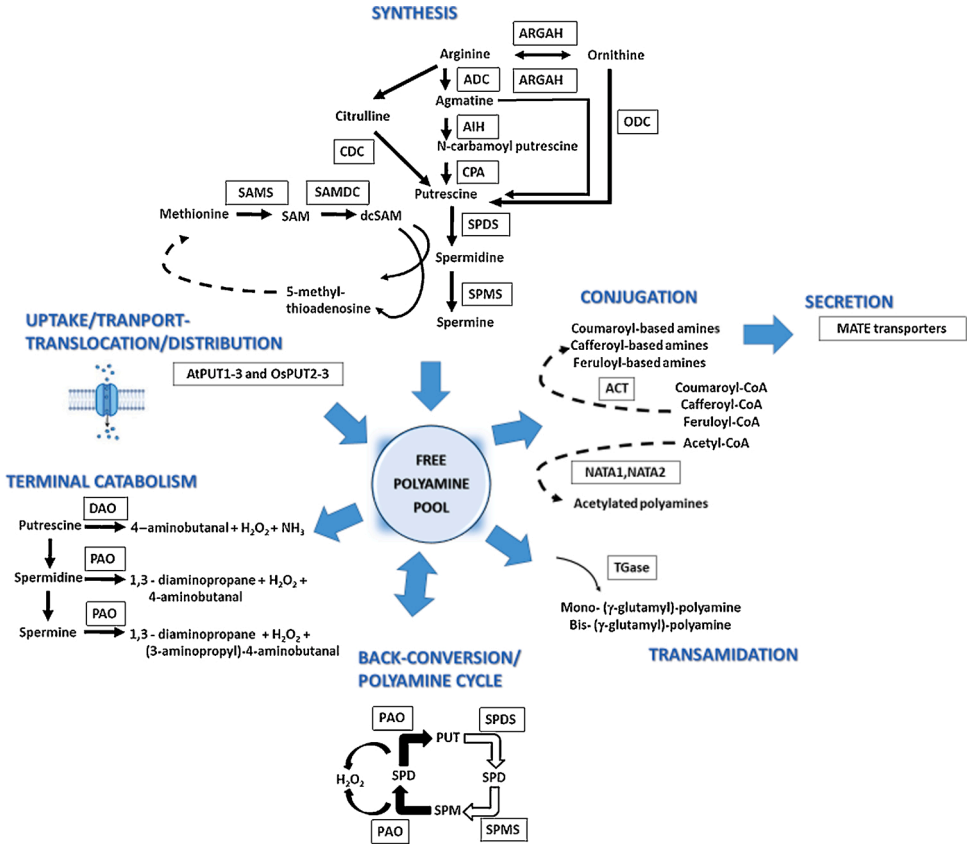

Fig. 1. Schematic figure of processes involved in the formation of the free polyamine (PA) pool in plant cells. For details see text.

compartment-specific metabolite redistribution has a role in cold acclimation processes [28]. Dynamic changes in the amount of PA can be observed in the polyamine cycle [5]. In addition, their metabolism may overlap with the synthesis of other protective compounds, such as proline and phytochelatins, the latter being heavy metal chelators [12,29,30]. If the key role of PAs in plant development and stress responses is to be better understood, it is important not only to consider the actual PA pool and the expression level of genes encoding enzymes involved in the synthesis and catabolism, but also other processes related to PA metabolism (Fig. 1). Many of these regulatory mechanisms are broadly conserved in cells, suggesting that the regulation of the free endogenous PA pool is of great importance [31].

Earlier works generally emphasised the importance of PA accumulation in order to cope better with environmental challenges. Changes in the PA pool in plants under stress conditions were well documented and reviewed [7,32,33]. Later, the picture became more nuanced, as it turned out that the "the more, the better" principle did not always work. The regulated synthesis and metabolism of PAs in the PA-cycle also suggested they might have a signalling function [5]. The present review goes even further, drawing attention to the importance of changes in the free PA pool, the distribution and transport of PAs, and the relationship between light-related processes and the PA metabolism, thus highlighting the complex regulation of PA levels in plant processes, and suggesting new ways in which the PA metabolism could be modified. Recent findings have shed light on the extraordinary complexity of the function of polyamines in plant development and stress tolerance. The fine tuning of the PA metabolism, resulting in an optimum free PA pool, is linked to developmental and stress-related processes. It should also be emphasised that in addition to PA metabolism itself (synthesis and catabolism), the role of PA conjugation and the importance and regulation of PA uptake transporters should also be investigated in detail. Other important questions are the relationship between light perception and PA metabolism, and the putative involvement of PAs in the circadian rhythm, which will be discussed here based on the current available knowledge.

