

Secondary metabolites during early development in plants

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Abstract Early development is a critical stage in a plant's life, as the plant must establish itself in the ecosystem during this period. The secondary metabolites (SM) during this phase is a strategy that contributes to the survival of plant species. Through a review of the literature, a number of reports were found that investigated the presence of SM during germination and early plant development (phases 0 and 1 according to the Zadoks and BBCH scales). A total of 250 reports were found that investigated 99 species and nearly 200 SM that accumulate during this period of the plant life cycle. A large portion of the SM are biosynthesised *de novo*, whereas the remainder are derived in part or in total from the mother plant. In many cases, the resources for biosynthesis are supplied only by the reserve material of the endosperm or cotyledons, which

allows for independent photosynthesis. The presence of SM at these stages confers characteristics of more advanced stages, such as tissue-specific distribution, spatio-temporal regulation, and the individual regulation of all of the biosynthesised SM. The amount and diversity of SM are not universally related to the progress of plant development, but it is a widespread phenomenon. The early production of SM has ecological implications that involve defence mechanisms, relationships with microorganisms, and the role of these compounds as nitrogen reserves. This review contributes to the systematisation of studies on SM in the early stages of development.

Keywords Natural products · Early metabolism · Early defence · Germination · Seedling development

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Introduction

Germination and subsequent plant development are the initial stages for establishing a new individual of any plant species. The germination process begins with the consumption of water by the seed (imbibition) and ends in the *strict sense* according to Nonogaki et al. (2007) and Weitbrecht et al. (2011) when a part of the embryonic axis (usually the radicle) extends and crosses the seed coat (emergence). This emergence is the first evidence of seedling growth, and this initial development depends on the energy reserves of the endosperm and cotyledons (Bewley and Black 1994). These processes

have been studied since the middle of the last century with lengthy discussions about the genetic, physiological, metabolic, and ecological aspects that surround new plant development. The following are a few well-organised reviews on the topic: Koller et al. 1962; Thomas 1993; Bewley and Black 1994; Bewley 1997; Baskin and Baskin 1998; Bove et al. 2001; Koornneef et al. 2002; Bradford and Bewley 2002; Kucera et al. 2005; Finch-Savage and Leubner-Metzger 2006; Bradford and Nonogaki 2007; Nonogaki 2010; Weitbrecht et al. 2011; Linkies and Leubner-Metzger 2012.

Among the rarely studied metabolic events are those related to the presence of secondary metabolites that until now were considered to be non-essential for cells but that often have ecological functions (Dixon 2001; Hartmann 2008) and may therefore be involved in the establishment and communication of plants in/with the environment in which they grow.

Germination and seedling development represent critical stages that are perhaps the most vulnerable stages for any plant. During these stages, it is evident that the tissues that initiate the growth and differentiation of the embryo or zygote are the most vulnerable to latent environmental dangers. Among these dangers are the presence of phytopathogens and herbivores, as well as competition with other plants for nutrients (Bewley 1997; Jurado and Moles 2003). The intake of water by the seed and degradation of polymers from the accumulated reserves (primarily starch, proteins, and lipids) for seedling establishment create a “generous” scenario of simple and energetic molecules available to insects and phytopathogens.

If SM are produced as a means of communication between plants and the environment, then it is natural to think that these molecules may be present in the stages mentioned, not only implementing defence mechanisms for the new individual but possibly also developing other functions (such as attraction or nitrogen reserves) that have already been characterised in later stages. The SM in these stages may be contributions from the mother plant that accumulate in the endosperm or cotyledons of the embryo. As the plant develops, these SM can distribute themselves in the seedling during growth or be biosynthesised *de novo*; both of these situations have been poorly documented. In any case, the SM represents an advantageous resource in early plant development that, in turn, provides an interesting perspective on the role and biology of SM in the plant kingdom.

Search method

The literature review included a retrospective review from 2012 using search engines and traditional databases with combinations of the following terms: early plant development, early ontogeny, ontogenic development, germination, seedling, seedling development with secondary metabolism, secondary metabolites, natural products, plant secondary products, plant secondary metabolites, alkaloids, anthocyanins, anthocyanidins, cyanogenic glycosides, flavonoids, hydroxamic acids, phenols, terpenes, terpenoids, polyketides, phenylpropanoids, pigments, flavours, essential oils, volatile oils, acetogenins, coumarins, and allelopathy, as well as (separately) metabolism early plant development, metabolism germination, and metabolism seedling. The developmental stages considered in this review are seedling germination and development, which correspond to the Zadoks et al. (1974) and BBCH (Hess et al. 1997) decimal scale stages 0 (1–9) and 1 (10–15), which physiologically range from the dry seed to when the plant achieves photosynthetic capacity.

Results

There were ~200 SM recorded in 99 species: 72 phenols (41 species), 80 alkaloids (48 species), and 36 terpenoids (18 species) (Tables 1, 2, 3). Of these metabolites, 48 % are found in the germination stage and 52 % during seedling development. In the reports that evaluated both stages (10 % of the citations), 80 % of the SM appear at germination and are maintained in the seedling stage.

The earliest reports found on SM in early plant development are that of Leete and Marion in 1951, who described the biosynthesis of the alkaloid *gramine* derived from tryptophan in *Hordeum vulgare*, Van Haga in 1954 on the alkaloids of *Atropa belladonna*, and Tso and Jeffrey in 1956 on the alkaloids nicotine and nornicotine from *Nicotiana tabacum* and *N. rustica*, respectively.

