Signaling and Communication in Plants

Nabil Semmar

Secondary Metabolites in Plant Stress Adaptation

Analytic Space of Secondary Metabolites

Springer

Signaling and Communication in Plants

Series Editor

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This book series will be devoted to diverse aspects of signaling and communication at all levels of plant organization, starting from single molecules and ending at ecological communities. The individual volumes will interlink molecular biology with plant physiology and the behavior of individual organisms, right up to the system analysis of whole plant communities and ecosystems.

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The integrative view of this book series will foster our understanding of plant communication throughout the individual plant and with other communicative systems such as fungi, nematodes, bacteria, viruses, insects, other plants, and predatory animals.

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Introduction

Environment constitutes a complex space characterized by a multidimensional (multifactorial) structure varying dynamically under the effect of continuously changing physical–chemical and biological factors leading to subsequent adaptive responses of biological populations at different system scales (molecular, cellular, tissue, physiological, intraspecific, interspecific scales). Biotic and abiotic factors continuously exert stresses on living organisms and populations leading to the need of adaptive (defensive, communicative) strategies for survival and co-development. Consequently, biological compositions and biochemical patterns of ecological populations are closely associated with different abiotic and biotic stressing factors occurring at different manifestation levels, frequencies (dominant, systemic, sudden, sporadic) and scales (local/global) of environment.

Identifying the types and quantifying the levels of changing/stressing factors in environment usefully help for evaluation of living states, variation trends and working ways of biosystems (organisms, populations, communities) favoring subsequently the management of natural resources at different spatial-temporal scales.

Identification and quantification of environment stresses require reliable recording ways of dynamical and cumulative variations of abiotic factors with subsequent (associated) responses of biological organisms living in such conditions. As sessile organisms, plants are continuously exposed to local environment stresses and consequently, their metabolism tends to be highly (reliably) associated with abiotic and biotic variations at different spatial, temporal and biological scales. Correlations between plant metabolism and environment conditions are efficiently highlighted by qualitative and quantitative variations of secondary metabolites (SMs) that are widely distributed in the plant world.

SMs represent a wide field of specialized small molecules showing high structural diversity, many biological activities and not uniform botanical distributions. They are produced at low amounts because of their reactivity and not body constitutive aspects (by opposition to primary metabolites: amino acids, fatty acids, saccharides). About 200,000 SMs have been elucidated from plants, whereas the total number of plant species exceeds 350,000. This makes to conclude about the relatively small number of known SMs compared with the potential number of not discovered yet in the plant world. SMs are mainly classified into three wide metabolic classes including phenolic compounds (hydroxylated benzene structures), terpenes (C5-multiple hydrocarbon chains or cyclic structures) and nitrogen-containing compounds represented by alkaloids, cyanogenic glycosides and glucosinolates (containing sulfur in addition to nitrogen). They play key roles in defense/protection of plants against harmful abiotic and biotic factors.

Abiotic stresses can be categorized into two main types including oxidative and osmotic processes which can be induced by different environment factors. Oxidative stresses involve the formation of reactive oxygenated species (ROS) that can be caused by high radiation levels, extreme temperatures, atmospheric ozone, as well as other oxidant compounds (e.g. heavy metals). Osmotic stress is essentially linked to drought (water deficit, saline middle) and cold (freezing) conditions. These stresses occur both in air and soil strata. This book focuses essentially on air-occurring abiotic stresses due to their direct involvement in the climate change (a current worry at planetary scale).

Biotic stress includes essentially pathogen infections and herbivore attacks of plants in addition to interspecific competitions (allelopathy) between spatially neighbor plants.

Plants respond to different environment stresses by the production and regulation of different types of SMs having appropriate structural and functional characteristics. Oxidative stresses are overcome by antioxidative SMs including essentially phenolic compounds (phenol acids, flavonoids, coumarins, tannins, etc.). Antioxidative properties of these SMs are due to the structural occurrence of hydroxyl groups and conjugated double bonds favoring electronic changes and transitions required for stopping radical chain reactions. Also, phenols show original antioxidative properties through ortho-di-hydroxylated structures able to chelate metals through electrostatic interactions. SMs with conjugated double bonds are also found in terpenes (sesquiterpenes, tetraterpenes) which represent electron sources for stopping oxidative chain reactions.

Osmotic stresses, however, are managed by osmoregulatory metabolites (osmolytes) helping for water retention in plant cells living in water-deficient environments (drought) or with unavailable form of water (freezing conditions). Osmoregulatory SMs include glycosylated compounds making the aqueous intra-cell space to be more concentrated resulting in the decrease of its osmotic potential and, subsequently, the reduction (avoidance) of water loss.

Oxidative and osmotic stresses tend to disturb and fragilize cell membranes by affecting its fluidity and integrity. Due to their lipophilic character, terpenes can interact with cell membrane contributing to the regulation of its fluidity and subsequent functional stabilization.

Oxidative stress can be systematically induced by radiative stress essentially caused by UV-light range. Harmful radiations and excess of non-photosynthetic light are treated by different specialized photoreceptors (chromophores made by conjugated nitrogen heterocycles and benzene) leading to attenuate and canalize the radiative energy for next use. Under radiative stress, antioxidants (e.g. phenolic compounds, carotenoids) are produced at different relative levels depending on radiation type, intensity and ratio.

Apart from abiotic stresses, plants should overcome biotic pressures due to pathogens and herbivores. For that, different SMs-based protective strategies were developed leading to immobilization, toxication or repellence of plant enemies. Pathogens are confronted by production of phytoanticipins and phytoalexins which can interact with proteins or cell membranes to alter their functional or structural aspects. These plant defensive compounds are concerned with various metabolic classes including phenolics, terpenes and nitrogen-containing SMs (alkaloids, cyanogenic glycosides, glucosinolates). Herbivore attacks are confronted by plants through production of individual or mixed SMs causing toxication or repellence of herbivores. Toxication can occur at different biological scales including (i) cytotoxicity via mitosis-blocking SMs or cell membrane attack and (ii) physiological disorder (e.g. paralysis, adverse nervous behaviors) via neural signal perturbation. Repellence of herbivore can occur through mixtures of volatiles (terpenes) attributing specific repulsive odors to the host plant and making the herbivore to avoid it. Astringent and antifeeding compounds provide another anticipative deterring way for plants against enemies. Interestingly, when plants are attacked by specialized herbivores able to detoxify, sequester or eliminate plant toxins, they can manifest indirect defense strategy by releasing mixtures of volatile compounds attracting the natural enemy of herbivore. Sesquiterpenes and monoterpenes were revealed to play key communicative roles in this indirect defense strategy.

