Available online at www.sciencedirect.com
ScienceDirect
South African Journal of Botany 76 (2010) 612–631
SOUTH AFRICAN JOURNAL OF BOTANY
www.elsevier.com/locate/sajb

Sites of synthesis, biochemistry and functional role of plant volatiles

M.E. Maffei *

Plant Physiology Unit, Department of Plant Biology, Innovation Centre, University of Turin, Via Quarello 11/A, 10135 Turin, Italy

Received 7 January 2010; received in revised form 3 March 2010; accepted 8 March 2010

Abstract

All plants are able to emit volatile organic compounds (VOCs) and the content and composition of these molecules show both genotypic variation and phenotypic plasticity. VOCs are involved in plant–plant interactions and for the attraction of pollinating and predatory insects. The biochemistry and molecular biology of plant VOCs is vast and complex, including several biochemical pathways and hundreds of genes. In this review the site of synthesis, the biosynthesis and the functional role of VOCs are discussed.

Keywords: Chemical defense; Molecular biology; Physiology; Plant secretory structures; Terpenes; Volatile organic compounds (VOCs)

1. Introduction

Volatile organic compounds (VOCs) are products emitted into the atmosphere from natural sources in marine and terrestrial environments (Guenther et al., 1995; Lerdau et al., 1997; Chappell, 2008) and the majority of VOCs entering the atmosphere are of biogenic origin. In fact, over 90% of natural emission of VOCs is related to plants species with dominant sources of VOCs being forests all over the world; the most important among them is the Amazonian rainforest. Plants emit 400–800 Tg C/yr as hydrocarbons, an amount equivalent to the sum of biogenic and anthropogenic methane emissions (Guenther et al., 1995), while up to 36% of the assimilated carbon is released as complex bouquets of VOCs (Kesselmeier and Staudt, 1999; Kesselmeier, 2001; Kesselmeier et al., 2002). Unlike methane, plant-produced VOCs are extremely reactive in the troposphere, with life-times ranging from minutes to hours (Lerdau et al., 1997), contributing to the aerosol that scatters the light to produce the blue sky.

VOCs are released from leaves, flowers and fruits into the atmosphere and from roots into the soil. To humans, pollinator-attracting floral VOCs have been a source of olfactory pleasure since antiquity, and we also use a large number of aromatic plants as flavorings, preservatives, and herbal remedies (Pichersky and Gershenzon, 2002; Pichersky et al., 2006).

The primary functions of airborne VOCs are to defend plants against herbivores and pathogens, to attract pollinators, seed dispersers, and other beneficial animals and microorganisms, and to serve as signals in plant–plant communication (Dudareva and Pichersky, 2008). In some plants, released VOCs may also act as wound sealers (Penuelas and Llusia, 2004).

Some VOCs might be dangerous for human's health when present at higher concentrations (Jahodar and Klecakova, 1999), and plant-emitted VOCs are also major precursors of tropospheric phytotoxic compounds (Padhy and Varshney, 2005). Since some VOCs can act as precursors of photochemical smog, their level is one of the fundamental parameters for the assessment of atmosphere quality (Ulman and Chilmonczyk, 2007). VOCs can regulate the oxidative capacity of the troposphere, carbon monoxide, O_3 and aerosol budgets, and together with high concentration of nitrogen oxides in the sunlight they form more phytotoxic O_3 (Vuorinen et al., 2005). Furthermore, VOCs have also been shown to be involved in the formation of secondary aerosols in the atmosphere, which have implications for the radiative balance of the earth (Padhy and Varshney, 2005).

Routine measurements of VOCs in air have shown that average concentrations are very much smaller than those used in laboratory experiments designed to study the effects of VOCs on plants. However, maximum hourly concentrations of some

* Tel.: +39 0116705967; fax: +39 0112365967.
E-mail address: massimo.maffei@unito.it.

0254-6299/$ - see front matter © 2010 SAAB. Published by Elsevier B.V. All rights reserved.
doi:10.1016/j.sajb.2010.03.003

VOCs can be 100 times larger than the average, even in rural air (Cape, 2003).

This review aims to collect most of the information available on the ability of plants to produce VOCs and to explore their sites of synthesis, biochemistry and functional role.