The most frequent metabolites in the scientific literature that allude to aspects of chemical structure and biological significance are the hydroxamic acids in cereals, studied by a group led by H. Niemeyer; the quinolizidine alkaloids of the *Lupinus* genera, studied by a group led by M. Wink (initiated in the 1980s with

Table 1 Alkaloids and other nitrogen compounds during early plant development

| Species | Compound | Stage | References |
|--------------------------------|---|-----------------------|---|
| <i>Atropa belladonna</i> | Total alkaloids | Seedling | Van Haga (1954), Abdel-Hady et al. (2008) |
| <i>Camellia sinensis</i> | Caffeine & theobromine | Germination | Suzuki and Waller (1987) |
| <i>Camptotheca acuminata</i> | Camptothecin | Germination | López-Meyer and Nessler (1997), Valletta et al. (2007) |
| | Camptothecin y 10 hydroxycamptothecine | Seedling | Zu et al. (2003) |
| <i>Catharanthus roseus</i> | Cabersonine, catharantine vindoline | Germination | Aerts et al. (1994), Aerts et al. (1996), Shukla et al. (2006) |
| | Ajmalicine, catharantine, tabersonine, vinblastine, vincristine, vindoline | Seedling | Bonzom et al. (1998), Magnotta et al. (2006), Vázquez-Flota et al. (2004), Guo et al. (2007), Miranda-Ham et al. 2007 |
| <i>Cinchona ledgeriana</i> | Cinchonine, dehydro-cinchonine | Germination, Seedling | Aerts et al. (1990), Aerts et al. (1991), Aerts et al. (1994) |
| <i>Coffea arabica</i> | Caffeine, theophilina, trigonelline | Germination | Friedman and Waller (1983), Baumann and Gabriel (1984), Shimizu and Mazzafera 2000. |
| | Trigonelline, theobromine, caffeine | Seedling | Zheng and Ashihara (2004) |
| <i>Crotalaria scassellatii</i> | N oxido-(axillaridine, axillarine, desoxiaxillarine) | Seedling | Toppel et al. (1988) |
| <i>Cytisus scoparius</i> | Lupanine, 13-hydroxylupanine, 13-tigloyloxylupanine, tetrahydrohombifoline, 17-oxosparteine, (–)-3 β -hydroxy-13 α -tigloyloxylupanine | Seedling | Wink and Witte (1985), Saito et al. (1994) |
| <i>Datura innoxia</i> | Atropine, scopolamine | Seedling | Petri (1982) |
| <i>Festuca pratensis</i> | Loline | Seedling | Justus et al. (1997) |
| <i>Glycine max</i> | Trigonelline | Seedling | Cho et al. (2008) |
| <i>Heimia salicifolia</i> | Phenylquinolizidines (2-hydroxy-4-(3-hydroxy-4-methoxyphenyl) quinolizidines (3 and 9a) | Seedling | Rother and Schwarting (1975) |
| <i>Hordeum distichum</i> | Hydroxamic acids | Seedling | Argandoña et al. (1980) |
| <i>Hordeum vulgare</i> | Gramine, hordenine, N-methyltyramine | Germination, Seedling | Leete and Marion (1954), Tyler (1958), Mann et al. (1963), Liu and Lovett (1993), Åhman et al. (2000), Matsuo et al. (2001) |
| <i>Laburnun anagyroides</i> | Cytisine, N-methylcytisine, 5,6 dehydrolupanine, anagyrine, lupanine, rhombifoline, 13-hydroxyanagyrine, N-metilcytisine, ammondendrine | Seedling | Wink and Witte (1985) |
| <i>Lupinus albus</i> | Albine, α -isolupanine, lupanine, 13-hydroxylupanine, 13-angeloyl-oxylupanine, 13-tigloyloxylupanine, 13-benzoyloxylupanine, angustifoline, 17-oxolupanine, N-methylalbine, multiflorine | Germination | Wink (1983), Wink and Witte (1985), de la Cuadra et al. (1994), de Cortes et al. (2005) |
| | 13-Tigloyloxylupanine, lupanine | Seedling | Wink (1983) |
| <i>Lupinus angustifolius</i> | Ester 13-tigloyloxylupanine | Germination | de Cortes et al. (2005) |

