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Database on mycosporines and mycosporine-like amino acids (MAAs) in fungi, cyanobacteria, macroalgae, phytoplankton and animals

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Abstract

A database on UV-absorbing mycosporines and mycosporine-like amino acids (MAAs) has been constructed that provides information on various mycosporines and MAAs reported in fungi, cyanobacteria, macroalgae, phytoplankton and animals from aquatic and terrestrial habitats. It also contains information on biosynthetic routes of MAAs as well as on the absorption maxima and molecular structures of different mycosporines and MAAs (Table 1S). This database provides necessary information for scientists working in the field of photoprotective compounds in fungi, cyanobacteria, macroalgae, phytoplankton and animals (Table 2S). (Tables 1S and 2S are available online as Supplementary material in the electronic copy of the journal as well as on our server <http://www.biologie.uni-erlangen.de/botanik1/html/eng/maa_database.htm>.)

Keywords: Phytoplankton; Macroalgae; Mycosporines; MAA; Data base

1. Introduction

Solar UV-B and UV-A radiation are detrimental for most sun-exposed organisms. To counteract the photodamage various organisms including microorganisms, plants and animals have developed a number of photoprotective compounds such as phenylpropanoids and flavonoids (in higher plants), melanins (in humans and animals), scytonemins (exclusively in cyanobacteria), mycosporines (in fungi), mycosporine-like amino acids (MAAs, in cyanobacteria, algae and animals) and several other UV-absorbing substances of unknown chemical structures [1,2].

Mycosporine-like amino acids have received much attention for their putative role in UV photoprotection, which were originally identified in fungi as having a role in UV-induced sporulation [3]. These MAAs are small (<400 Da), colorless, water-soluble compounds composed of a cyclohexenone or cyclohexenimine chromophore conjugated with the nitrogen substituent of an amino acid or its imino alcohol [4,5], having absorption maxima ranging from 310 to 362 nm. Generally, the ring system contains a glycine subunit linked to the third carbon atom. Some MAAs also contain sulfate esters or glycosidic linkages through the imine substituents [6,7]. Differences between the absorption spectra of MAAs are due to the attached side groups and nitrogen substituents. Mycosporines differ from MAAs in exclusively having an aminocyclohexenone unit bound to an amino acid or amino alcohol group and having absorption maxima between 310 and 320 nm. The most common method for detection and quantification of these compounds is high-performance liquid chromatography (HPLC) based on their retention times and their absorption maxima or obtaining entire UV scans via diode array detection (DAD) [5,8,9]. The electrospray ionization

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mass spectrometry (MS) coupled with liquid chromatography (LC/MS) has also been used to analyze the MAAs in several organisms [10–12]. Recently, Torres et al. have reported the structure and molecular formula of porphyra-334 by the application of MS in conjunction with ^{1}H and ^{13}C NMR data [13].

The biosynthesis of MAAs has been predicted to occur *via* the first part of the shikimate pathway but concluding evidences are lacking. It has been found that 3-dehydroquinate, which is formed in the center of the shikimate pathway, acts as a precursor for the synthesis of fungal mycosporines and MAAs *via* gadusols [14–16] (Fig. 1). The primary MAA mycosporine-glycine, synthesized in the shikimate pathway, is then transformed into other secondary MAAs [17,18]. The synthesis of mycosporines and MAAs occurs in fungi, bacteria, cyanobacteria, phytoplankton, macroalgae (red, brown and green algae) but not in animals, because they lack the shikimate pathway. Studies have shown that in animals MAAs are derived from their algal diet [19,20]. Thus, MAAs provide protec-