2. Ratio, distribution and forms of PAs

PAs are found in all living organisms in free soluble, non-covalently conjugated, or covalently conjugated forms, the latter can be divided into perchloric acid-soluble and perchloric acid-insoluble fractions [4]. The uptake and translocation of Put were studied in tomato, maize and pine plants by feeding the roots with [^{3}H] Put. Put translocated rapidly and appeared in the upper parts of the plants within 30 min, where the Put concentration continued to increase for up to 24 h. The Put taken up was partly metabolized to Spd and Spm within 24 h [34]. PAs show organ-specific distribution patterns in plants. Based on the results obtained in wheat, maize, rice and *Arabidopsis*, it can be generally concluded that Spd is the most dominant PA in the leaves, followed by Spm and Put, while in the roots the order is: Spd $\geq$ Put $>$ Spm [10,11,29,35,36]. Seasonal changes in free and non-free Spd and Spm in vegetative and reproductive organs of olive were also determined in relation to floral initiation, anthesis and fruit development [37]. In summary, the dominant PA differs from one species to the other. Some examples are presented in Table 1.

The ratio of different PAs may even change during plant development, as found in the case of triticale, where Spd was the most abundant in the leaves at tilling and anthesis, and Put at heading [3]. Dominance may also differ for the free and conjugated fractions; for instance in wheat leaves, the Spd content was higher in the free form, and the Put content in the conjugated form [44]. Similarly, in triticale leaves during anthesis, the Spd level was the highest in the free form, while the Spm level was evident in the cell wall-bound form [3]. In seagrass (*Cymodocea nodosa)* seedlings Put was dominant, followed by Spd and Spm, in the free and soluble-bound fractions, and Spd in the insoluble-bound fraction [48]. However, it should also be taken into consideration that the regulation of the Spd and Spm levels in plants is more efficient than that of Put, so the concentration of the latter may fluctuate more widely, especially under stress conditions [54]. Very interesting results were gained from a complex temporal and spatial distribution analysis of the most abundant PAs (Put, Spd and Spm) in tobacco plants. The roots were found to contain a lower level of PAs than the shoots, while the highest total PA synthesis capacity was detected in the apical meristem. A negative correlation was also shown between leaf ontogenic stage and the PA level; in addition, young vascular tissues were found to mediate the basipetal transport of PAs. Interestingly, in the secondary roots, the free fraction was dominant followed by the soluble-conjugated fraction, while this order was reversed in the primary roots. In the oldest leaves the ratio was similar to that of the primary roots, but from the base to the apex of the plant the soluble-conjugated fraction became the most dominant fraction at the expense of the insoluble-conjugated fraction, which decreased. In tobacco plants the highest Put biosynthetic capacity was found in the underground apical meristems followed by the shoot apex and young leaves, while the highest biosynthetic capacity of Spd and Spm was determined in the shoot apex and youngest leaves, although these can also be synthesized in the roots [55]. When the PA content was monitored at different developmental stages in seagrass, it was found that among the seeds, cotyledons, seedlings and fruit, the highest total PA content was measured in the seedlings. In all the organs the soluble-bound fraction was present in the highest ratio [46].

Table 1
Dominant polyamines in different organs of various plant species. Cad: cadaverine; Put: putrescine; Spd: spermidine; Spm: spermine.

Species	Organ	Dominant polyamine	Reference
Creeping bentgrass	Leaves	Spd	[38]
Maize	Leaves	Spd	[39]
	Roots		[11]
Rice	Leaves	Spd	[35,40]
Wheat	Leaves	Spd	[41,42,43]
	Roots	Put	[42]
Oat	Leaves	Put	[44,45]
Triticale	Leaves	Spd	[3]
	Seeds	Spd	
Seagrass	Cotyledons		[46]
	Seedlings	Put	
	Fruit		
Pumpkin	Leaves	Spd	
Broccoli	Leaves	Put	
	Stalks	Spm	
Carrot	Leaves	Spd	
Collard	Leaves	Spd	[47]
	Stalks	Spm	
Radish	Leaves	Spm	
Cassava	Leaves	Spm	
Grape	Leaves	Spm	
Spinach	Stalks	Spd	
	Leaves	Spd	[48]
Common ice plant	Leaves	Spd	[49]
Bean	Leaves	Spd	[50]
Arabidopsis	Seedling cotyledons	Spd	[51]
	Seedling roots		
	Rosetta leaves		
	Flowering plant leaves		
	Flowers		
	Stalks		
Tobacco	Leaves	Spd	[52]
Soybean	Roots	Cad	[53]

3. Conjugated PAs

Although conjugated PAs were discovered a considerable time ago, it was previously thought that conjugated PAs were only inactive, and very few studies reported the role of this fraction, except in connection

with plant biotic stress responses, food analyses or human health [2,56]. Most investigations investigated the free PA content, and even when the conjugated fraction was mentioned in relation to the PAs released after acidic hydrolysis, these were again determined in the free form. Since then more and more evidence has indicated that the conjugated fraction may have an essential role in plant development and responses [57,58].