Table 1 continued

| Species | Compound | Stage | References |
|--|---|-----------------------|---|
| <i>Lupinus campestris</i> | Hydroxyaphylline, hydroxyaphyllidine | Germination | de Cortes et al. (2005) |
| <i>Lupinus harwegii</i> | Gramine | Germination, Seedling | Leete (1975) |
| <i>Lupinus hirsutus</i> | (+)-(Trans-4'-acetoxycinnamoyl) epilupinine, (–)-13 α -tigloyloxymultiflorine, (–)-multiflorine, (+)-epilupinine | Germination, Seedling | Takamatsu et al. (1991) |
| <i>Lupinus luteus</i> | Lupinine, sparteine, lupanine | Germination | de la Cuadra et al. (1994) |
| <i>Lupinus polyphyllus</i> | 4-Hydroxylupanine, 13-tigloyloxylupanine | Germination, Seedling | Wink and Witte (1985) |
| <i>Nicotiana rustica</i> | Nicotine, nornicotine, anabasine, anatabine, | Germination | Week and Bush (1974) |
| <i>Nicotiana tabacum</i> | Nicotine, nornicotine, anabasine, anatabine, | Germination | Tso and Jeffrey (1956), Week and Bush (1974) |
| <i>Nicotiana glutinosa</i> | Nicotine | Germination | Tso and Jeffrey (1956) |
| <i>Papaver bracteatum</i> | Thebaine, sanguinarine | Germination | Rush et al. (1985) |
| <i>Papaver somniferum</i> | Thebaine, sanguinarine, | Germination, Seedling | William and Ellis (1989), Facchini et al. (1996), Huang and Kutchan (2000) |
| <i>Phaseolus aureus</i> | Trigonelline | Germination | Zheng et al. (2005), Zheng et al. (2008) |
| <i>Pinus ponderosa</i> | Pinidine & other piperidine alkaloids | Germination | Tawara et al. (1995) |
| <i>Pisum sativum</i> | Trigonelline | Germination, Seedling | Evans et al. (1979), Evans and Tramontano (1984) |
| <i>Psychotria brachyceras</i> | Brachycerine | Seedling | Gregianini et al. (2004) |
| <i>Lolium spp.</i> | Perloline, halostachine | Seedling | Aasen et al. (1969) |
| <i>Ricinus communis</i> | Ricinine | Seedling | Dubeck and Kirkwood (1952) |
| <i>Secale cereale</i> | Hydroxamic acids (DIBOA, DIMBOA) | Germination, Seedling | Argandoña et al. (1980) |
| <i>Senecio jacobaea</i> , <i>S. vulgaris</i> | Pyrrolizidine alkaloid | Germination, Seedling | Schaffner et al. (2003) |
| <i>Triticum aestivum</i> , <i>T. durum</i> , <i>T. carthlicum</i> , <i>T. compactum</i> , <i>T. macha</i> , <i>T. dicochum</i> , <i>T. monococcum</i> , <i>T. polonicum</i> , <i>T. spelta</i> , <i>T. sphaerococcum</i> , <i>T. turgidum</i> , <i>T. zhukovskyi</i> | Hydroxamic acids (DIBOA, DIMBOA) | Germination, Seedling | Argandoña et al. (1980), Argandoña et al. (1981), Niemeyer (1989 ^a), Thackray et al. (1990), Gianoli and Niemeyer (1997), |
| <i>Zea mayz</i> | Hydroxamic acids (DIBOA, DIMBOA) | Germination, Seedling | Klun and Robinson (1969), Collantes et al. (1998) |

biosynthesis studies); the indole alkaloids of *Catharanthus roseus*, studied by a group led by V. de Luca; and the benzyloisoquinoline alkaloids in Papaveraceae and Berberidaceae, studied by a group led by P. Facchini circa 1990. In recent decades, the studies

of chemical ecology that explain the function of hydroxamic acids against herbivorous aphids during the early development of wheat, barley, and maize (~20) and the allelopathic activity of *Lupinus* alkaloids (~15) are notable due to their abundance.

Table 2 Phenols during early plant development

| Species | Compound | Stage | References |
|--|--|-----------------------|--|
| <i>Arabidopsis thaliana</i> | Anthocyanin, cyanidin 3-glucosides, sinapate, sinapoylmalate | Germination, Seedling | Kubasek et al. (1992), Martin et al. (2002), Poustka et al. (2007), Pourcel et al. (2010), Milkowski and Strack (2010) |
| | Caffeic acid, cinnamic acid, rutin, ferulic acid, benzoic acid | Seedling | Scheible et al. (2004) |
| <i>Arachis hypogaea</i> | Trans-caffeic, chlorogenic, cis-caffeic, protocatechuic, cis-p-coumaric, p-hydroxy benzoic, trans-p-coumaric, trans-ferulic, sinapinic, vanillic acid, cis-ferulic acids | Germination, Seedling | Devi and Reddy (2002), Wu et al. (2011) |
| <i>Betula pendula</i> | Anthocyanin, myricetin-3-galactoside, myricetin-3-glucoside chlorogenic acid, quercetin 3-galactoside, quercetin 3-rhamnoside, kaempferol 3-rhamnoside, chlorogenic acid | Seedling | Tegelberg et al. (2004) |
| <i>Betula pubescens</i> | Phenolic acids, salidroside, rhododendrins, ellagitannins, flavan-3-ols, soluble condensed tannins | Seedling | Keski-Saari and Julkunen-Tiitto (2003), Keski-Saari et al. (2007) |
| <i>Brassica napus</i> | Phenolic compounds, sinapate, sinapoylmalate | Germination | Zobel et al. (1994), Wronka et al. (1994), Milkowski and Strack (2010) |
| <i>Brassica oleracea</i> , <i>Brassica rapa</i> | Anthocyanin | Germination | Siegelman and Hendrichs (1957), Zhou et al. (2007) |
| <i>Capsicum annuum</i> | Ferulic acid, caffeic acid, chlorogenic acid | Germination, Seedling | Díaz et al. (1997) |
| <i>Coffea arabica</i> | Chlorogenic acid (5-O-caffeoyl-quinic acid) | Seedling | Aerts and Baumann (1994) |
| <i>Cypripedium macranthos</i> var. <i>rebunense</i> | Lusianthrin, chrysin | Germination | Shimura et al. (2007) |
| <i>Daucus carota</i> | Quercetin, kaempferol, rutin or quercetin 3-rutinoside) and two flavones (apigenin, luteolin) | Seedling | Poulin et al. (1993) |
| <i>Dolichos lablab</i> | Tannins, total polyphenols | Germination | Ramakrishna et al. (2006) |
| <i>Fagopyrum esculentum</i> | Rutin, quercitin | Germination | Kim et al. (2004), Choi et al. (2007) |
| <i>Fagus crenata</i> | Catechin, epicatechin | Seedling | Yamaji and Ichihara (2012) |
| <i>Glycine max</i> | Anthocyanins, proanthocyanins, luteoline | Seedling | Zabala et al. (2006) |
| | Kampferol, quercetin, isorhamnetin, daidzein, genistein | Germination | Grahamn (1991) |
| <i>Hordeum vulgare</i> | (+)-catechin, ferulic acid | Germination | Lu et al. (2007) |
| <i>Lactuca sativa</i> | Chlorogenic acid | Seedling | Narukawa et al. (2009) |
| <i>Lens culinaris</i> | p-Hydroxybenzoic aldehyde, p-hydroxyphenylpropionic acid, vanillin, T4 (Procyanidin tetramer) ferulic acid, B5 [(±)-epicatechin-(4-6)-epicatechin] | Germination | Bartolome et al. (1997) |
| <i>Lotus japonicus</i> | Kaempferol glycosides | Seedling | Suzuki et al. (2008) |
| <i>Lupinus luteus</i> | Apigenine 7-O-beta-neohesperidoside, Genistein 8-C-beta-glucoside, Genistein 7-O-beta-(6-malonyl) glucoside | Seedling | Katagiri et al. (2002) |
| <i>Lycopersicon esculentum</i> | Anthocyanins | Germination, Seedling | Huub et al. (1997), El-Araby et al. (2006), Guo and Wang (2010) |