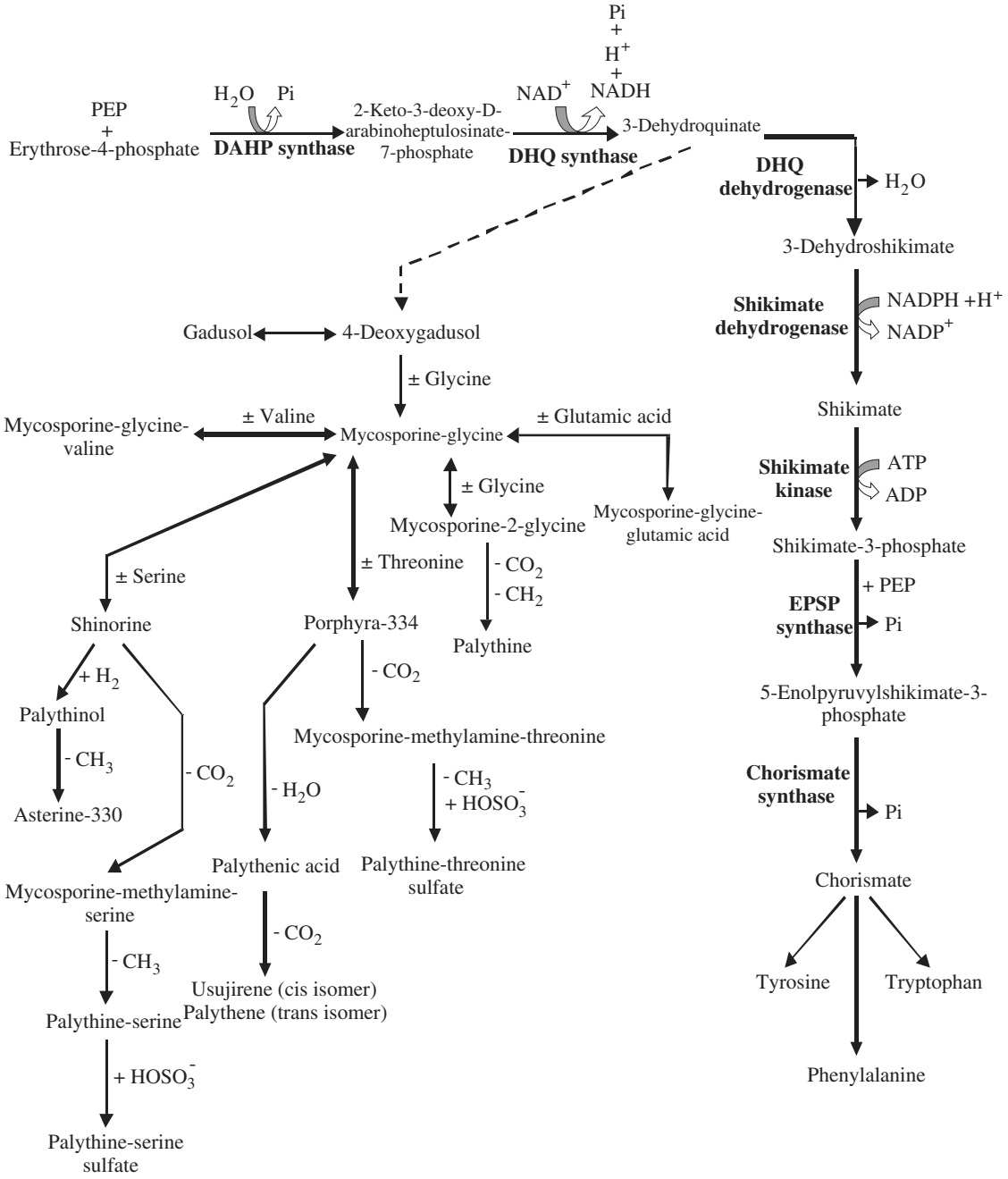

Fig. 1. Biosynthetic routes for the formation of MAAs *via* the shikimate pathway and their feasible chemical and/or biochemical conversion. Broken line represents the putative biosynthetic connection between Dehydroquinate, gadusols and MAAs. PEP: Phosphoenolpyruvate; DAHP: 3-deoxy-D-arabinoheptulosinate-7-phosphate; DHQ: dehydroquinate; EPSP: 5-enolpyruvylshikimate-3-phosphate.