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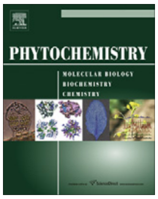

Molecules of Interest

Phenolamides: Bridging polyamines to the phenolic metabolism

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ABSTRACT

Phenolamides constitute a diverse and quantitatively major group of secondary metabolites resulting from the conjugation of a phenolic moiety with polyamines or with deaminated aromatic aminoacids. This review summarizes their bioactivities and their reported roles in plant development, adaptation and defence compared to those of their polyamine precursors. The most conclusive recent developments point to their contribution to cell-wall reinforcement and to direct toxicity for predators and pathogens, either as built-in or inducible defence. Phenolamides were often considered as accumulated end-chain products. Recent data bring a light on their biosynthesis and suggests their possible contribution in the branching of the phenylpropanoid metabolism.

1. Introduction

Phenolamides are frequently referred to as hydroxycinnamic acid amides (HCAA) or phenylamides. They have been reported throughout the plant kingdom, usually as main phenolic constituents of reproductive organs and seeds. They are regarded either as products of polyamine catabolism or as polyamines or phenolics storage forms. However, they seem to have specific functions in plant development and defence, as metabolic intermediates and final products. This review sums-up HCAAs occurence, biosynthesis and potential functions in plants in connection with polyamines and phenolic metabolism.

2. Polyamines

The name "polyamines" refers to aliphatic organic compounds with more than one amino group. Putrescine, spermidine and spermine are the most widespread in all living organisms especially in actively proliferating tissues. They are also the most common in plants, while cadaverine was also reported in legumes. Recent data suggest that the spermine isomer thermospermine might be also widespread and was present before spermine in aerial plants (Kakehi et al., 2008; Minguet et al., 2008). Norspermidine, norspermine and homospermine on the other hand were described as taxonomic markers of Bryophytes, Pteridophytes, Gymnosperms and Fungi (Hamana and Matsuzaki, 1985). The positive charge of polyamines at physiological pH confers them the property to bind negatively charged macromolecules or to modulate the activity of some ion channels. In plants, polyamines are found not only in the cytoplasm but also in vacuoles, plastids and mitochondria (Kumar et al., 1997). Several recent reviews provide a good overview on the current knowledge on polyamine biosynthesis, catabolism and bioactivity, including their roles in plant development and adaptative responses. Those will thus be just summarized briefly.

2.1. Biosynthesis and catabolism

Intracellular concentrations of polyamines are quite high and range from several hundreds of micromolar to a few millimolar. Due to their important biological functions, polyamine concentrations are very tightly controlled. While biosynthesis, catabolism, conjugation and transport contribute to polyamines homeostasis, catabolism also contributes to their bioactivity.

Polyamine biosynthesis involves similar pathways in bacteria, animals and plants (Kusano et al., 2008). Two alternative pathways starting from L-arginine have been confirmed in plants (Fig. 1). The ornithine decarboxylase pathway is favoured in meristematic and dividing cells, while the arginine decarboxylase pathway predominates in mature tissues and in response to environmental stress (Flores, 1991). Only one of these pathways was proposed to be operating in *Arabidopsis thaliana* since no ornithine decarboxylase has been predicted from its annotated genome (Hanfrey et al., 2001). However, Tassoni and coworkers (2003) reported ornithine decarboxylase activity associated with the plastid membranes in *Arabidopsis* leaves. In legumes, cadaverine is derived from lysine

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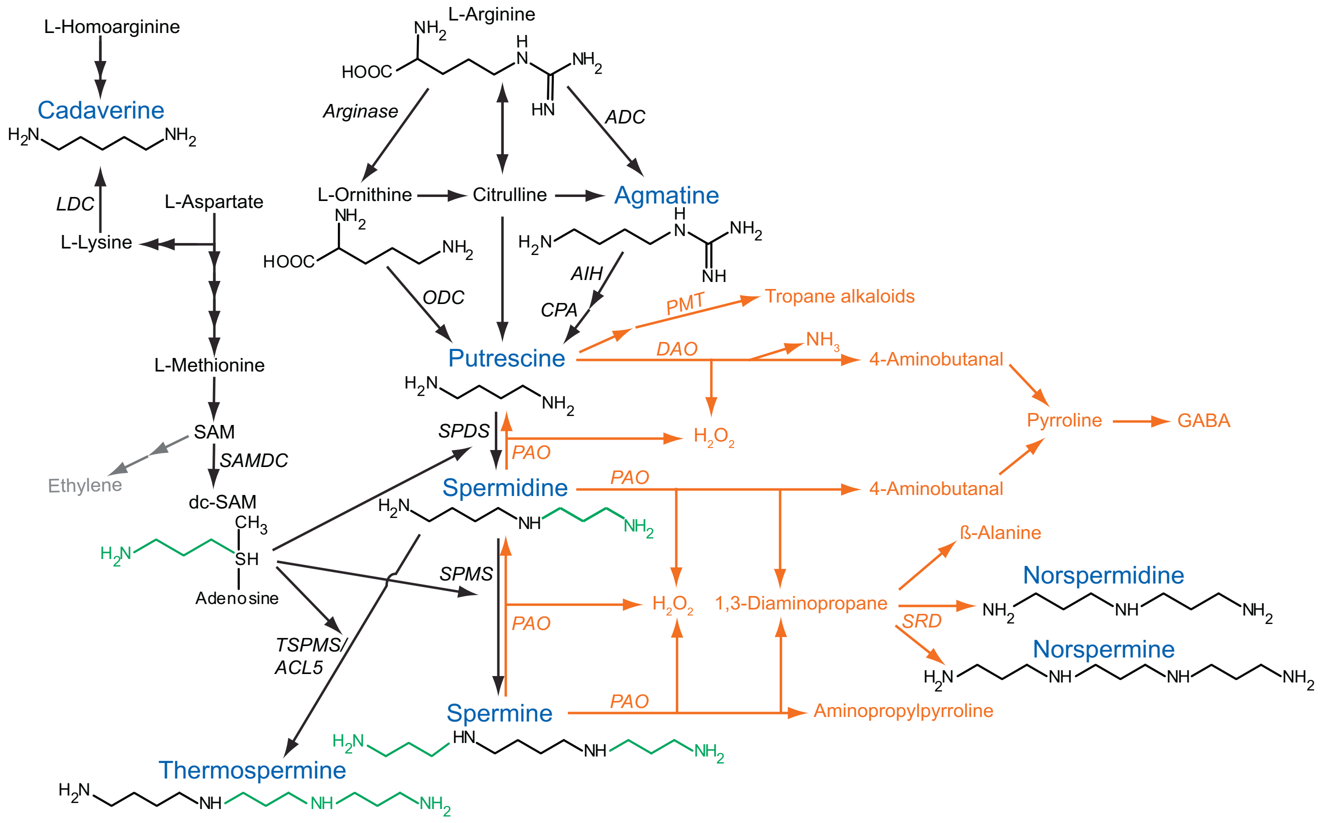