Table 2 continued

| Species | Compound | Stage | References |
|--|---|-------------------------|--|
| <i>Medicago sativa</i> | 4',7-Dihydroxyflavone, 4'-7-dihydroxyflavanone, and 4,4'-dihydroxy-2'-methoxychalcone, ononin, malonylononin | Germination | Maxwell et al. (1989), Zuanazzii et al. (1998) |
| | Daidzein, 7,4-dihydroxyflavone, formononetin, isoliquiritigenin, liquiritigenin, 2-methoxy-isoliquiritigenin, ononin, malonylononin | Seedling | Zuanazzii et al. (1998) |
| <i>Oriza sativa</i> | Ferulic acid, sinapinic acid | Germination | Tian et al. (2004) |
| <i>Pangium edule</i> | Total phenol | Germination | Andarwulan et al. (1999) |
| <i>Pennisetum glaucum</i> | Total polyphenol | Germination | Abdelrahman et al. (2007) |
| <i>Pennisetum typhoideum</i> | Total polyphenol | Germination | Abdelrahman et al. (2007) |
| <i>Phaseolus, Lens, Pisum spp</i> | Total phenol | Germinación | López-Amorós et al. (2006) |
| <i>Raphanus sativus</i> | Sinapate, sinapoylmalate | | Strack (1981) in Milkowski and Strack (2010) |
| <i>Ricinus communis</i> | Flavonoids, anthocyanins | Germination Seedling | Khogali et al. (1993) |
| <i>Sesamum indicum</i> | (+)-Pinoresinol, (+)-sesaminol | Germination | Ono et al. (2006) |
| <i>Sesbania vesicaria, S. drummondii</i> | Total flavonoids, total condensed taninns | Germination | Ceballos et al. (1998) |
| <i>Sesbania virgata</i> | (+)-Catechin | Germination | Simões et al. (2008) |
| <i>Sinapis alba</i> | Flavonoids | Seedling | Zenner and Bopp (1987) |
| <i>Solanum lycopersicum</i> | Petunidin 3-(caffeoyl) rutinoside-5-glucoside, petunidin 3-(p-coumaroyl) rutinoside-5-glucoside, malvidin 3-(p-coumaroyl) rutinoside-5-glucoside, quercetin, kaempferol | Seedling | Bovy et al. (2002) |
| <i>Sorghum bicolor</i> | Dhurrin, apigeninidin, luteolinidin, 3-anthocyanins | Seedling | Nicholson et al. (1987), Weiergang et al. (1996), Huang and Backhouse (2005) |
| <i>Trapa natans</i> | Total phenol | Seedling | Baldisserotto et al. (2007) |
| <i>Vicia faba</i> | Catechin derivative, flavone, flavonone, phenolic acid | Seedling | Bekkara et al. (1998) |
| <i>Vigna radiata</i> | Anthocyanins | Seedling | Dumortier and Vendrig (1982a, b) |
| <i>Vitis amurensis</i> | (+) Catechin, (–) epicatechin | Germination | Weidner et al. (2007) |
| <i>Zea mays</i> | Anthocyanin | Seedling | Duke and Naylor (1976) |

Variation of SM during early development

SM, as has previously been mentioned, can be provided directly by the mother plant (Baumann and Gabriel 1984; Suzuki and Waller 1987) or biosynthesised de novo (Aerts et al. 1990; Niemeyer 1988; Aerts et al. 1996; Huub et al. 1997; Schaffner et al. 2003; Matsuda et al. 2005; de la Cruz Chacón and González-Esquinca 2012). In any case, these two

conditions imply a considerable investment of energetic resources and biosynthetic machinery, first during embryogenesis and/or the maturation of seeds and later during germination or seedling growth. There are species that employ both strategies; they accumulate SM in the seeds, and subsequently during early development they increase and/or decrease the quantity and diversity of SM (Takamatsu et al. 1991; Wink 1983; de la Cuadra et al. 1994; Gregianini et al. 2004;