Apart from their functional aspects contributing in plant protection against abiotic and biotic stresses, SMs provide highly useful metabolic patterns helping for (i) chemical characterization/classification of productive plants, and (ii) assessment of plant living conditions and environment states. This attributes to phytochemical patterns a great advantage for biodiversity and environment management. Phytochemical patterns can be characterized (interpreted) under different qualitative and quantitative aspects of SMs including occurrence–absence of metabolite(s), co-occurrence of different chemical compounds with variable regulation ratios. Further pattern analysis is made by correlations or variation trends between different metabolites leading to highlight their sensitivity levels and responsiveness ways in relation with different inductive abiotic factors and biological taxa. In biodiversity field, phytochemical pattern analysis provides a strong tool for chemotaxonomic classification of plant populations representing key resiliency components of ecosystems. Environment management via phytochemical pattern analysis can be deepened by considering interaction effects of different co-manifesting environment factors on SM production profiles in different plant taxa.

A synthesis picture on involvement ways of SMs in environment management is given in Fig. 1.

Phytochemical management of environment represents an integrative field associating variable plant metabolic patterns with many structural states and functional aspects of plant growing conditions by means of multifactorial and multiscale computational analyses (Fig. 2). Phytochemical data can be of different types including identified molecular structures (chemical compositions) by spectroscopic ways,

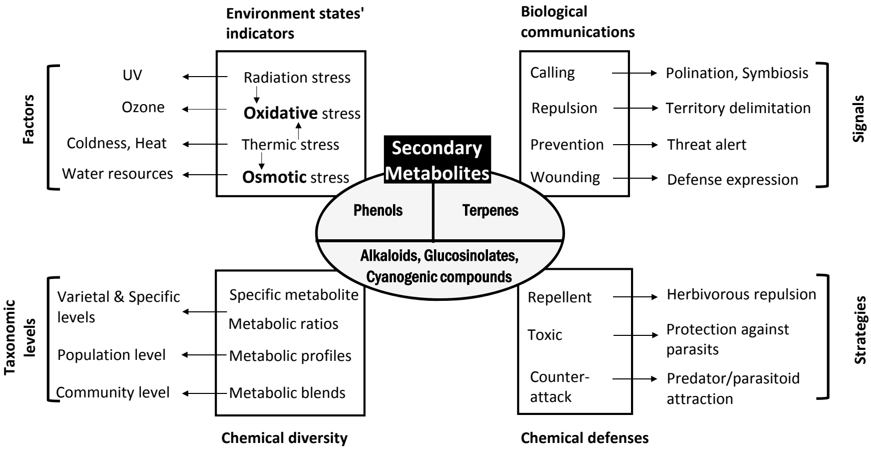

Fig. 1 Synthesis presentation on the book content focused on the interests of secondary metabolites and their patterns (production levels, regulation ratios) in the chemical assessment, monitoring and management of biological populations and natural spaces

quantified amounts by chromatographic ways (in different biological or environment matrices), *in silico* calculated molecular interaction energies, *in vitro* evaluated biological activities, etc. (Fig. 2a). Statistical analysis of these different types of data requires different appropriate methods including correlation or trend analysis between metabolites, population classification of phytochemical patterns, link analysis between biological systems and phytochemical patterns (discrimination or pattern recognition), causal–effect relationship analyses between metabolic structures/compositions and activities or functional characteristics of biological systems (Fig. 2b). Biological systems are highly diversified by their structural and functional aspects (Fig. 2c, d): under structural aspects, biosystems can be phytochemically studied for biodiversity evaluation and chemical polymorphism analysis by treating them at different scales and with different conceptions leading to hierarchical, embedded, mixture and chained systems (Fig. 2c). Under functional aspects, quantitative and qualitative analyses of SMs help for highlighting different variation trends governing biosynthesis (increase), distribution, regulation, elimination (decrease), defensive and adaptive reactions (interaction), chemical and biological activities and signaling (communicative) roles of phytocompounds in different ecological niches of plant species (Fig. 2d). Integrative combination between these three fields (phytochemistry-biology-biostatistics) provide flexible and efficient way for assessment, monitoring, control and understanding environmental systems (Fig. 2e). These steps are fundamental for protection and optimal use of natural resources helping for management strategies of complex environment in favor of sustainable development.

