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Review

S-Adenosyl-L-methionine: Beyond the universal methyl group donor

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Dedicated to Prof. Rodney Croteau at the occasion of his 60th birthday.

Abstract

S-Adenosyl-L-methionine (AdoMet or SAM) is a substrate in numerous enzyme-catalyzed reactions. It not only provides methyl groups in many biological methylations, but also acts as the precursor in the biosynthesis of the polyamines spermidine and spermine, of the metal ion chelating compounds nicotianamine and phytosiderophores, and of the gaseous plant hormone ethylene. AdoMet is also the source of catalytic 5′-deoxyadenosyl radicals, produced as reaction intermediates by the superfamily of radical AdoMet enzymes. This review aims to summarize the present knowledge of catalytic roles of AdoMet in plant metabolism.

Keywords: *S*-Adenosyl-L-methionine; Methyltransferases; Polyamines; Nicotianamine; Phytosiderophores; Ethylene; 5′-Deoxyadenosyl radicals

Contents

1. Introduction

The number of known enzymes that utilize *S*-adenosyl-L-methionine (**1**) (AdoMet or SAM, Fig. 1) has increased steadily in recent years. It is now clear that the transfer of methyl groups is only one role of this metabolite. Because of the vast number of methylated secondary products, methyltransferases are the most numerous among the AdoMet-utilizing enzymes in plants. Considering the richness of flora on Earth, and the fact that many identified or yet to be identified secondary products are produced only

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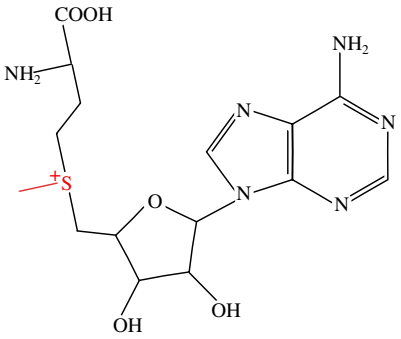


S-Adenosyl-L-Methionine, **1**

Fig. 1. Chemical structure of AdoMet. The sulfonium and the *S*-bound methyl group are highlighted in red. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

by some plant species, many more AdoMet-utilizing methyltransferases will likely be discovered in the future. AdoMet (**1**) is also recognized as the substrate of a decarboxylase, of enzymes that catalyze transfer of aminopropyl or carboxypropyl groups, and of enzymes that catalyze generation of 5′-deoxyadenosyl radicals in plants. Reactions catalyzed by these enzymes lead to the biosynthesis of ethylene, polyamines, nicotianamine, phytosiderophores, and biotin. Finding enzymes that use AdoMet (**1**) as a substrate for entirely novel reactions in plants would not be surprising, as such enzymes are still being found in other organisms. For example, the recently discovered enzyme aclacinomycin-10-hydroxylase from *Streptomyces purpurascens* catalyzes an AdoMet-dependent hydroxylation reaction (Jansson et al., 2005).

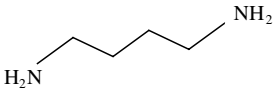
AdoMet (**1**) is synthesized from methionine and ATP in a reaction catalyzed by the enzyme AdoMet synthetase (Aarnes, 1977; Espartero et al., 1994; Izhaki et al., 1995; Konze and Kende, 1979; Schröder et al., 1997; Van Breusegem et al., 1994). The biosynthesis of methionine, and other members of the aspartate family of amino acids, is regulated by AdoMet (**1**) in plants. AdoMet (**1**) inhibits an isozyme of aspartate kinase in the presence of lysine (Azevedo et al., 1997), activates threonine synthase (Curien et al., 1998; Madison and Thompson, 1976), and affects stability of the mRNA for cystathionine γ-synthase (Chiba et al., 2003). Through these interactions, AdoMet (**1**) also regulates its own biosynthesis. This review focuses on AdoMet (**1**) as substrate in enzyme-catalyzed reactions in plants. Other related reviews have dealt with the biosynthesis of aspartate-derived amino acids and AdoMet (**1**) (Amir et al., 2002; Azevedo et al., 1997; Azevedo and Lea, 2001; Galili and Höfgen, 2002; Hesse et al., 2004; Hesse et al., 2001; Ravanel et al., 1998).

2. AdoMet as the precursor of polyamines

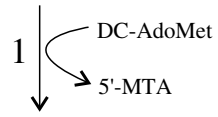
As the aminopropyl group donor in the biosynthesis of the polyamines spermidine (**3**) and spermine (**4**), AdoMet (**1**) is first decarboxylated to *S*-adenosyl-methioninamine in a reaction catalyzed by AdoMet decarboxylase (Dresselhaus et al., 1996; Hao et al., 2005; Mad Arif et al., 1994; Thu-Hang et al., 2002). Spermidine synthase (Yoon et al., 2000) then catalyzes transfer of the aminopropyl moiety of *S*-adenosyl-methioninamine to putrescine (**2**), yielding spermidine (**3**). Addition of another aminopropyl moiety to spermidine (**3**), catalyzed by spermine synthase (Hanzawa et al., 2000), yields spermine (**4**) (Fig. 2). Putrescine (**2**), spermidine (**3**), and spermine (**4**) are positively charged at cellular pH values, and are known to chemically interact with DNA, RNA, phospholipids, and some proteins. Abnormal phenotypes of plant mutants modified in polyamine metabolism suggest that these molecules are involved in the regulation of plant development (Clay and Nelson, 2005; Hanzawa et al., 2000; Imai et al., 2004a). Polyamines also appear to be involved in plant stress responses (Imai et al., 2004b; Kasukabe et al., 2004). Yet, their exact mode of action is unknown.

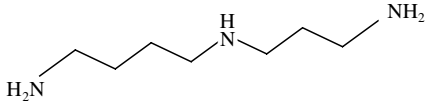
3. AdoMet as the precursor of nicotianamine and phytosiderophores

Nicotianamine (**5**) (Fig. 3), a strong chelator of iron and various transition metals, occurs widely in higher plants

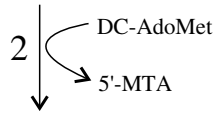


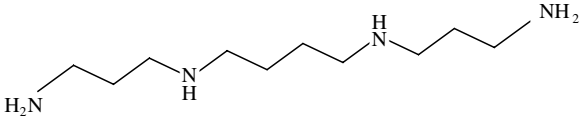
Putrescine, **2**





Spermidine, **3**





Spermine, **4**

Fig. 2. Biosynthesis of spermidine and spermine. Abbreviations: 1, spermidine synthase; 2, spermine synthase; DC-AdoMet, *S*-adenosyl-methioninamine; 5-MTA, 5-methylthioadenosine.