In *Arabidopsis* the NATA1 activity has been reported to be responsible for the acetylation of ornithine and Put, resulting in competition with SPDS for Put as a common substrate [24,59], while NATA2 prefers ornithine and spermine as substrates [60]. Although N^1-acetylspermidine was found to be as abundant as Spd, peroxisomal and cytosolic polyamine oxidases (PAOs), which catalyse the oxidation of Spm and Spd to Put, have lower affinity for N^1-acetylspermine and N^1-acetylspermidine [61,62]. Hence, the acetylation of higher PAs could be responsible for the lower defence-related H_2O_2 accumulation, suggesting that the effector molecule produced by the *Pseudomonas syringae* pathogen suppressed antimicrobial defence by inducing NATA1 expression [59]. However, it was also hypothesised that the acetylation of 1,3-diaminopropane, the catabolite product of PAOs, may act as an antagonist in the inhibition of abscisic acid-induced stomatal closure, thus facilitating the entry of the pathogen into the leaves [59]. In addition, acetylated PAs has a smaller net positive charge, which in turn decreases their interaction with other molecules [31]. N^1-acetylspermine, N^1-acetylspermidine and N^8-acetylspermidine have been found in several plant species [63], and the various acetylated forms of PAs may have a role in biotic stress responses [64] (Fig. 1). It has recently been revealed that exposing Arabidopsis to heat stress also induced the accumulation of PAs, particularly acetylated Spd and Spm, especially when applied together with a specific inhibitor of HSP90 activity. The resulting deregulation of the PA pool induced the gene expression of PAOs, responsible for PA oxidation-back-conversion that, in turn, decreasing the amount of substrate available for acetylation [65]. Despite these novel aspects, the distribution and role of acetylated polyamines in plants have not yet been investigated in detail.

Phenolamides, also known as hydroxycinnamic acid amides (HCAAs) [2,66] form a class of secondary metabolites. Hydroxycinnamic acids are conjugated with amines by hydroxycinnamoyltransferases to yield HCAAs [67–69]. The first amine N-hydroxycinnamoyltransferase identified was the barley agmatine coumaroyltransferase (ACT) [70]. Since then, several acyltransferases have been characterized, including putrescine N-hydroxycinnamoyltransferase [71], Spd hydroxycinnamoyltransferase [72] and spermine hydroxycinnamoyl transferase [67]. There was much debate on the putative physiological roles of HCAAs, but the fact that these compounds crosslink various cell wall polymers via ester and ether linkages, suggests they have a role in pollen maturation and pollen tube elongation [72]. As their polymerization into the plant cell wall modulates the rigidity of the cell wall, they are also involved in plant defence responses to pathogen attack or wounding [73,74]. The rapid accumulation of HCAAs in response to infection, along with their antimicrobial and antioxidant activity, indicate that these compounds can be classified as phytoalexins [2,66]. This is supported by the discovery that *p*-coumaroylagmatine, which is the major HCAA accumulated in *Arabidopsis* and is secreted via membrane-localized multidrug and toxin extrusion (MATE) transporters, inhibits *P. infestans* spore germination *in vitro* [75]. The accumulation of cinnamic acid amides has also been reported after infection with *Fusarium* in barley [76]. Hydroxycinnamoylagmatines are the direct precursors of hordatines, which together with their glycosides form a special group of HCAAs detected in *Hordeum* species [77].

Besides *p*-coumaroylagmatine and feruloylagmatine, the hydroxycinnamic acid conjugates of PAs, including *p*-coumaroylputrescine and feruloylputrescine have also been identified in *Arabidopsis* leaves after infection with *Alternaria brassicicola,* accumulating due to the reaction catalysed by AtACT [78]. N-p-coumaroylputrescine and N-feruloylputrescine accumulation has also been reported after the inoculation of rice roots with various rhizobacteria belonging to the *Azospirillum* genus, when two genes involved in the synthesis of N-feruloylputrescine were also up-regulated. In contrast to the results obtained after inoculation with beneficial strains, decreased HCAA content and the down--regulation of synthesis genes were found after pathogen infection [79].

Although Put mainly forms monomers with coumaric acid, caffeic acid or ferulic acid, dimers or trisubstituted HCAAs may also occur [80], different gene products may be responsible for monoacetylation and for the second acetylation, as found in tobacco [81]. Hydroxycinnamic acid-Put and hydroxycinnamic acid-Spd are predominant in the plant kingdom, while only a few plants are rich in hydroxycinnamic acid-Spm compounds [82,83]. A recently developed method has made it possible to identify HCAAs in the seeds of maize, wheat and rice, in the roots of rice, and in the leaves of rice and tobacco. Among the 79 HCAAs detected, 42 were identified in these plants for the first time, and 20 have not previously been reported in plants [83]. Studies have been published on the spatiotemporal accumulation patterns of phenolamides in rice [82], and natural variation has been revealed in the HCAAs in maize landraces [84]. Changes in the relative proportions of hydroxycinnamic acids were detected in grapes infected with the gray mold (*Botrytis cinerea*). Coumaric acid was the predominant hydroxycinnamic acid at the beginning and end of gray mold infection, whereas caffeic acid predominated during the middle stage [85]. It has been suggested that HCAAs may have a major function in plant adaptation to stress via their antioxidant properties and radical scavenging activities [2] under ozone [86] or cold stress conditions [87]. In recent studies various isomers of this group showed different changes under drought stress conditions or phosphorus deficiency [88,89]. In detached barley leaves dark-induced senescence was accompanied by the accumulation of conjugated Put, but not of Spd or Spm [90]. In summary, phenolamides should not only be seen to be regulators of the free PA content, but also to have important roles in plant growth and development, as well as in senescence (Fig. 1). However, very limited information is available on the abundance and natural variation of HCAAs in crop plants during plant development and under different growth or stress conditions, so further detailed analysis will be required to reveal their complex role.