Fig. 1. Polyamine metabolism. Schematic biosynthetic pathways for common polyamines and related metabolites are indicated by black lines and catabolic processes in red. Common polyamines are in blue and enzymes in italics. Abbreviations: ACL5, ACAULIS5; ADC, arginine decarboxylase; AIH, agmatine iminohydrolase; CPA, *N*-carbamoylputrescine amidohydrolase; DAO, diamine oxidase; dc-SAM, decarboxylated *S*-adenosylmethionine; GABA, γ-aminobutyric acid; LDC, lysine decarboxylase; ODC, ornithine decarboxylase; PAO, polyamine oxidase; PMT, putrescine *N*-methyltransferase; SAM, *S*-adenosylmethionine; SAMDC, *S*-adenosylmethionine decarboxylase; SPDS, spermidine synthase; SPMS, spermine synthase; SRD, Schiff-base reductase/decarboxylase; TSPMS, thermospermine synthase.

via a lysine decarboxylase (EC 4.1.1.18). Most of the genes in the polyamine biosynthetic pathway are duplicated in plants. In *Arabidopsis*, two spermidine synthases and a spermine synthase associate to form a metabolon (Panicot et al., 2002). *ACL5*, one of the predicted *A. thaliana* spermine synthase genes was recently shown to encode a protein with thermospermine synthase activity (Knott et al., 2007). This suggested the presence of this spermidine isomer in plants and may explain the characteristic phenotypes in stem elongation and vascular development observed upon *ACL5* defect (Hanzawa et al., 1997; Clay and Nelson, 2005; Kakehi et al., 2008). Interestingly, a duplication of the genes encoding spermidine/spermine synthases has led to the evolution of putrescine *N*-methyltransferases, catalyzing the first step to the secondary metabolites nicotine and tropane alkaloids in Solanales (Minguet et al., 2008).

S-adenosylmethionine carboxylase (SAMDC) seems a critical point of regulation of polyamine homeostasis in all organisms (see e.g. Kumar et al., 1996; Martin-Tanguy, 1997) and might be responsible for antagonism between synthesis of higher polyamines and ethylene. Polyamine-controlled upstream ORF-mediated translational regulation of SAMDC was reported in mammals and plants. In *Arabidopsis*, two uORFs contribute to SAMDC regulation and translation repression at reduced levels of polyamines (Hanfrey et al., 2005).

Plant polyamine catabolism was recently reviewed by Moschou et al. (2008a) and is also summarized in Fig. 1. The main polyamine catabolic pathway, via both diamine and polyamine oxydases, generates H_2O_2. Catabolism of putrescine via diamine oxydase (DAO) also generates γ-aminobutyric acid, often considered as a mediator of plant defence. Plant polyamine oxydases (PAOs) catalyze the retroconversion from spermine and spermidine to spermidine and putrescine, respectively. They do not require acetylation of their substrates as shown for animal enzymes. Several DAO and PAO genes are found in plant genomes. Some of these enzymes were shown to be targeted to peroxisomes (Moschou et al., 2008a; Kamada-Nobusada et al., 2008) or the vacuole (Cervelli et al., 2004). This raises the question of their specific roles in the plant.

Polyamine homeostasis further relies on their conversion into secondary metabolites such as nicotine or tropane alkaloids in Solanaceae (Kusano et al., 2008) or in their conjugation with hydroxycinnamic acids (see below) or with proteins, hemicellulose or lignin (Creuss et al., 1991). Cross-linking mediated by transglutaminases might play a significant role in polyamine bioactivity for flower development and compatibility in reproduction (Serafini-Fracassini and Del Duca, 2008). Extracellular transglutaminases are expected to support organization of the cell-wall and pollen tube growth. For cytosolic enzymes, tubulin and actin have been identified as substrates (Del Duca et al., 1997), while chloroplastic forms would protect thylakoid proteins and Rubisco.

2.2. Role in plant growth and development

Polyamines, in particular spermidine, are essential for plant viability. Double insertional mutants of both arginine decarboxylase genes, both spermidine synthase genes, or of *SAMDC1* and *SAMDC4* *S*-adenosylmethionine carboxylases are embryo lethal in *A. thaliana* (Urano et al., 2005; Imai et al., 2004a; Ge et al., 2006). Mutants defective in spermine synthesis however grow normally (Imai