



Volatile isoprenoids and their importance for protection against environmental constraints in the Mediterranean area



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ABSTRACT

Among plant secondary metabolites, volatile isoprenoids have received increasing attention because they are involved in a range of physiological and ecological interactions, often helping plants cope with abiotic and biotic stressors, and potentially affecting the chemistry of the troposphere once they are emitted in the air. We review evidence about the beneficial functions of volatile isoprenoids in leaves, principally as antioxidants and membrane stabilizing agents, avoiding heat damage. Because the Mediterranean environment is characterized by prolonged dry and hot seasons, and recurrent heat-waves, we surmise that volatile isoprenoids are particularly widespread, and play an important physiological role, in Mediterranean woody plants. Based on a review of available inventories, isoprene emission characterizes deciduous woody plants, whereas evergreens are more often monoterpene emitters. Monoterpene emitters may be better fit to the Mediterranean climate, and, in general, to climate conditions favoring evergreens.

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1. Introduction

According to the definition given by Verpoorte and Alfermann (2000) secondary metabolites are bioactive plant compounds, which have a restricted occurrence in taxonomic groups and are not necessary for a cell (organism) to live, but ensure the survival of the organism in its ecosystem. Based on the biosynthetic pathway from which they derive, secondary metabolites are divided in three groups: terpenoids (= terpenes = isoprenoids), alkaloids and phenylpropanoids (Croteau et al., 2000).

The terpenoids derive from the isoprenoid biosynthetic pathway, which uses building blocks of five carbon (C5) compounds. Terpenoids are classified, based on the number of the isoprenic units, as hemiterpenes (C5), monoterpenes (C10), homoterpenes (C11,

C16), sesquiterpenes (C15), diterpenes (C20), triterpenes/steroids (C30) and tetraterpenes (carotenoids) (C40). Within major classes (e.g. monoterpenes, sesquiterpenes) a myriad of terpenoids can be formed, based on oxidation, reduction, isomerization and conjugation reactions (Croteau et al., 2000). Volatile terpenoids, more often called volatile isoprenoids (VIPs), include hemiterpenes, homoterpenes, monoterpenes and sesquiterpenes. Di-, tri- and tetra-terpenes form the group of non-volatile terpenoids. The diterpene compounds arise from geranylgeranyl diphosphate. One of the simplest and most important of the diterpenes is phytol, which forms the lipophilic side-chain of the chlorophylls (Vetter and Schröder, 2011). Triterpenes arise from squalene, a coupling of two farnesyl diphosphate units (Abe, 2007). Cyclization of squalene, or squalene oxide leads to a large number of diverse structural triterpene skeletal types, such as lupane, oleanane, ursane (Tantillo, 2011). Finally, tetraterpenes (carotenoids) constitute the largest group of natural dyes. Carotenoids are substances with very special properties possessed by no other group of substances, such as xanthophylls, and which allow protection of all kinds of living organisms (Britton, 1995).

Most of the alkaloids are nitrogen-containing compounds derived through the decarboxylation of amino-acid precursors (ornithine, lysine, tyrosine, tryptophan, and histidine) and they are end-products of different biosynthetic pathways. Contrary to terpenoids, alkaloids are relatively stable. They represent the most potent class of compounds of the chemical defense arsenal used by

Abbreviations: CCN, cloud condensation nuclei; DMAPP (C5), dimethylallyl diphosphate; ER, endoplasmic reticulum; FPP, farnesyl diphosphate; G3P, glyceraldehyde 3-phosphate; GGPP, geranylgeranyl diphosphate; GPP, geranyl diphosphate; IPP, isopentenyl pyrophosphate; MEP, 2-C-methyl-D-erythritol 4-Phosphate; NOx, nitric oxides; PSII, photosystem II; ROS, reactive oxygen species; SOA, secondary organic aerosol.

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plants against herbivore and micro-organism attacks (Schowalter, 2006).

Phenylpropanoids originate from aromatic amino acids, from phenylalanine to cinnamic acid and from tyrosine to *p*-coumaric acid, by the action of phenylalanine ammonia-lyase (PAL) and tyrosine ammonia-lyase (TAL), respectively. A series of enzymatic hydroxylations and methylations leads to production of monolignols, *p*-coumaryl, coniferyl and synapil alcohols. Their further hydroxylation and cyclization lead to phenolic acids, lignans, lignins and flavonoids (Vogt, 2010).

While all secondary metabolites influence ecological interactions between plants and the environment (Croteau et al., 2000), this review will only focus on isoprenoids, and particularly on volatile isoprenoids, whose presence is widespread in the Mediterranean and might have important ecological roles in protecting plants against environmental constraints.

Isoprenoids are associated with both primary and secondary metabolism. Primary isoprenoids, i.e. gibberellins, abscisic acid and brassinosteroid phytohormones, phytosterols and carotenoids, are involved in basic and indispensable functions, such as the regulation of plant growth and development, photosynthesis, membrane permeability and fluidity (Vranová et al., 2012). However, the majority of the plant isoprenoids are secondary, often volatile metabolites that play a crucial role in the interaction of plants with the environment, e.g. by serving as pollinator attractants, herbivore repellents, anti-feedants, toxins or antibiotics (Gershenzon and Dudareva, 2007). All plants produce isoprenoids as secondary metabolites, but the spectrum of constitutive isoprenoids is very diverse among the different plant species, and within the single species. Moreover, isoprenoid biosynthesis can be induced by stresses (Dicke and Loreto, 2010). Plants may opportunistically allocate carbon resources either to primary metabolism and essential isoprenoid biosynthesis, or to volatile isoprenoids that are used for defensive purposes when coping with stressors (Owen and Peñuelas, 2005). In other cases, volatile isoprenoids simply proxy the activation of biosynthetic pathways that lead to other stress-defensive compounds, e.g. abscisic acid (ABA, Barta and Loreto, 2006). In turn, ABA formation may alter phenylpropanoid metabolism, thus regulating a general and yet under-investigated cross-talk among secondary metabolites (Tattini, personal communication).