4. Role of polyamine transporters

The biosynthetic compartmentalisation and subcellular localisation of PAs have physiological importance, suggesting that PA transport may have a significant influence on the role of PAs. Substantial information is available on the PA transport systems in bacteria, yeast, and mammals, but the PA transport systems in plants have not yet been satisfactorily described. The first study on a *PA Uptake Transporter* (PUT) in plants was the characterisation of the Spd-preferential OsPUT1 in rice, which is encoded by a gene expressed in all plant tissues except seeds and roots [91]. Five more PUTs, AtPUT1-3 and OsPUT2-3, were later identified and confirmed in *Arabidopsis* and rice [92] (Fig. 1), and AtPUT homologs are predicted in almost all microalgal genomes, too [93]. Transient expression analysis using *Arabidopsis* protoplasts revealed that AtPUT1–3 could be isolated from the endoplasmic reticulum, Golgi apparatus and plasma membrane, respectively, and OsPUT2 from the Golgi apparatus [94,95]. These findings support the hypothesis that PUTs are involved not only in PA transport across the plasma membrane, but also in intracellular translocation, resulting in the fine tuning of the optimal organellar PA pool in the cells [94]. Investigations on a transporter belonging to the L-type amino acid transporter (LAT) family, named RMV1 (resistant to methyl viologen 1) and responsible for the uptake of PA and its analog paraquat (PQ), showed that the natural variation in PQ tolerance in 22 accessions of *Arabidopsis* was correlated with the polymorphic variation of RMV1 [96]. Recently, PUT3 from *Arabidopsis* has been identified as a polyspecific transporter, responsible for the transport of PAs, vitamin B1 and paraquat in the phloem. Interestingly, PUT3 exhibited polymorphic differences in the ecotypes Columbia and Landsberg erecta, resulting in differences in the PA composition of the phloem saps [97]. The phenotypic changes observed

when *Os* PUT3 was overexpressed in *Arabidopsis* resembled those detected after the exogenous application of PA: increased biomass, yield and drought tolerance [98]. The transient expression of *Arabidopsis* and rice PA transporter genes in tobacco revealed that AtPUT5 and OsPUT1 are localised in the endoplasmatic reticulum, while AtPUT2-3 and Os PUT3 are in the chloroplast. The constitutive expression of *OsPUT1* and *Os* PUT3 in tobacco is associated with an extreme delay in both flowering and plant senescence [99]. It was also revealed that in *Arabidopsis* the PUT3 localised in the plasma membrane is required for the uptake of extracellular PAs and plays an important role in stabilizing the mRNAs of several crucial heat-stress-responsive genes, including *HSPs* at high temperature [100]. Investigation on allelic variations in *Arabidopsis* found that 5 of the 22 ecotypes tested had a non-functional PUT3 allele, and that these 5 ecotypes all originated from northern latitudes or high mountains, suggesting that the loss of PUT3 function may be related to the lack of high temperature stress, and that these ecotypes need vernalisation treatment for flowering [96]. Recently, it has also been revealed that PUT3 is able to interact with SOS1 (plasma membrane Na^+/H^+ transporter) and SOS2 (protein kinase), two signalling molecules critical for salt tolerance. These interactions synergistically activate PUT3 transport activity, indicating that SOS1 and SOS2 are required for PUT3 activity [101].

These results suggest that besides influencing PA biosynthesis, PA transporters could be useful targets for the regulation of the PA pool and distribution. Unfortunately, very few detailed investigations have so far been published on the expression and polymorphic variation of PUTs in plants during growth, development and stress.