Table 3 Terpenes during early plant development

| Species | Compound | Stage | Reference |
|---|---|-------------|---|
| <i>Chrysanthemum cinerariaefolium</i> | Piretrine | Seedling | Matsuda et al. (2005) |
| <i>Brassica</i> | Steroids triterpen | Germination | Ingrams et al. (1968) In: Baisted (1971) |
| <i>Calendula officinalis</i> | Steroids triterpen | Germination | Kasprzyk et al. (1971) In: Baisted (1971) |
| <i>Cheiranthus cheiri</i> | Steroids triterpen | Germination | Ingram et al. (1968) In: Baisted (1971) |
| <i>Eucalyptus nitiens</i> | α -Pinene, sideroxytonals, cineole | Seedling | McArthur et al. (2010) |
| <i>Gossypium hirsutum</i> | Desoxyhemigossypol, desoxy-6-methoxyhemigossypol, hemigossypol, 6-methoxyhemigossypol, gossypol, 6-methoxygossypol, and 6,6'-dimethoxygossypol | Seedling | Hunter et al. (1978) |
| | (Z)-3-hexenyl acetate, hexyl acetate, (E)- β -3-ocimene, (3E)-4,8-dimethyl-1,3,7-nonatriene, and (Z)-3-hexenyl butyrate | Seedling | McCall et al. (1994) |
| | α -Pinene, β -pinene, (E)- β -ocimene, myrcene, α -humulene, β -bisabolol, (E)- β -ocimene, (E)- β -caryophyllene | Seedling | Opitz et al. (2008) |
| <i>Happlopappus heterophyllus</i> | Steroids triterpen | Germination | Bennett et al. (1967) In: Baisted (1971) |
| <i>Melaleuca alternifolia</i> | α -Pinene, β -pinene, terpinolene | Seedling | Southwell and Russell (2003) |
| <i>Melaleuca alternifolia</i> var rich oil | 1,8-Cineole, α -pinene, β -pinene, & terpinolene | Seedling | Southwell and Russell (2003) |
| <i>Nicotiana tabacum</i> | Stigmasterol, campesterol | Germination | Bush and Grunwald (1972) |
| <i>Phaseolus vulgaris</i> | Steroids triterpen | Germination | Duperon and Duperon (1965), In: Baisted (1971) |
| <i>Plantago lanceolata</i> , <i>P. major</i> | Iridoid glycosides, | Seedling | Barton (2007) |
| <i>Pisum sativum</i> | Steroids triterpen | Germination | Vil'yams and Krochina (1966) In: Baisted (1971), Green and Baisted (1971) |
| <i>Raphanus sativus</i> | Steroids triterpen | Germination | Ingram et al. (1968) In: Baisted (1971) |
| <i>Ricinus communis</i> | Sasbene | Seedling | Sitton and West (1975) |
| <i>Sinapis alba</i> | Steroids triterpen | Germination | Ingram et al. (1968) In: Baisted (1971) |
| <i>Zea mays L.</i> | Stigmasterol, β -sitosterol | Germination | Kemp, Goad and Mercer (1967) |
| | Linalool, (E)- β -farnesene, sesquiterpenoid naphthalene, 1,2,4a,5,8,8a-hexahydro-4,7-dimethyl-1-(1-methylethyl)-, (1a,4ab,8aa) | Seedling | Turlings et al. (1998), Shen et al. (2000) |

Zheng and Ashihara 2004; Zheng et al. 2005; Poustka et al. 2007; Valletta et al. 2007; Pourcel 2010; Milkowski and Strack 2010). This increasing and/or decreasing result in a significant characteristic of SM dynamics, namely, that the gene expression of all SM

for a species is not a reflection of each particular plant. This difference indicates different genetic regulation for each molecule. *Coffea arabica* provides a good example of SM variation during germination (Ashihara 2006; Baumann 2006). This seeds of this

species contain the alkaloids caffeine and trigonelline, as well as chlorogenic phenolic acid, composing approximately 1 and 2 % of the dry weight, respectively. Immediately upon the initiation of germination (between 1 and 5 days), these compounds travel from the cotyledons to other embryonic tissues during growth or are excreted into the surrounding medium. A calculation of the quantities in each tissue or excretion reveals that the level of caffeine is 2.5 times greater than that found before germination; the trigonelline remains essentially unchanged; and the level of chlorogenic acid is reduced to a third of the initial content. Almost all of the trigonelline accumulated in the cotyledons is transported to the seedling during development such that the caffeine and chlorogenic acid are detected in the seedling and surrounding medium. The differences between the original quantities of caffeine and those calculated later (between 51 and 86 % more) indicate that not all of the caffeine detected in the plant is supplied by the mother plant but that *de novo* synthesis also must have occurred, contrary to what occurs with chlorogenic acid (Baumann and Gabriel 1984; Aerts and Baumann 1994; Zheng and Ashihara 2004). Another similar case is that of the alkaloids nicotine, nornicotine, anabutine, and anabasine in *Nicotiana tabacum*. The initial nicotine and nornicotine levels (183 and 74 $\mu\text{g/g}$ dry weight, respectively) in the seeds decrease to 30 and 60 $\mu\text{g/g}$, respectively, during hours 24–96 of germination, although these levels later increase to 1325 and 119 $\mu\text{g/g}$, respectively, just as the radicle emerges (48 h after having decreased), whereas the amount of anabutine (32 $\mu\text{g/g}$) diminishes to undetectable levels. The opposite effect occurs with anabasine levels, which reach 127 $\mu\text{g/g}$ (Weeks and Bush 1974).