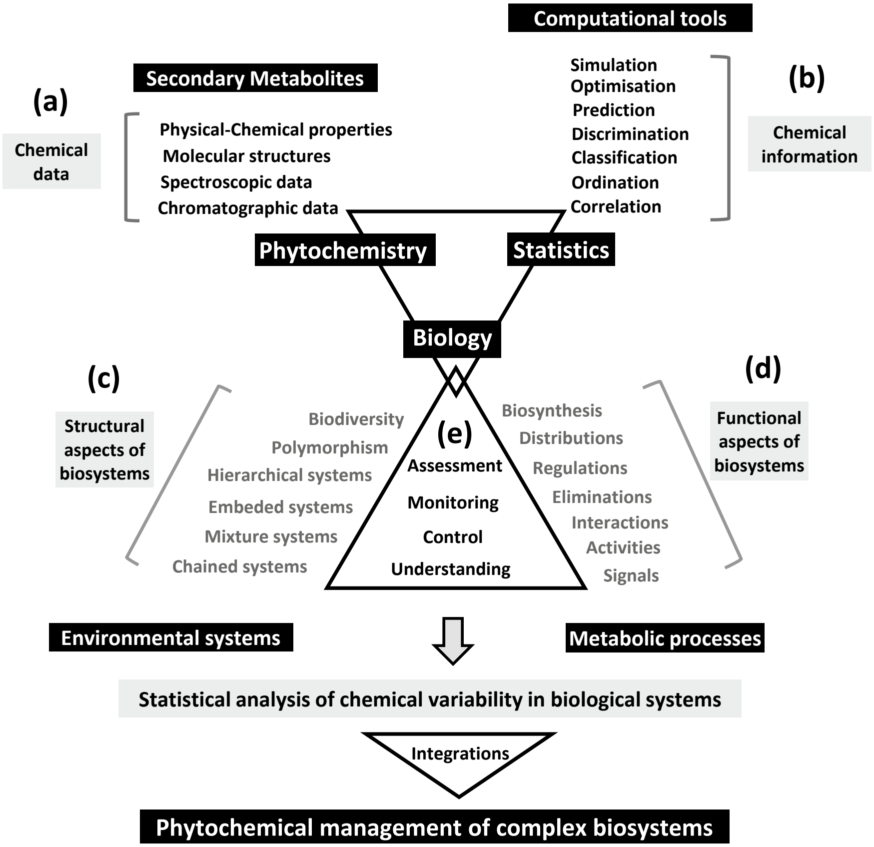

Fig. 2 Overview on the integrative aspect of variability analysis of different phytochemical data by means of different statistical tools aiming for multifactorial and multiscale assessment and monitoring of structural and functional aspects of biosystems and helping for optimal management of environment

This book is organized into four parts presenting respectively:

(1) An overview on the interest of phytochemical diversity under multiscale and multifactorial aspects. Phytochemical diversity represents the backbone of this book and is used as basis to highlight causal–effect trends between complex environment conditions and chemical composition (chemical responses) of plants.

(2) Biosynthesis pathways, structural variability and distribution of secondary metabolites in plant world. This section focuses on functional aspects of metabolic pathways and their flexible variability between plant taxa leading to specific characteristic metabolic patterns (metabotypes or chemotypes) that usefully help for assessment and monitoring of biodiversity by chemical way.

(3) Phytochemical responses of plants to abiotic stresses including high and low temperatures, water deficit, excessive or harmful radiations (e.g. UV) and ozone. These factors are mainly involved in assessment and monitoring of climate changes. The book gives several illustrative study cases on associations (correlations) between upstream abiotic variations and downstream phytochemical responses including biosynthesis of specific (signaling) molecules, variations of regulation ratios between metabolites, variable shapes of response (e.g. kinetic) curves, etc.
(4) Phytochemical responses of plants to biotic stresses due to pathogen infections and herbivore attacks. This book part provides an overview on different communicative and defensive strategies in plants through either anticipative or curative ways. These strategies involve the use of different toxic, repelling or attracting phytocompounds including phytoanticipins, phytoalexins, astringent or deterrent molecules, olfactory volatile mixtures, etc.

Better and differential understanding of the effects of different abiotic and abiotic factors on phytochemical patterns is provided by many complementary experiments based on separated or combined factors concerning plants growing under controlled (e.g. in greenhouse) or in field conditions. These multidisciplinary researches joining phytochemistry to ecology via statistical data analyses provide integrative field helping for flexible management of natural resources and sustainable development.

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Part I
Overview on Governing Factors of Phytochemical Diversity

Chapter 1
Variational Aspects of Secondary Metabolites

1.1 Overview on Multifactorial, Multiphasic and Multiscale Variations of Secondary Metabolites

Phytochemistry refers to the quantitative and qualitative analysis of plant metabolites including more particularly secondary metabolites (SMs). SMs provide specialized tasks to productive plants in terms of defense and communication. They are characterized by their sensitive variations in responses to external (environmental) factors and internal (physiological, genetic) states of producer organisms. This sensitivity involves the synthesis of specific metabolites, regulation ratios of metabolites and particular sets of co-occurring metabolites (metabolic profiles) as adaptive chemical responses or protective strategies [Fig. 1.1(1)]. Environmental (biotic, abiotic) stresses exert continuous, regular or sudden disturbances to plants; consequently, plants react by defense/adaptation ways based on quantitative and qualitative variations of SMs [Fig. 1.1(1)]. Such defensive and adaptive chemical reactions are modulated by varying regulation ratios between different metabolites [Fig. 1.1(2)]. The set of all the metabolites participating in chemical responses to stress form a metabolic profile that provides an integrative picture (phytochemical pattern) on the effects of a given stress on a considered plant (taxon) [Fig. 1.1(3)].

Phytochemical patterns are associated with adaptive strategies that can be better understood by analyzing the relative variations of different metabolites involved in plant-environment interactions [Fig. 1.1(4)]. The shapes and variation ranges of such profiles provide key information on plant physiological states, chemical polymorphisms within and between populations, adaptive trends or interactive relationships at community or ecosystem scale helping for better environment management and agricultural production improvement [Fig. 1.1(5)]. At lower scale, different plant tissues show different phytochemical patterns in relation to plant states, organs' roles and living environment (soil, air; floor; light vs. shade space; etc.). At high scale, phytochemical profiles are correlated with environmental conditions (variations) leading

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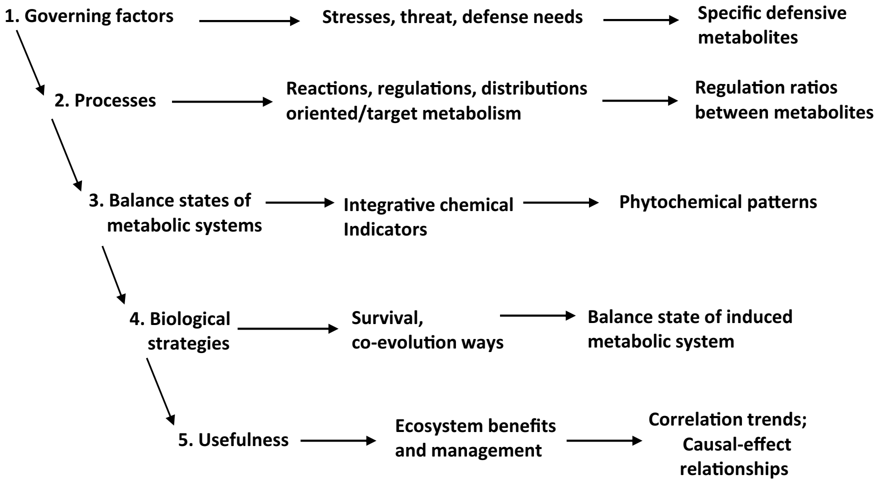

Fig. 1.1 Overview on different functional spaces governing the variability and the use of secondary metabolites in biological world

to highlight causal-effect trends governing structural and functional variability of SMs.