5. Relationship between light conditions and the PA pool/metabolism

Plant stress responses are significantly influenced by light [102–104], and the relationship between PAs and photosynthesis is well-documented. In experiments performed on chloroplasts prepared from spinach leaves [48], all three main PAs (Put, Spd and Spm) were detected, but Spm was present in the highest quantity, despite the fact that Spd is usually the most abundant PA in spinach leaves. However, Put was the dominant PA in fractionated thylakoid membranes, Photosystem II (PS II) membranes, the light harvesting complex (LHC), and PS II complexes, while the highly resolved PS II core and the PS II reaction centre contained only Spm, and no Put or Spd. It has been demonstrated that PAs are involved in stabilizing the structure and function of the photosynthetic apparatus in response to stress factors. In salt-stressed *Scenedesmus obliquus*, a reduction in Put content was correlated with changes in the structure and function of the photosynthetic apparatus, manifested as an increase in the size of the antenna and a reduction in the density of PS II reaction centres, but exogenously applied Put was able to compensate for these changes [105]. The important role of Put in chloroplasts has also been proved by the high activity of ADC [106] and of transglutaminase (TGase), which catalyses the covalent binding of PAs to proteins [107,108]. The overexpression of the maize *TGase* in *Arabidopsis* increased the activation threshold of photoprotection [109], while in tomato it promoted the CO_2 assimilation rate by activating the Calvin cycle enzymes [108]. Exogenous Spm not only stabilized the chloroplast ultrastructure, but induced he expression of the chlorophyllase gene and, in turn, chlorophyllase activity in stressed tomato seedlings [110]. Although the uncharged forms of PAs represented less than 0.1 % of the total PA pool, the physiological role of this fraction has been demonstrated to be crucial in chemiosmosis [111]. Exogenous Put treatment can also provide protection during salt or osmotic stress conditions by improving photosynthetic activity in maize and wheat plants [11,14]. While Spd and Spm alleviated photoinhibition in isolated thylakoid membranes [112].

It is thus clear that PAs are able to influence photosynthesis in several ways. They can increase the photosynthetic pigment content by retarding chlorophyll destruction and/or by increasing their biosynthesis. They bind to photosynthetic complexes, leading to the conformal modification of the secondary structure of LHCII, PS I and II and their buffering role in the thylakoid lumen leads to increased chemiosmotic ATP synthesis, etc. (review: [113]). On the other hand, PA biosynthesis is also controlled by light [114]. It has been suggested that the photoregulation of the PA content during chloroplast development is linked to the existence of three photoreceptor systems. A protochlorophyllide photoreceptor is possibly responsible for the inhibition of Put and Spd formation during chloroplast development, while a blue-light photoreceptor probably mediates the formation of PAs, while a red-light photoreceptor could be responsible for inducing of an increase in PA [115]. The rapid up-regulation of ODC activity was also observed when dark-adapted *Chlamydomonas reinhardtii* cells were transferred to light conditions, but this increase in ODC activity was terminated by the PSII inhibitor, DCMU and by the inhibition of protein biosynthesis [116]. However, light may influence not only the synthesis, but also the catabolism of PAs. A phytochrome-mediated increase in *PAO* expression has been reported in maize mesocotyls, where it plays a role in the photomodulation of growth and cell wall differentiation [117]. The expression of *OsPAO5* also increased in the presence of light and was inhibited by darkness in rice, suggesting that light is important for the fine tuning of the PA metabolism, which in turn has a role in the regulation of mesocotyl elongation [118]. The PAO-mediated catabolism of Spd and/or Spm is involved in dark-induced senescence [119], and PAOs have also been found to play a key role in light- or developmentally-regulated maturation and programmed cell death as a source of H_2O_2 [120]. Diamine and PA oxidases exhibited higher activity and gene expression levels in tomato seedlings growing under controlled light conditions than in plants kept in the dark [121]. It should also be taken into consideration that the terminal catabolism and back-conversion of PAs may take place in the same plant. PAs are metabolised through the activity of amine oxidases, including both the CuAOs, which have high affinity for Put and cadaverine, and the FAD-dependent PAOs that oxidize Spd and Spm by cleaving their secondary amino groups, leading to terminal catabolism. Another group of PAOs are responsible for the back-conversion of higher PAs to Put [120].

While the amount of PAs in tomato leaves tend to accumulate to a greater extent in the light (diurnal rhythm), their concentrations frequently fluctuated under dark conditions [121]. The PA diurnal rhythm was also described in the leaves of tobacco plants, where the PA content exhibited a maximum after 9 h of light [122]. TGase activity was also modulated by the presence of light [108], which has been proved to play an important role in inducing the accumulation of conjugated/-bound PAs under salt stress in tomato, resulting in increased antioxidant activity and improved salt tolerance [123]. However, the relationship between light perception and PA metabolism has still not been fully clarified.

Besides light intensity, the spectral quality also has a great effect on the photosynthesis and metabolism of plants. Phytochromes are plant photoreceptors that control development in the ever-changing environment throughout the whole plant life cycle. Light-induced conformational changes enable phytochromes to interact with other signalling molecules, such as transcription factors and proteins [124]. Phytochromes also control the abundance of the transcription factor PHYTOCHROME-INTERACTING FACTOR 1 (PIF1), a key germination repressor in seeds [125]. It was recently found that recessive mutations in the gene that codes for the Golgi- and chloroplast-localised PUT2 resulted in the overaccumulation of PAs in mutant *put2* seeds due to the defective cellular distribution of PAs, which in turn increased PA synthesis as a compensatory mechanism. This *put2* mutation led to enhanced germination, as PA accumulation stimulated phytochrome A (phyA), which in turn overcame the repressive effect of PIF1 on germination. It was also established that endogenous PA accumulation is repressed by PIF1 in wild-type seeds exposed to an early far red pulse [126].