In 2007, Choi et al. described another study examining flavonoids during the germination of *Fagopyrum esculentum* and *F. tataricum*. In that study, the total amount of flavonoids increased during germination from 8 to 145 mg/g dry weight. As a result, rutin increases tenfold (from 4.5 to 52.67 mg/g of dry weight), whereas quercetin apparently disappears. Simultaneously, quercetin and another unidentified flavonoid are biosynthesised *de novo* to such a degree that 48 h after germination, taken together, they account for nearly 50 % of the flavonoid content.

A further interesting aspect over interconversion compounds is documented with sinapoyl ester metabolism. Members of the Brassicaceae family

accumulate specific sinapate esters, i.e. sinapine (sinapoylcholine) during seed development and this compound is hydrolysed and mobilized during seed germination to liberate sinapate and choline. In young seedlings, the liberated sinapate is conjugated via sinapoylglucose to sinapoylmalate (Milkowsky and Strack 2010). For example, during early seedling development of *Brassica napus*, the amount sinapine (140 nmol seed⁻¹) decreased until to trace amounts in 10 days, followed by accumulation of sinapoylmalate (zero to 100 nmol seedling⁻¹). This conversion is important, because both sinapoylmalate and sinapoylglucose should be implicated in UV-B tolerance (Milkowsky et al. 2004; Milkowsky and Strack 2010).

Another aspect to highlight is that this metabolic variation is distinct, including between neighbouring plants that initially possess similar profiles, i.e., the movement of a particular SM might also be regulated by the species. Various species of *Lupinus* have been documented to deposit quinolizidinic alkaloids in their seeds. For example, *L. angustifolius*, *L. albus*, and *L. campestris* accumulate nearly 2.5 % of the dry weight (15, 23.6, and 24.5 mg/g, respectively) (de Cortes et al. 2005), of which a large portion are typically lupanine and hydroxylupanine (Wink and Witte 1985). During the first several days of germination, the total alkaloid amount decreases by 20, resulting in 50 % of original levels. Nevertheless, this apparent loss is recovered in the following days, coinciding with the beginning of the photosynthetic capacity (Wink and Witte 1985). This general behaviour does not represent the activities of each particular SM. For instance, in *L. albus*, lupanine increases and albino and 13-hydroxylupanine decrease substantially, whereas in *L. angustifolius*, only 13-hydroxylupanine decreases. In *L. campestris*, hydroxyaphylline and hydroxyaphyllidine increase, whereas epihydroxyaphylline and dehydroepi-hydroxyaphylline decrease, and lupanine remains constant (de Cortes et al. 2005). It is also observed that the free alkaloids decrease, and their ester derivatives increase, of which the most important is 13-tigloiloxylupanine (which has an antimicrobial activity 20 times greater than that of its precursor, 13-hydroxylupanine), which increases in a progressive manner during the germination of *L. angustifolius* (from 0 to 4.4 mg/g) and *L. albus* (from 10 to 200 $\mu\text{g/g}$) (Wink and Witte 1985; de Cortes et al. 2005).

The number of SM does not always increase, nor is this increase proportional to seedling development.

For example, the lentil (*Lens culinaris*) shows a decrease in the diversity and quantity of phenols. The seeds contain 45 phenols that account for 41.27 µg/g of the dry weight, but during germination (6 days later), the quantity and diversity of phenols decreases to 4.47 µg/g and 15 SM, an 89 and 67 % decrease, respectively. In this phenomenon, as in others, there are specific regulations, such that on one side (+) catechins and the primary proanthocyanidins from seeds cease to be detected upon forming a tetramer (Bartolomé et al. 1997).

In the previous examples, the species referred to contain certain SM in the seeds that are formed during embryogenesis. Nevertheless, there are species that appear to biosynthesise de novo essentially all of their SM during early development. Among these species are the seedlings of *Arabidopsis thaliana*, which produce anthocyanins 3–5 days after germination (Ehmann et al. 1991; Kubasek et al. 1992; Shirley et al. 1995; Kubasek et al. 1998; Murphy et al. 2000; Jeong et al. 2010), and *Catharanthus roseus*, which accumulate the alkaloids catharanthine, tabersonine, vindoline, and vincristine 7–10 days after germination; these SM account for up to 2 % of their biomass (Balsevich et al. 1988; De Luca et al. 1986; Aerts et al. 1994; Guo et al. 2007). *Zea mays*, *Secale cereale*, *Triticum durum*, and *T. aestivum*, among other grasses, biosynthesise hydroxamic acids from the second day of germination, with the highest level of production being detected on the fourth day (15.2 mmol/kg from fresh biomass each day in maize, 7.4 in rye, 5.0 and 3.2 in *Triticum*). After the fifth day, the production decreases (1–3 mmol/kg wet weight), but the total content of hydroxamic acids continues to increase as seedling development progresses (Argandoña et al. 1981). In the cases mentioned, the seeds apparently do not contain indications of the SM biosynthesised later during the early stages of the species.