2. Impacts of biogenic emissions on global and Mediterranean climate

At a global level, estimated natural volatile organic compound (VOC) emissions are of the order of 1300 Tg(C)/yr, with volatile isoprenoids contributing >50% of total VOC, and about 10 times more than other classes of volatiles (Pichersky and Gershenzon, 2002; Loreto and Schnitzler, 2010; Guenther et al., 2006). The major components of volatile isoprenoids are isoprene (44%) and monoterpenes (11%) (Guenther et al., 1995). Semi-volatile sesquiterpenes are estimated to make up to 28% of overall plant isoprenoids (Helmig et al., 1999).

Volatile isoprenoids play a key role in determining atmospheric chemistry and composition. Through reactions with the major atmospheric oxidizing agents and NO_x, volatile isoprenoids control the oxidizing capacity of the atmosphere, with monoterpenes and sesquiterpenes mostly producing secondary organic aerosols (Bonn and Moortgat, 2002; Joutsensaari et al., 2005) (Fig. 1), which affect local air quality and global climate. Isoprene, on the other hand, can be directly oxidized by O₃ and NO_x; thus, depending on the level of these pollutants, isoprene may affect both the rates of production and of destruction of tropospheric ozone. Namely, at low levels of NO_x, isoprene is oxidized by ozone, thus contribute to scavenging

atmospheric ozone concentration, whereas at high concentrations of NO_x, isoprene oxidation produces NO₂ which increases O₃ level, as photolysis of NO₂ leads to formation of monooxygen that rapidly reacts with O₂ to form O₃ (Chameides et al., 1988; Taraborrelli et al., 2009). The Mediterranean area seems to be a particularly relevant hot spot for VIP-driven atmospheric chemistry (Fowler et al., 2009). At least two factors contribute to this effect: (i) the large and diverse emissions of VIPs by Mediterranean vegetation, as detailed below, also elicited by optimal weather conditions (high temperature and sunny summer days); and (ii) the position of coastal forests (a major source of biogenic VIPs) and cities (a major sources of anthropogenic NO_x) with respect to prevailing wind circulation, which makes it possible mixing of these reactive compounds at optimal rates to trigger reactivity and formation of atmospheric pollutants (Fares et al., 2009).

Finally, volatile isoprenoids alter climate by expanding the residence time of greenhouse gases which more slowly react with hydroxyl radicals in air, such as methane (Kwan et al., 2012; Taraborrelli et al., 2009), and by the formation of aerosols and cloud condensation nuclei (e.g. Kesselmeier et al., 2002; Peñuelas and Llusia, 2003). In all cases, volatile isoprenoids indirectly contribute to altering climate and favor global warming (Grote et al., 2006).

3. Volatile isoprenoids biosynthesis

In plants, all isoprenoids are synthesized from two C5 precursors: isopentenyl diphosphate (IPP) and its isomer dimethylallyl diphosphate (DMAPP), via two main biosynthetic pathways (Fig. 1): the MEP (2-C-methyl-D-erythritol 4-phosphate) pathway in plastids, and the MVA (mevalonic acid) pathway in cytosol and perhaps also in peroxisomes (Sapir-Mir et al., 2008) and in the endoplasmic reticulum membranes (Vranová et al., 2012). The MEP and MVA pathways are often alternative in the formation of volatile isoprenoids, though they seem to cooperate under stressful conditions that reduce photosynthesis. Both biosynthetic pathways are responsible for the formation of the IPP and DMAPP from pyruvate and glyceraldehyde 3-phosphate in the plastids, and from acetyl-CoA in the cytosol. Once the C5 units are formed, isoprenyl diphosphate synthases (part of the prenyltransferase enzyme family), catalyze condensations of IPP and DMAPP into GPP (geranyl diphosphate, C10), FPP (farnesyl diphosphate, C15) and GGPP (geranylgeranyl diphosphate, C20) (Liang et al., 2002). Finally, diverse terpene synthases (TPSs) convert DMAPP, GPP and GGPP into hemiterpenes (C5), monoterpenes (C10), diterpenes (C20) and tetraterpenes (C40) in plastids; whereas other TPSs convert FPP to sesquiterpenes (C15) and triterpenes (C30) usually in the cytosol (Bohlmann et al., 1998; Lange et al., 2000).

Multiple studies using different approaches have shown that an exchange of isoprenoid precursors takes place among different sub-cellular locations (Flores-Perez et al., 2008; Vranová et al., 2012). Also, it has been shown that a flow of intermediates between both pathways occurs (Hemmerlin et al., 2003; Laule et al., 2003; Schuhr et al., 2003; Dudareva et al., 2005) especially from the chloroplasts toward the cytosol (Laule et al., 2003). The intermediate FPP, once thought to be confined to the cytosol, is also present in the plastid (Aharoni et al., 2003; Schuhr et al., 2003). Sesquiterpene formation occurs not only in the cytosol, but also in plastids, endoplasmic reticulum systems, and mitochondria (Dudareva et al., 2005; Sapir-Mir et al., 2008; Sallaud et al., 2009). At the regulatory level, substrate availability, gene regulation, enzyme activity, sub-cellular compartmentation and other factors may control the rate of volatile isoprenoids formation. For example, it has been shown that light and sugar signaling down-regulate the MVA pathway but up-regulate the MEP pathway (Flores-Perez et al., 2008; Vranová et al., 2012).

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