In *Arabidopsis,* it was found that the quality of light was perceived by

the light receptor phytochromes phyB and phyA, and that the phyA photoreceptor regulated PA biosynthesis [127], while in *Arabidopsis* plants exposed to relatively strong light and a low R:FR ratio the *phyB* mutation resulted in lower PA content, revealing that phyB acts as a major regulator of the leaf metabolic status in response to light intensity [128]. When white light was combined with low-blue and deep-red, but without far-red spectra, the endogenous PA content increased in *Cariniana legalis* shoots, leading to greater elongation compared to those grown under white light only [129]. Light quality also influenced the PA pool in lettuce, as the Put:Spd ratio was lower under white or red light and higher under blue light [130]. In wheat plants grown in plant growth chambers with different spectral distributions provided by LED light sources, the light quality and quantity were found to affect both the amount and composition of free amino acids [131], which could in turn regulate the PA level via Glu or Arg, the precursors of PA synthesis. Recently, it was also found that growing *Cedrela fissilis* Vell. *in vitro* under LED light with white plus blue, deep red and far red instead of fluorescent lamps increased the protein and free Put contents and resulted in higher shoot elongation of [132]. However, very little direct information is available as yet about how light quality and the duration of light conditions influence the PA metabolism. Table 2 provides an overview of the changes in PA content of and parameters related to their metabolism (enzyme activity, gene expression) under different light conditions, based on the available literature [116–117, 121, 126–130, 133–137].

6. Relationship between PA metabolism and the circadian rhythm

The cellular redox state and the circadian rhythm have been shown to influence each other continuously, and both are affected by environmental stressors [138]. In rodents the connection between the circadian clock and stress responses is well documented [139]. Interestingly, in mice the decline in PA levels with age was found to be associated with a longer circadian period, which could be reversed by PA supplementation to the diet, suggesting crosstalk between circadian clocks and PA biosynthesis [140]. In photosynthetic organisms, daily changes in light availability constitute a major metabolic change in the cells, and the circadian clock strictly regulates rhythmic photosynthesis. Moreover, it regulates responses to environmental stress, as well as rhythmic oscillations in ROS production and plant hormonal signalling. Hormone levels themselves oscillate, so the effect of a hormone stimulus will be more or less dependent on the circadian clock [141]. Cyanobacteria are the simplest photosynthetic organisms with well-defined circadian rhythms. A circadian clock consisting of three clock proteinsKaiA, KaiB, and KaiC, is responsible for their robust oscillation [142]. In a recent study, it was found that in an established *in vitro* reconstitution system, PAs disrupted the robustness of the cyanobacterial circadian clock by inducing the protein-dependent denaturation of the Kai proteins, thus reducing the thermal stability of the clock [143].

PA levels have also been reported to vary rhythmically in tomato seedlings, the growth of which was correlated with the PA composition. In addition, the diurnal rhythm of PA levels proved to be controlled by the temperature cycle rather than by the light cycle, as PA accumulation persisted when the same temperature program was continued in the dark, suggesting that PA levels are regulated endogenously [144]. It has long been known, that changes in the expression level of the *SAMDC* gene are under circadian control in *Pharbitis nil*. In addition, the transcript level of the gene encoding the S-adenosylmethionine decarboxylase (SAMDC) enzyme, which is involved in the synthesis of higher PAs, increased after exposure to red, green, blue or UV light, but not after far-red light, suggesting that the expression of the *SAMDC* gene is

Table 2
Summary of changes in PA content, and in the enzyme activity and gene expression related to their metabolism under different light conditions in various plant species. (na: data not available, + : increment; : no change; - : decrement).