The abundance of SM in early development in certain species is relatively high; cotton seedlings (*Gossypium hirsutum*) biosynthesise 10 terpenes at 10–20 days of age and thirteen anthocyanins were found in *Arabidopsis* wild-type seedlings with 4–5 days of germination, whereas *Lupinus* produce up to 13 alkaloids at 9 days of age, and only 7 days later, 23 flavonoids appear (Hunter et al. 1978; Wink 1983; Bednarek et al. 2001; Pourcel et al. 2010). Others species, such as *Camptoteca acuminata*, accumulate the majority of certain SM during the early

stage. For example, the alkaloid camptothecin is deposited in the hypocotyls at 4.23 mg/g, which is 50 times more than in any later stage (Valletta et al. 2007).

In other plant stages, the SM are distributed in an organ-specific manner. Murphy et al. (2000) and Peer et al. (2001) demonstrated that the localisation of the specific flavonoids quercetin, kaempferol, and naringenin in *Arabidopsis* plants is concentrated only in three parts of the plant: in the cotyledon node, hypocotyl-root transition zone, and hypocotyl. In *Phaseolus aureus*, from the second day of germination forward, nearly all of the trigonelline accumulated in the seed cotyledons (~240 nmol) is transported via the hypocotyl of the embryonic axis, and on the fifth day, when trigonelline reaches its highest level (380 nmol), the most critical proportion (~35 %) is observed in the apical hypocotyls (Zheng et al. 2005). *L. albus* also transfers its alkaloid content in its cotyledons toward the forming hypocotyls, leaves, and developing roots during germination (Wink and Witte 1985). In *L. luteus* some alkaloids are higher in the cotyledons than in the leaves (Wang et al. 2000). In the plants of *C. arabica*, caffeine is distributed primarily in the leaves and cotyledons, and only trace quantities are found in the radicles and foliage blooms (Zheng and Ashihara 2004). The essential oils formed at these stages accumulate in the aerial components of the plants of *Chrysanthemum*, *Citrus*, *Echinacea*, and *Zea* (McCall et al. 1994; Turlings et al. 1998).

Importance of SM during early development

The germination and development of seedlings are critical life stages that allow the plants to become established in the environment. The presence of SM during these stages and their spatio-temporal distribution can be important survival strategies. In this section, the roles of SM as reservoirs of nitrogen, defence substances against phytopathogens and insects, allelopathic agents, molecules with photoprotective roles, and attraction signals for nitrogen-fixing microorganisms are documented (Niemeyer et al. 1989a; Zuanazzii et al. 1998; Weir et al. 2003; Gregianini et al. 2004; Zheng et al. 2008; Milkowski and Strack 2010; Yamaji and Ichihara 2012).

Nitrogen and water deficits are the primary factors that limit biomass production, and they therefore impact plant development. From their studies on

C. arabica, *P. aureus*, and various species of *Lupinus*, Wink and Witte (1985) proposed that certain nitrogenous SM, particularly alkaloids, can constitute reservoirs of nitrogen. By working with these species of *Lupinus* at different points during germination and plant development, these investigators followed (with classical spectrometric techniques) the motility of quinolizidinic alkaloids (QAs) and determined that 20–50 % of the initial QA quantity in the seed cotyledons is transferred to the roots and hypocotyls during germination, and after two weeks, the cotyledons have almost no QAs. The quantity used for plant growth during this period (6–10 days) decreases by 60 %, and only 4 % of the total is excreted into the environment. For this reason, the authors suggest that the remaining 54 % must have been catabolised, and the nitrogen must have been utilised for plant growth. A more certain result is that of Shimizu and Mazzafera (2000), who analysed changes in the content of the alkaloid trigonelline at various germination stages *C. arabica*. Using radioactive substrate assays, these researchers determined that the seedlings can convert trigonelline (carboxyl- ^{14}C) to nicotinic acid during germination, which can be used to synthesise NAD, suggesting that trigonelline acts as a nitrogen reserve during these stages (Ashihara 2006).

However, Zheng et al. (2005) and Zheng et al. (2008), using 1- to 2-day-old *P. aureus* seedlings, determined that the inverse phenomenon (the biosynthesis of trigonelline from nicotinic acid (carboxyl- ^{14}C) and NAD) occurred in the cotyledons and embryos in this stage, incorporating 60 to 70 % of the marked molecule into trigonelline. Because plant growth is inhibited by the exogenous application of nicotinic acid and nicotinamide but not trigonelline, this result suggests that the alkaloid is biosynthesised from nicotinic acid, possibly with the goal of eliminating the toxicity of the excess nicotinic acid and nicotinamide liberated during the cellular NAD cycle (Zheng et al. 2005). In any case, it appears that trigonelline may be an interchangeable SM involved in nucleotide metabolism, depending on the characteristics of the species. Certain authors have additionally indicated that trigonelline also functions as a phyto regulator during germination because it potently induces cell cycle arrest in the G2 phase (Evans et al. 1979; Evans and Tramontano 1984; Minorsky 2002). This SM appears to be a common molecule among various legumes (Table 1) (Rozan et al. 2000).