1.2 Overview on Stress Concept

Stress refers to adverse environmental conditions affecting growth, reproduction and yields in biological organisms (including plants). It was also referred as process or symptom associated with a critical or suffering situation (Heiser and Elstner 1998). Inductive stress and induced SMs are often connected through oxygen activation resulting in reactive oxygen species (ROS) that should be controlled by antioxidative compounds including essentially SMs. Stress factors including drought, temperature changes, light variations, biological infections, air pollution, and soil contamination lead to metabolic disturbances due to the generation of ROS including free radicals. To face oxidative stress, plants must counteract these harmful reactions by increasing antioxidative compounds or processes. SMs play key role in these defensive processes. However, if stress impacts continue, they cause the loss of control followed by harmful radical processes leading to cellular decompartmentalizations and lytic/necrotic reactions. Harmful and defense processes vary with stress type, plant species and tissue.

1.3 General Structural and Functional Characteristics of SMs

SMs differ from primary metabolites (PMs) by quantitative and qualitative characteristics leading to complementary roles under both structural and functional aspects [Fig. 1.1(2)]: PMs are constitutive of biological bodies and include saccharides, amino acids and fatty acids. They are structurally limited but quantitatively abundant leading to uniform distribution in biological world [Fig. 1.2(1)]. By their constitutive aspects, PMs are deeply involved in growth systems, but they are less sensitive to environment variations compared with SMs.

However, SMs are not constitutive of biological bodies making they are quantitatively minor [Fig. 1.2(2a)]. They are occasionally synthesized under need conditions for protection or communication signals [Fig. 1.2(2b)]. Occasional or conditional syntheses of SMs are favored by their excitable or inducible character [Fig. 1.2(2c)]. The low amounts of SMs (compared with PMs) make their small variations to be efficiently detected as chemical signals in biosystems.

The needs and ways of plant protection against many stress conditions are species- and environment-dependent resulting in high structural diversity of SMs in the plant world [Fig. 1.2(2d)]. Moreover, minor levels, occasional synthesis and high structural diversity of SMs result in their not uniform distributions with many specific or specialized roles [Fig. 1.2(2e)]. These characteristics attributes to SMs a strong usefulness for chemical characterizations of different plant taxa at different taxonomic levels [Fig. 1.2(2f)]. This refers to the chemotaxonomy field and is important for chemical identification of plant varieties associated with different production trends and potentials (types, levels, rhythms) [Fig. 1.2(2g)]. Chemical profiles of SMs are associated with different tissue and cell compartments in individual plants [Fig. 1.2(2h)]. Compartmentation results in multiple differentiation ways and subsequent specific phytochemical patterns within and between plants. Also, compartmentation represents an essential process to control activities of SMs leading to self-protection in plants.

SMs show sensitive variations with plant age, physiology and development states [Fig. 1.2(2i)]. Beyond the time-dependent variations of SMs associated with natural plant growth, SMs are involved in many interactions between plants and environment including defense, adaptation and communication signals [Fig. 1.2(2i)]. Wide chemical diversity of SMs implies flexible metabolic regulation ways resulting in different response profiles which satisfy different biological roles and signal trends [Fig. 1.2(2e, f)]. Their low amounts attribute sensitive aspects to their variations; this makes small variations to provide reliable information on plant-environment system [Fig. 1.2(2c, k)]. Also, micro-molecular nature of SMs makes their quantitative variations to be reliably converted into signals associating reactional plants and stimulant environment conditions.

By this way, SMs are implied in homeostasis processes including stabilization, regulation and survival states of biosystems [Fig. 1.2(2i, j)].