Publication	Genotype	Experiment	Light regime		*ADC*	*ODC*	Put	*SPMS*	Spd	*SPDS*	Spm	SAM	*SAMDC*	DAO	PAO	*DAO*	*PAO*
[121]	*Solanum lycopersicum* L.	Plants were exposed to 24 h continuous white light conditons	1h	200 μmol m^{-2} s^{-1}	-				-	-		na	na	-		-	-
			3h		-			+	-	-		na	na	-	-	-	-
			6h		-	-	+	+		-	+	na	na	+	-	-	+
			12h		-	-	+	-	+	+	+	na	na	+	-	-	-
			24h		+		+	+	+	+	+	na	na	-	+	-	+
[133]	*Pisum sativum* L.	Etiolated seedlings after transfer to white light	100 μmol m^{-2} s^{-1}		na	na	na	na	na	na	na	na	na	na	na	+	na
[116]	*Chlamydomonas reinhardtii*	Dark adapted cultures 3 h after transfer to white light	40 μmol m^{-2} s^{-1}		+	+	na	na	na	na	na	na	na	na	na	na	na
[117]	*Zea mays* L.	Etiolated seedlings 1 h after transfer to light	9 W m^{-2}	White	na	na	na	na	na	na	na	na	na	na	na	na	+
			3 W m^{-2} red light	Red	na	na	na	na	na	na	na	na	na	na	na	na	+
[134]	*Pharbitis nil*	Dark adapted plants were exposed to red and blue light exposure	60 μmol m^{-2} s^{-1}	Red	na	na	na	na	na	na	na	na	+	na	na	na	na
				Blue	na	na	na	na	na	na	na	na	+	na	na	na	na
[135]	*Glycine max* L.	Blue or red and far-red irradiance or their combination at lower and higher PAR level compared to the combined irradiance at lower PAR level	300 μmol m^{-2} s^{-1}	Blue	na	na		na		na	-	na	na	na	na	na	na
			300 μmol m^{-2} s^{-1}	Red, far-red	na	na	+	na	+	na		na	na	na	na	na	na
			600 μmol m^{-2} s^{-1}	Blue and red, far-red	na	na		na		na	-	na	na	na	na	na	na
			600 μmol m^{-2} s^{-1}	Blue	na	na	+	na	+	na	+	na	na	na	na	na	na
			600 μmol m^{-2} s^{-1}	Blue and red, far-red	na	na	+	na	+	na	-	na	na	na	na	na	na
[129]	*Cariniana legalis*	Treatments with LED lamp compared to fluorescent white	55 μmol m^{-2} s^{-1}	White, low blue and deep red	na	na	+	na	+	na	na	na	na	na	na	na	na
[130]	*Lactuca sativa*	18 days of continuous white, red or blue light	35 μmol m^{-2} s^{-1}	White	na	na	+	na	+	na	+	na	na	na	na	na	na
				Red	na	na	+	na	+	na	+	na	na	na	na	na	na
				Blue	na	na	-	na	-	na	-	na	na	na	na	na	na
[136]	*Triticum aestivum* L.	Light intensities and spectral compositions compared to normal white conditions (250 μmol m^{-2} s^{-1})	50 μmol m^{-2} s^{-1}	White	-	na	na	na	na	na	na	na	na	na	na	na	na
			500 μmol m^{-2} s^{-1}		+	na	na	na	na	na	na	na	na	na	na	na	na
			250 μmol m^{-2} s^{-1}	Blue	-	na	na	na	na	na	na	na	na	na	na	na	na
			245 μmol m^{-2} s^{-1}	Blue-red (pink)	-	na	na	na	na	na	na	na	na	na	na	na	na
			250 μmol m^{-2} s^{-1}	Far-red	-	na	na	na	na	na	na	na	na	na	na	na	na
[127]	*Arabidopsis thaliana*	*phyA* mutant was compared to the wild type	10 μmol m^{-2} s^{-1}	White	+	na	+		na	+	na	na	na	na	na	na	na
			10 μmol m^{-2} s^{-1}	Far-red	+	na	+		na	-	na	na	na	na	na	na	na
[126]	*Arabidopsis thaliana*	Far-red (3.69 μmol m^{-2} s^{-1}) followed by red (14.92 μmol m^{-2} s^{-1}) or far-red pulse compared to far-red alone	Far-red/far-red		na	na		na		na		na	na	na	na	na	na
			Far-red/red		na	na	+	na	+	na	+	na	na	na	na	na	na
[128]	*Arabidopsis thaliana*	*phyA, phyB* and *phyAphyB* double mutant compared to the wild type	*phyA*	251 μmol m^{-2} s^{-1} Red:far-red ratio: 11.8	na	na		na	+	na	na	na	na	na	na	na	na
			phyB		na	na		na		na	na	na	na	na	na	na	na
			phyAB		na	na		na		na	na	na	na	na	na	na	na
			phyA	136 μmol m^{-2} s^{-1} Red:far-red ratio: 11.8	na	na		na		na	na	na	na	na	na	na	na
			phyB		na	na		na		na	na	na	na	na	na	na	na
			phyAB		na	na		na		na	na	na	na	na	na	na	na
			phyA	251 μmol m^{-2} s^{-1} Red:far-red ratio: 14.3	na	na	-	na	-	na	na	na	na	na	na	na	na
			phyB		na	na		na		na	na	na	na	na	na	na	na
			phyAB		na	na		na		na	na	na	na	na	na	na	na
			phyA	136 μmol m^{-2} s^{-1} Red:far-red ratio:14.3	na	na		na		na	na	na	na	na	na	na	na
			phyB		na	na		na		na	na	na	na	na	na	na	na
			phyAB		na	na		na		na	na	na	na	na	na	na	na
[137]	*Oryza sativa*	*phyAphyBphyC* triple mutant compared to the wild type	530 μmol m^{-2} s^{-1}		na	na	+	na	na	na	na	+	na	na	na	na	na

