New Synthesis—Systems Chemical Ecology

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Secondary metabolites are enigmatic in terms of costs and benefits for their producers and how their ontogenetic accumulation or timely induction affects the evolution of single species and co-evolution of interacting species. More than 50 years ago, Gottfried Fraenkel dispelled the notion of secondary metabolites as waste products: “Thus, the animal world which surrounds the plant is deeply influenced not only by their morphology, but also by their chemistry”.

Today, in the post-genomic era, with huge amounts of data generated by functional genomic, metabolomic, and proteomic studies, the emerging picture of secondary metabolites is more complex. Also, the recognition has grown that one of the ultimate challenges in the life sciences is not just to understand component parts, but rather the systems comprised of these parts. This has led to the establishment of a new discipline - *systems biology* - which advocates an integrative rather than reductionist approach.

The relations between plants and the microbes and herbivores that colonize and eat them once were described as a “wobbling triangle” of interactions that occur both below- and above ground. In this scenario, a reliable and flexible signalling system is mandatory to coordinate gene expression in separate tissues accordingly. Present knowledge suggests that in plants, as in other organisms, co-ordinated redox chemical reactions between reactive oxygen species (ROS) and hormones represent the upstream part of this signalling system which, further downstream, is continued by MAP kinases, helping to maintain the homeodynamics of micro- and macro-molecules required during ontogenesis (Mittler et al., 2011).

One important recognized component is retrograde (organelle to nucleus) signalling. Abiotic and biotic stresses impair the functionality of electron transport chains in chloroplasts and mitochondria. As a consequence, instead of four electrons that are required to reduce molecular oxygen to water, incorrectly transferred single electrons lead more quickly to the formation of superoxide anion radicals, $O_2^{\cdot-}$, than upregulated enzyme expression, e.g. NADPH oxidase, which is involved in systemic ROS production (Kerchev et al., 2011). So far, metabolomic studies have revealed extensive reprogramming of primary metabolites in context with retrograde signalling. The fact that no single cytosolic component yet has been identified unequivocally as a retrograde signal induced Thomas Pfannschmidt (2010) to ask a heretical, albeit justified question: “Maybe a single metabolite is not sufficient to work as a signal, but what about a metabolite signature?”. In terms of a systems biological approach, we may also consider whether secondary metabolites function as ensemble components of a metabolite signature. Although GC–MS is far from ideal for detecting non-volatile secondary metabolites, no single analytical method satisfactorily provides

the comprehensive metabolic profiling needed to evaluate this question, especially if secondary metabolites are part of a complex mixture of predominantly unknown analytes.

If specific patterns of primary metabolites, such as sugars, amino acids and organic acids, function as components of a metabolite signature, chemical reactions with ROS that are generated in the upstream part of the signal cascade have to be possible. This is the case. Atoms such as oxygen nitrogen and sulphur are characteristic for primary metabolites. Under aqueous reaction conditions, all molecules that contain these elements are reactive and can undergo redox chemical reactions, in which one or more electrons can be transferred either from them (oxidation) or to them (reduction). These properties characterize all plant metabolites that have been recognized as antioxidants. The lone-pair electrons of oxygen, nitrogen and sulphur not only add to the reactivity of molecules containing them, but also enable them to be ligands of transition metals, such as iron, copper and manganese. Transition metals, conversely, can exist in various oxidation states, which allows them to function as catalysts of electron transfer reactions, amongst others of the reduction of ROS to water and molecular oxygen to ROS. Organic acids and phenolic secondary metabolites are especially recognized for these chemical properties and illustrate that, at least in this respect, primary and secondary metabolites do not differ fundamentally and are equally equipped to function as components of metabolite signatures.

Following Gottfried Fraenkel, chemical ecologists predominantly view secondary metabolites as chemical defences against predators. Adding a systems biological perspective, considering secondary metabolites as system components with potential to improve chemical cell homeodynamics, might provide one alternative approach to better understand how secondary metabolites contribute to the survival and successful reproduction of their producers in a world of rapidly changing stresses, in which herbivory is only one of many possible challenges. Signalling functions of secondary metabolites in bi- and tritrophic interactions, however, represent another, probably more recently evolved facet of secondary metabolite evolution.

References

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