2. Plant VOCs

Chemically, VOCs belong to the large group of terpenoids (homo-, mono-, di-, sesquiterpenoids), fatty acid derived C_6-volatiles and derivatives, phenylpropanoid aromatic compounds (like methyl salicylate, MeSA, and indole), as well as certain alkanes, alkenes, alcohols, esters, aldehydes, and ketones (Pichersky and Gershenzon, 2002; Holopainen, 2004; Arimura et al., 2005, 2009; Baldwin et al., 2006; Wu and Baldwin, 2009). Today more than 1700 volatile compounds have been isolated from more than 90 plant families, constituting approximately 1% of all plant secondary metabolites (Pichersky and Gershenzon, 2002). The composition of VOCs emitted by plants also depends on the mode of damage such as single wounding, continuous wounding (Mithöfer et al., 2005), herbivore feeding (Paré and Tumlinson, 1996), and egg deposition (Hilker and Meiners, 2002). Some VOCs emitted after insect feeding can serve as repellents to the attacking insect itself as a direct defense, as well as attractants to the natural enemies of the attacking insect as indirect defenses (Kessler and Baldwin, 2001). An herbivore-induced VOC blend may comprise more than 200 compounds (Dicke and Van Loon, 2000). In addition to attracting the natural enemies of the egg and larval stages, herbivore-induced plant volatiles (HIPVs) can also decrease the oviposition rates of the attacking herbivores and thus can be considered both direct and indirect defense systems (Dicke and Van Loon, 2000; Kessler and Baldwin, 2001). Besides addressing organisms from other trophic levels, induced VOCs also act on neighbored leaves of other plants (Arimura et al., 2000; Engelberth et al., 2004; Heil and Silva Bueno, 2007). Moreover, the volatile production generally shows a pronounced rhythmicity by emitting the volatiles mostly during the light phase (Arimura et al., 2008b). Furthermore, the production of VOCs is activated by elicitors from oral secretions of the attacking insect herbivore (Truitt et al., 2004; Truitt and Pare, 2004; Schmelz et al., 2006).

Although defenses might benefit plants, the expression of plant resistance can be costly in the absence of plant enemies (Bergelson and Purrington, 1996; Strauss et al., 2002). Since the synthesis of a chemical represents an investment of energy and resources for the organism if the benefits it gets from this investment are reasonable, evolution will keep this trait, yet the opposite is also true: if the use of resources does not benefit the organism, this adaptation may persist or it will eventually disappear (Macias et al., 2007). Since the production of VOCs can be limited by both light and soil nutrients is likely to incur considerable costs, at least under certain growing conditions (Heil, 2008).

3. Sites of synthesis of plant VOCs

Plants express different types of secondary metabolites as defense strategy against biotrophs, ranging from the constitutive and inducible synthesis of bioactive natural products to the production of structural traits (Ballhorn et al., 2008). Many VOCs, particularly most monoterpenes and sesquiterpenes, are synthesized and stored in special secretory tissues, which occur in most vascular plants. The secreted material is usually eliminated from the secretory cells outside the plant or into specialized intercellular spaces (Fahn, 1988). Certain plant species accumulate VOCs in resin ducts, or glandular trichomes and such compounds can be released in large amounts as soon as these structures are ruptured by herbivore feeding or movements on the plants' surface (Duke et al., 2000). Since many of the constitutive defense compounds may be toxic at high concentrations to the plant itself, the plant must be able to generate and store such substances without poisoning itself. The obvious strategy to overcome this problem is to store VOCs as inactive precursors, for instance as glycosides (Jerkovic and Mastelic, 2001), or in extracellular compartments, as in the case of glandular trichomes. Secretory tissues are usually classified according to the substance they produce and trichomes, ducts and cavities are mainly involved in VOC production.

3.1. Glandular trichomes

Several plant species store VOCs in specialized glandular trichomes (Gershenzon et al., 2000) which release their contents in response to tissue damage, thus deterring herbivores or inhibiting microbial growth (Langenheim, 1994). Glandular trichomes secreting VOCs are present in Lamiaceae, Asteraceae, Geraniaceae, Solanaceae and Cannabinaceae. Their morphology may vary among families although two general types of trichomes are frequently present: capitate trichomes, which consist of a basal cell, one to several stalk cells and one to few secretory cells (Fig. 1A–B) and peltate trichomes, comprising a basal epidermal cell, a short stalk cell and a secretory head consisting of several secretory cells arranged in one layer (Fig. 1C–F). Whatever the exact nature of the capitate gland secretory products, it is clear that the bulk of the VOCs is produced by and stored in the peltate glandular trichomes (Maffei et al., 1989; Turner et al., 2000). This general scheme of glandular trichome structure can reach a further complexity in some families where trichomes are multicellular and biseriate, with one to several pairs of cells in the stalks and the secretory heads (Fahn, 1988) (Fig. 1C). In many cases, VOCs are accumulated inside the cuticular layer but outside the plant cell wall, either alone or along with other compounds which can be of a very different chemical nature and lipo-hydrophilicity. Being protodermal extrusions, glandular trichomes are present on plant surfaces, with particular reference to leaf blades, flowers and, in some cases, seeds. Although the presence of terpene synthases in trichomes has been well documented (Bertea et al., 2006), the regulation of their expression in trichomes remains obscure. In tomato (*Lycopersicon esculentum* Mill.), the expression of the monoterpene synthase *LeMTS1* in stems and petioles was predominantly detected in trichomes and could be induced by jasmonic acid (JA) treatment (Van Schie et al., 2007). To elucidate the biosynthetic pathway and to isolate and characterize genes involved in the biosynthesis of