controlled by both the blue light photoreceptor- and phytochrome-mediated light regulation pathways [134]. It was later demonstrated that the SAMDC activity and its gene expression level changed diurnally in carnation leaves. The putative sites in the promoter region responsible for diurnal expression have also been identified [145]. Changes in PA levels in Scots pine seedlings were observed after the shortening of the day length, supporting the role of PAs in the initial stage of the cold hardening process [146]. The ADC, ODC and DAO activities were correlated with changes in PA content during the day/-night period in tobacco plants. Furthermore, data indicated that these parameters were not only light-affected, but also regulated by an internal rhythm [122]. In higher plants, endogenous oscillations and their relationship with the circadian clock have mostly been investigated in *Arabidopsis*. At dawn, two closely related transcription factors, Late Elongated Hypocotyl (LHY) and Circadian Clock Associated 1 (CCA1), are co-expressed, while in the afternoon and at night their expression is repressed by Pseudo-Response Regulator proteins PRR7 and PRR9, and especially by PRR1, which is also known as Timing of CAB Expression 1 (TOC1). The repression of the LHY and CCA1 genes is overcome by the "evening-complex" (EC), a complex of three proteins: Early Flowering 3 and 4 (ELF3 and ELF4) and Lux Arrhythmo (LUX), which down-regulates the PRR7 and PRR9 genes in the morning [147]. However, the link between the regulation of the circadian clock and the PA metabolism is still poorly understood.

The major secondary messengers in PA signalling may be H_2O_2 and NO, which are not only produced in the course of the PA metabolism, but also transmit signals that influence gene expression via an increase in the cytoplasmic Ca^{2+} level. PAs are also able to influence Ca^{2+} influx independently of the H_2O_2- and/or NO-mediated pathways; furthermore, these pathways may converge during other hormonal signalling processes. The circadian clock has been demonstrated to control daily fluctuations in the abscisic acid (ABA) level and to influence the sensitivity of plants to ABA, while changes in ABA concentration, in turn, influence the clock [148]. Diurnal light/dark cycles have also been found in the concentrations of other plant hormones, such as auxin, jasmonic acid, salicylic acid (SA), cytokinin and ethylene (ET), which reach their maximum at different time points [140]. The relationship between plant hormones, such as SA, ABA and ET, and PAs has been reported under different conditions, suggesting that PAs can also influence the hormonal balance [4]. PAs may thus be key hubs in the circadian network. However, no detailed information is yet available on how the changes in PA metabolism and its relationship with plant hormones are linked to plant clock responses.

7. Conclusions

Developments in our understanding of PA biosynthesis, and of metabolic routes and molecular mechanisms influenced by PAs offer new strategies for influencing plant development and stress tolerance by exploiting the PA metabolism. It is evident that the fine tuning of the PA metabolism plays an important role both in plant growth and stress tolerance. However, detailed investigations will be required not only on PA metabolism itself (synthesis and catabolism), but also on the role of PA conjugation. Another new aspect is the understanding of the precise mechanisms and regulation of PA transport in plants. These results could open up new targets, in the improvement of stress tolerance. Although a considerable body of data has been published on how the light regime influences PA metabolism, large gaps in our knowledge still remain with regards to perception and regulation. One new question in connection with the regulation of the PA pool by the circadian rhythm is the relationship between light perception and the PA metabolism (Fig. 2). In summary, the story of PAs is still unfinished. The present review is an attempt to provide new directions and aspects for research in this fascinating field.

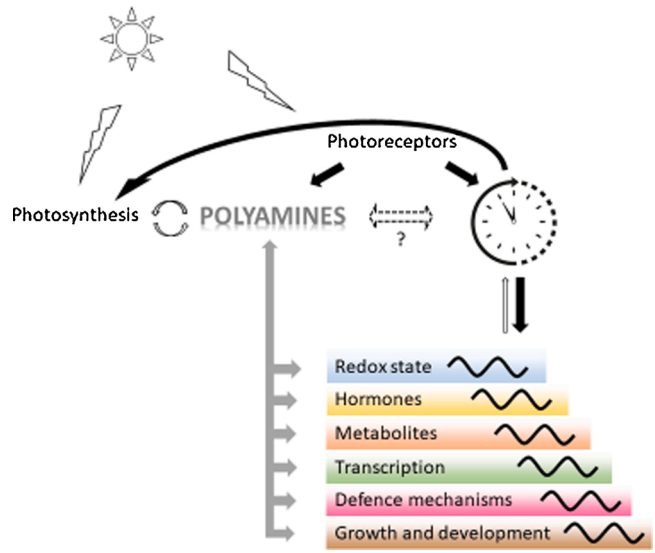

Fig. 2. Main processes in which light-regulated interactions can be assumed between polyamines and the circadian rhythm.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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