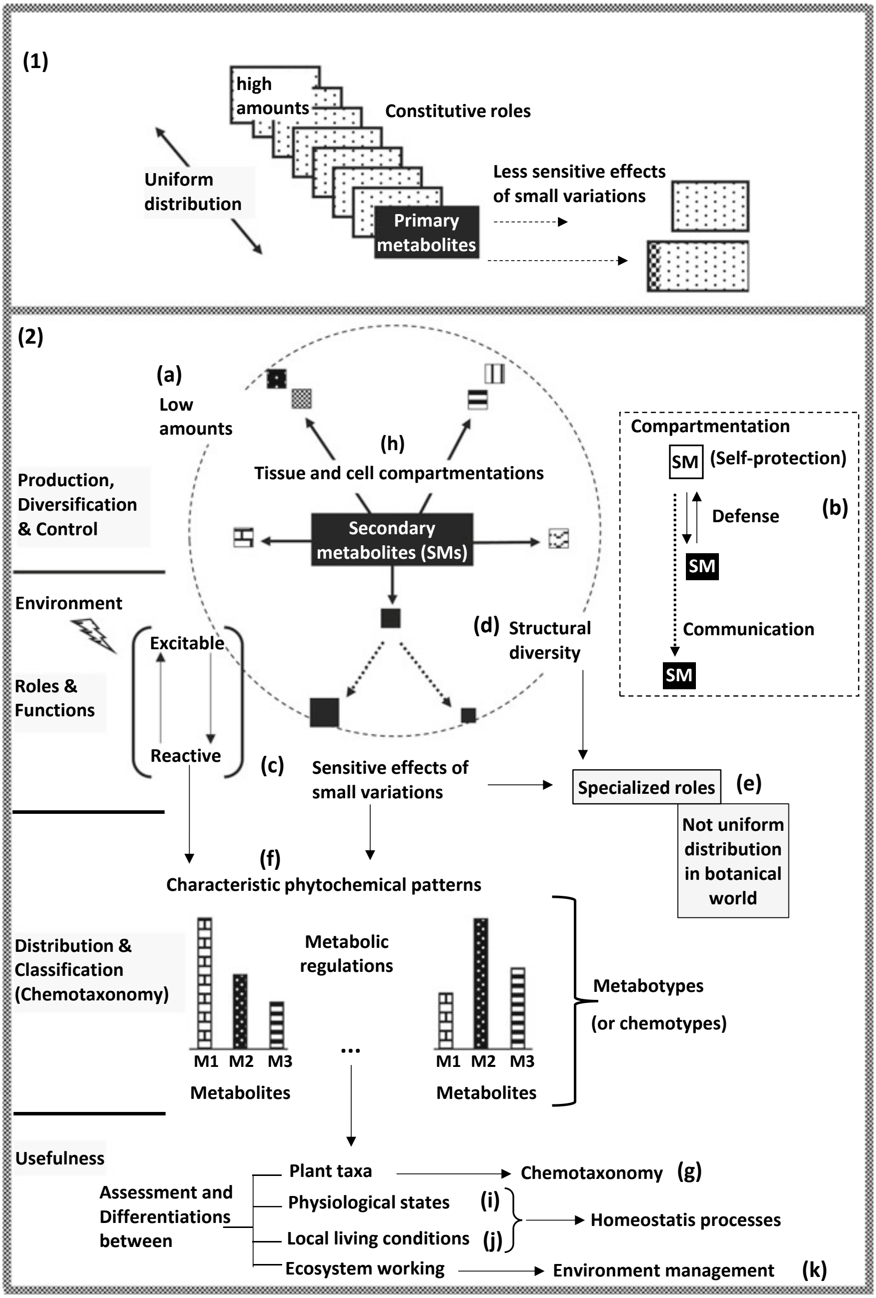

Fig. 1.2 Different quantitative and qualitative characteristics of secondary metabolites (compared with primary metabolites) helping for assessment and monitoring of biotic and abiotic states in ecosystems

Multifactorial and multidirectional variations of SMs attribute them strong usefulness for detection, correlation and classification analyses of plants responses and adaptive profiles in relation to different types and levels of inductive factors (living conditions) [Fig. 1.2 (2g, i-k)].

1.4 Overview on Variational Usefulness of SMs

Beyond development states and living conditions, SMs' patterns are helpfully used for chemical classifications and identifications of plants leading to chemotaxonomy [Fig. 1.2(2f, g)]. This usefulness is linked to the non-uniform botanical distributions of SMs at multi-taxonomical scales (class, family, genus, species, variety) [Fig. 1.2(2e)]. At the lowest taxonomical scale, individuals of a same plant species can be chemically differentiated into metabotypes defined by several metabolites produced at different regulation ratios [Fig. 1.2(2f)].

Sensitivity of SMs to abiotic factors provides an efficient way for climatic changes monitoring. For instance, protective role of polyphenolic compounds (a SM family) against UV and drought stress was highlighted in Mediterranean endemic plants through diurnal and monthly variations of their concentrations with peaks occurring in summer and at midday where UV radiations, temperature and drought reach maximal levels (Gori et al. 2019, 2020). Also, compositions of defensive compounds in plants tend to significantly vary with latitude and altitude (Moreira et al. 2014, 2018). Different Mediterranean populations of *Cistus ladanifer* living in different locations (different climatic conditions) showed different flavonoid profiles (compositions and contents) (Sosa et al. 2005).

Elevated temperatures result in higher emissions of volatile terpenes as consequence of more active synthesis in leaves and needles. Monitoring studies revealed increased emission rates of isoprene and monoterpenes (Penuelas and Staudt 2010; Holopainen et al. 2013). Subsequently to elevated night temperatures, isoprene, monoterpenes, sesquiterpenes and a homoterpene showed higher daytime emissions rates on a leaf-area basis in deciduous trees. This process associated increase in plant growth rate (influencing that of total leaf area) with increased terpenoid emissions under warmer living environment.

Environmental stresses tend to increase chemical resistances of plants. Stress-tolerant plants tend to produce more variable SMs than nontolerant ones (Sharkey et al. 2008; Loreto and Velikova 2001). In consequence, resistant or adapted plants provide a potential source of active metabolites favoring drug discovery (Macías et al. 2007).

Finally, biotic stresses in plant include pathogenic infections and herbivore attacks. These harmful situations are managed by plants via the production of SMs with both preventive and curative aspects including repelling, astringent, toxic and signalling volatile compounds.

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Chapter 2
Variational Factors and Regulation Processes of Secondary Metabolites

2.1 Multiple Induction Origins of Secondary Metabolites

Secondary metabolites are induced and vary in response to changes in environmental conditions or internal states of plants (Fig. 2.1(1, 2)). Plant sensitivity to quantitative and qualitative variations of external/internal conditions can be monitored through different phytochemical patterns characterizing different environmental conditions and biological states. By this way, downstream-formed phytochemical patterns are correlated with upstream-inducing factors associated with extrinsic or intrinsic origins. These causal-effect trends attribute high interest to secondary metabolites for understanding complex adaptive behaviors of plants on one hand, and for subsequent management of ecological and biological systems on other hand.

Inducing external conditions are associated with either abiotic or biotic stresses which have different and multiple effects on plants (Fig. 2.1(1a, b)):

- Abiotic stresses include air and soil physico-chemical factors exerting constraints through relatively high or low levels. Air-linked factors include temperature (heat, cold), water availability (humidity, rainfall, water deficit), light (sunlight, shade), UV-radiations (UV-A, UV-B) and ozone (O_3). These factors are closely involved in climatic changes representing a main current worry at planetary scale. Their effects on plants and subsequent phytochemical responses are particularly detailed and illustrated in this book. Soil-linked factors include drought, soil salinity and heavy metal attacks (Fig. 2.1(1a)).
- Biotic stresses imply cooperative or defensive interactions between plants and biological partners or enemies, respectively (Fig. 2.1(1b)). Cooperative interactions include symbiose and pollination requiring attraction processes using specific SMs or particular mixtures of SMs associated with recognizable color or odor by the expected biological partner. Some biological partners are attracted by specific odors to assist plants in their defense against herbivore attacks and parasit infections. These two biotic stresses are at the origin of production of SMs

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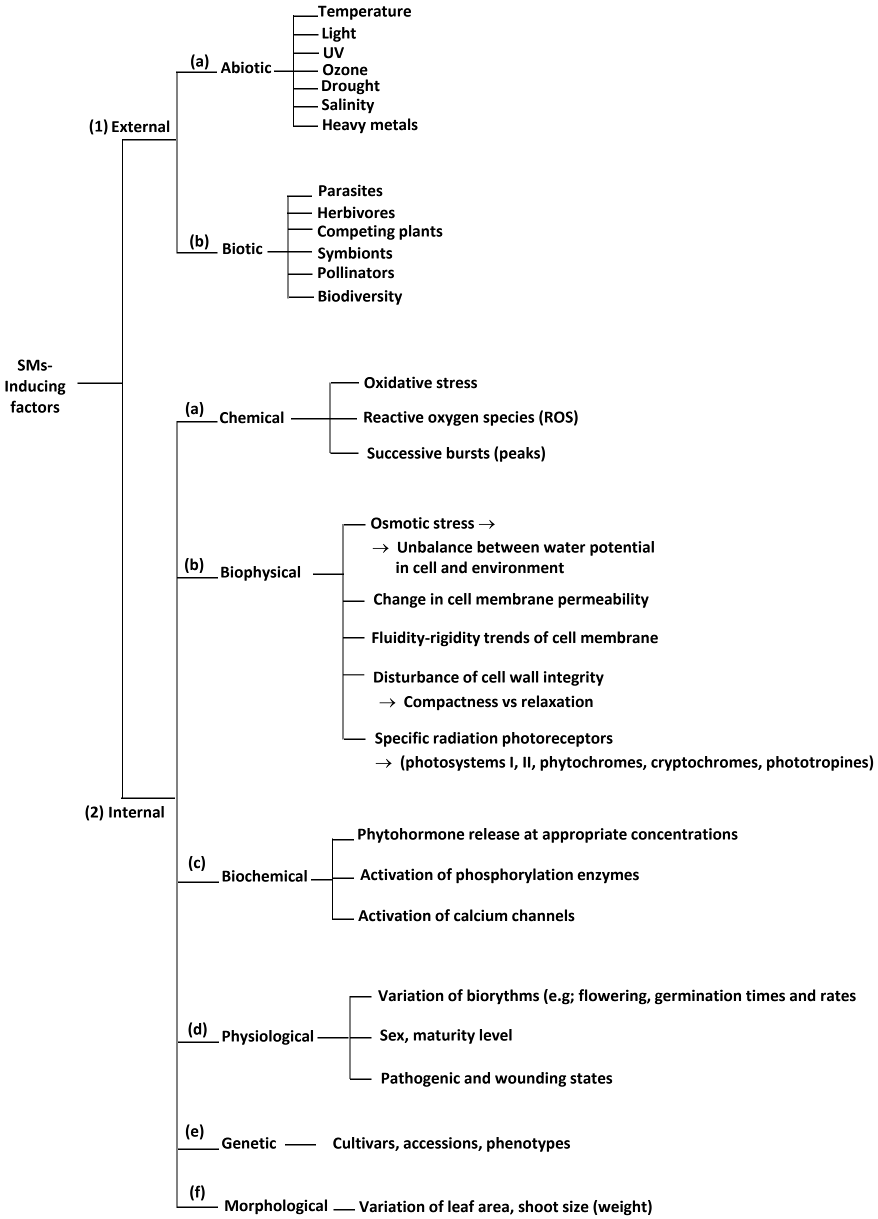


Fig. 2.1 Different types of external and internal factors involved in the production, diversification and distribution of secondary metabolites in plants

with toxic and repellent effects in plants. Futher structural diversity and patterns of produced SMs tend to be observed under more biological interactions. By this way, biodiversity in ecosystem represents a strong factor governing quantitative and qualitative productions of SMs in plants.

Plant internal factors involved in SM induction are of different types including chemical, biophysical biochemical, physiological, genetic and morphological factors/systems (Fig. 2.1(2)). SM induction occurs in downstream of stress management systems consisting of sensitive constitutional components involved in detection, transmission, transduction and conversion of stress signals from physical–chemical aspects to metabolic forms. Thus, SMs are synthesized as specialized metabolites through signals coupling harmful or alarming variations (in upstream) with protective or adaptive phytochemical patterns (in downstream). Intrinsic inducing factors of SMs include:

- Chemical factors consisting of oxidative stress due to the formation of reactive oxygen species (ROS) (Fig. 2.1(2a)). ROS and other oxidants (including radical and non-radial compounds) induce the formation of antioxidant SMs. The Inducing oxidative signal can be amplified and/or extended through double burst leading to higher efficiency of SMs' induction signal.
- Biophysical factors originated from osmotic balance disturbance and radiative excitation (Fig. 2.1(2b)). Osmotic stress is detected from unbalance between water potential of cell and that of environment. It results in different variation trends between fluidity and rigidity states of cell membrane. Osmotic stress can be amplified by some changes in cell membrane composition. Moreover, water deficit stress can result in disturbance of cell wall integrity leading to reinforce the inducing biophysical ways of SMs. Under radiative stress, SMs are induced through photoreceptors specialized in detection of different radiation ranges including photosystems I and II, phytochromes, cryptochromes and phototropines.
- SMs-inductions are also governed by biochemical processes involving phytohormones which are associated with cascades of transduction and gene expression signals in upstream or downstream steps (Fig. 2.1(2c)) (Murcia et al. 2017). Apart from their naturally endogenous aspect, phytohormones can be applied to plants as external factors (e.g. by spraying) to stimulate several protection or tolerance responses. SMs-inducing biochemical ways include also activation of trans-membrane calcium channels and phosphorylation enzymes (Fig. 2.1 (2c)).
- SMs-inducing physiological factors include changes in seasonal processes such as delayed or accelerated flowering and germination (Fig. 2.1(2d)). Inducing factors include also sex, maturity level, pathogenic and wounding states (e.g. following herbivore attacks).
- Genetic factors responsible for induction of SMs involve cultivars, accessions and/or phenotypes able to produce appropriate SMs for occurring stress adaptation (Fig. 2.1(2e)).

- Morphological factors are associated with plant growth and include leaf area and shoot size that are affected by leaf turgor pressure and mitosis impairment (Fig. 2.1(2f)).

2.2 Chemical and Cellular Factors Influencing Diversification, Distribution and Specialization Roles of Secondary Metabolites

Protective and communicative specialized roles of SMs in plants are fundamentally governed by their highly variable chemical structures involving several other aspects (Punetha et al. 2022; Yeshi et al. 2022; Hadacek 2002; Singsaas 2000):

- Hydrocarbon skeleton (called aglycone or genin) is responsible for the global shape (scaffold), elementary size and solubility properties of molecule (Fig. 2.2(1a)). Aglycones represent the initial steps in SMs' biosynthesis and basic identifiers of corresponding metabolic pathways. Metabolic pathways showing different biosynthesis rates and regulation ratios of SMs are correlated with different expression levels of key enzymes (Fig. 2.2(1b)). Biosynthesis enzymes work by promiscuity way, i.e. they are able to use different substrates to form a same product, or give different products from a same substrate (Fig. 2.3). Promiscuity system favors the development of metabolic diversity in plants leading to specialized metabolism (wide SMs' pool) in downstream of stimulating biotic and abiotic stress factors. Biosynthesis of aglycone is followed by intramolecular transformations leading to structural diversification of SMs within a same metabolic pathway (biochemical family) (Fig. 2.4a, b).
- Moreover, biosynthesis enzymes of SMs are subject to diversification through mutation processes occurring on encoding genes (Fig. 2.2(1c)). Such upstream processes favored the development of promiscuity enzymes (Leong and Last 2017; Kreis and Munkert 2019; Waki et al. 2021). Moreover, environmental constraints continuously exert selective pressures leading to further mutations which result in more phytochemical diversity where new SMs are subscribed (retained) because of their efficient roles against occurring stresses and changing conditions.
- In downstream of metabolism, SMs' diversification is favored by transformations of aglycones through chemical substitutions occurring at different carbons (positions) of molecules (Figs. 2.2 (2) and 2.4a). Aglycone can attach various chemical groups leading to the formation of new molecules with gradually varied sizes, physical–chemical properties and biological activities. This enlarges the phytochemical pools and results in more pathways and sub-pathways (Fig. 2.4b). Moreover, chemical substitutions result in steric variation of SMs leading to multiple interaction ways with other molecules.
- Substituted chemical groups can have hydrophilic or lipophilic characters resulting in different solubility properties and compartmentation ways of SMs (Fig. 2.2(3)). Compartmentation process concerns different biological structures

including cells, organs and tissues (Figs. 2.4c, 2.5 and 2.6) (Lipko et al. 2023). At cell scale, different organelles provide storage compartments of SMs according to their hydrophilic or lipophilic aspects. Hydrophilic compounds are stored in vacuole, laticifers and apoplast space of cell wall; lipophilic compounds are stored in cell membranes, cuticle, trichome, resin ducts, laticifers and oil cells (Fig. 2.6) (Cai et al. 2012). Hydrophily is favored by hydroxylation and glycosylation whereas lipophilic character is associated with hydrocarbon aspects. Further details on structures-solubility trends are presented in Sect. 3.2 of the current chapter. Cell compartmentation represents an efficient process protecting plants against self-toxication by their reactive metabolites. At higher scale, particular occurrence or accumulation of SMs in some tissues is linked to their local roles and specific needs for plant. Distribution of SMs extend beyond the plants through their emissions in environment for communicative strategies. This makes cell and tissue compartmentations to play key roles in the control of biological signals and reactivity linked to SMs (Figs. 2.2(3) and 2.5). For instance, terpenes are stored in resin ducts in conifers vs oil glands and leaf hairs in broadleaves (Singsaas 2000). Targeted communicative roles of SMs in plant-animal interactions requires their anticipated (preliminary) storages. Volatile compounds are emitted by plants from storage matrices under the effect of tissue temperature (Guenther et al. 1991). Also, SMs as phenylpropanoids tend to be relatively more distributed in leaves exposed to oxidative stress (e.g. ozone-linked) vs decreased storage in wood tissue (Richet et al. 2012).

- Metabolic diversification processes act in favor of stronger abilities of plants to face multiple types of disturbances. Initially, needed SMs are stimulated through cascade processes involving stress detection followed by specific gene induction, transduction and metabolism (Fig. 2.2(4)). In downstream, formed and stored SMs can be activated by enzymatic hydrolysis leading to release of active (toxic) components.
- Structural variability of SMs is responsible for a diversification of their activities. Different activities are associated with different target roles and fates of SMs (Fig. 2.2(5)). According to their structures, solubility properties and molecular weights, SMs will be dispatched to protect plants against specific harmful conditions or to communicate with well target biotic environment. Protective roles of SMs against abiotic stresses involve (Fig. 2.2(5)) (Kivimäenpää et al. 2022):

  (i) antioxidant activities by interactions with oxygen reactive species or heavy metals (oxidants),
  (ii) membrane protection via its fluidification favored by lipophilic SMs,
  (iii) strengthening of wall structures,
  (iv) water flux control by osmoregulation based on hydrophilic metabolites (osmolytes),
  (v) thermotolerance regulations by emission of volatile SMs that can form cooling (protecting) aerosol micro-cloud above plant tissues.

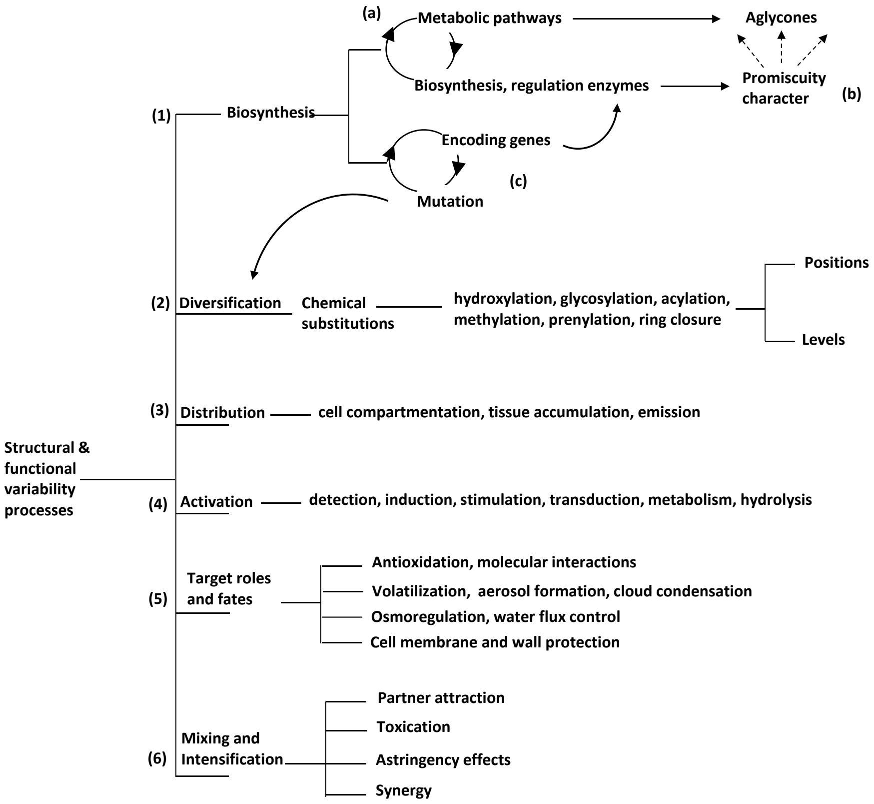


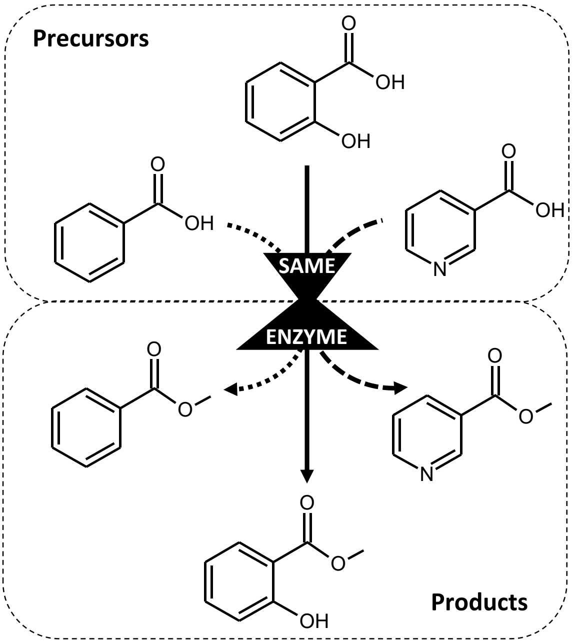
Fig. 2.2 Chemical and cellular factors influencing structural diversification, distribution and target roles of secondary metabolites against different biotic and abiotic stresses

- In biotic systems, plant SMs can be combined to provide well-defined mixtures playing key roles in (i) attraction of specific biological partners (symbiotic microorganisms, pollinators, parasitoids of herbivores) or (ii) in intensified (synergetic) repelling/toxic effects against herbivores and pathogens (Fig. 2.2(6)).

2.3 Roles of Phytochemical Variations/Patterns in Plant Adaptive Strategies and Environment Management

The interest of SMs in environment management strongly derives from their correlations or significant variation trends with different external (abiotic, biotic) conditions and internal plant states (Figs. 2.7 and 2.8). This results in more or less specific phytochemical patterns associated with different adaptive plant responses to different external conditions or internal states:

Fig. 2.3 Illustration of enzyme showing substrate promiscuity



Abiotic factors include temperature, radiations, ozone, drought, salinity and heavy metals (Fig. 2.7(1)). They are detailed in Part III. Biotic factors can be of offensive or cooperative types resulting in phytochemical patterns associated with defensive, alerting (wounding) or communicative messages (Figs. 2.7(2) and 2.8). In well-adapted plants, defensive SM-patterns are of anticipative type and can be highlighted by pre-existing SMs initially synthesized and stored as preventive strategy (Fig. 2.8(1)). Also, under unexpected or sudden stress, curative responses are manifested through repair and wound cue metabolites (Fig. 2.8(1, 2)). Defensive SMs can play toxication, repelling or deterring roles against biological enemies (e.g. herbivores, pathogens) (Fig. 2.8(1)).

Biological relationships between plants and other organisms involve specific SMs playing (i) attractive roles in symbioses, pollinations, calling of herbivores' enemies, or (ii) repulsive effects against competing neighbor plants (allelopathy) or animal or microbial harmful (Fig. 2.8(3)). Specific SMs and more generally phytochemical patterns vary with plant physiology and taxonomy (genetics) (Fig. 2.7(3, 4)). Physiologic states of plants vary with their reproduction phases and fitness, growth and maturation levels, circadian rhythms, health states and disease types (Fig. 2.7(3)).

Phytochemical patterns associated with different abiotic and biotic conditions provide key information on multiple interactions between plants and living conditions helping for environment protection and management. Also, environment management calls for optimal use of bioresources by identifying phytochemical patterns associated with high plant fitness. Such patterns could be potential candidates for agriculture development.