SM are also implicated in plant defence against diverse microorganisms aimed at depredation or microbial attacks; in early plant developmental stages, their role in defence has been documented. Classic work involved the early biosynthesis of hydroxamic acids (HXA) in grains as defence substances against insects (Argandoña et al. 1980; Bohidar et al. 1986; Xie et al. 1991; Assabgui et al. 1995; Davis et al. 2000). Argandoña et al. (1980) demonstrated that the susceptibility of three grass species (*H. distichum*, *S. cereale*, and *T. durum*) to aphids (*Metopolophium dirhodum*) is related to the presence or absence of HXA. After infesting rye, barley, and wheat seedlings of different ages (10, 16, 22, 28, and 34 days) with aphids, it was observed that the youngest seedlings contained a larger quantity of HXA and simultaneously showed greater resistance to aphids than plants at later developmental stages. In this same study, 20-day-old rye and wheat plants, after being infested with aphids, showed an increase in HXA biosynthesis, which was accompanied by a decrease in the number of insects, in contrast to the barley seedlings, which were less toxic because of their lower HXA production. In addition, DIMBOA (2,4-dihydroxy-7-methoxy-1,4-benzoxacin-3-one) was the most important active constituent of HXA in in vitro assays of aphids fed different diets of HXA at varying concentrations (Argandoña et al. 1980). Thus, HXAs act as natural defences against *M. dirhodum*. HXA is biosynthesised shortly after germination, suggesting that it participates in defence at this stage. Similar results have been found in maize and different wheat varieties when facing *Rhopalosiphum maidis*, *Schizaphis graminum*, and *Sitobion avenae* (Bohidar et al. 1986; Wratten et al. 1988; Niemeyer et al. 1989a, b).

It also appears that from the beginning of their lives, plants produce compounds that inhibit the growth of other plant organisms. Allelopathic activities have been documented in *Camellia sinensis*, *Coffea arabica*, *Ipomoea tricolor*, and *Lupinus albus* (Wink 1983; Suzuki and Waller 1987; Macías-Ruvalcaba et al. 2008). In *L. albus*, Wink (1983) examined the allelopathic properties of the excreted compounds in the aqueous form from the seed during germination at intervals 0 and 42 h and observed that part of the total alkaloids is excreted in an exponential manner from 0 to 3 mg over a period of 1 to 2 days. The excretions are composed primarily of lupinine (50–75 %), cytisine (5–10 %) and 13-tigloiloxylupanine (10–20 %)

(the first two substances are produced by the seed, whereas the third is produced de novo) during that germination period, presumably from the 13-hydroxylupanine present in seeds (Wink and Witte 1985). A single seed contains approximately 9 mg of alkaloids and liberates nearly 0.7 mg or more from the roots during germination (equivalent to ~ 2 mol alkaloids), which is a sufficient quantity to inhibit 90 % of the *Lactuca sativa* germination (Wink 1983). The author suggests that this phenomenon is similar to in vivo conditions in which an allelopathic activity is ascribed to these alkaloids. A study in which both species are grown together could confirm this hypothesis.

Weir et al. (2003) performed in vitro studies on *Centaurea maculosa* and determined that the secretion of (–)-catechin at phytotoxic levels (5 to 40 $\mu\text{g/mL}$) begins from the first and third week of seedling emergence for plants cultivated in liquid media. The authors compared the effects of different concentrations of (–)-catechin on *Digitalis purpurea*, *Papaver orientale*, three species of grass (*Festuca idahoensis*, *Stipa tenuissima* and *Koeleria cristata*) and itself (*C. maculosa*). The results indicated that, whereas concentrations of 10–50 $\mu\text{g/mL}$ caused burns on the radicle system in all of the species, only concentrations equal to or greater than 600 $\mu\text{g/mL}$ were sufficient to inhibit the growth of *C. maculosa* (20–60 times more), indicating that the natural secretion of (–)-catechin by seedlings occurs at levels that are not toxic to themselves but to other species.

Additionally, it has been documented that flavonoids are a defence mechanism against phytopathogens. These SM are generally inducible and produced prior to the lignification of tissues around the infection (Dixon et al. 1994; Dixon and Steele 1999). These phenomena have been observed with the induction of the antifungal flavonoid glyceollin in seedlings of different *Glycine max* varieties (Graham et al. 1990; Graham 1991; Mohr and Cahill 2001; Lozovaya et al. 2004). Graham et al. (1990) and Graham (1991) demonstrated that 7-day-old *G. max* seedlings accumulate the isoflavonoids daidzein and genistein in their cotyledons in conjugates of the glycosylated form. Daidzein is a direct precursor of glyceollin and genistein, the latter of which is antifungal in its free form. Upon exposing seedlings to the phytopathogen *Phytophthora megasperma*, isoflavonoids were observed to be liberated from their conjugates 24 h after the infection, and the biosynthesis of glyceollin was initiated. At 48 h, the level of glyceollin

reaches 700 nmol/g of wet weight in infected tissues, and the presence of daidzein increases to 6000 nmol/g, i.e., glyceollin is biosynthesised up to 7 times more than its effective dose (100 nmol/mL) on *P. megasperma*, 1 to 10 times more on genistein, and 2 to 75 times more on daidzein than the amount required to produce glyceollin in quantities approximating its average activity. Glyceollin is also partially responsible for the resistance to *Phytophthora sojae* in soy seedlings 7–10 days of age (Bhattacharyya and Ward 1985; Morris et al. 1991; Mohr and Cahill 2001). A role for glyceollin in plant defence is also supported by studies of Lozovaya et al. 2004. These authors determined that glyceollin is produced from the roots of *G. max* as a consequence of infection with *Fusarium solani* and that the quantities detected (100–200 $\mu\text{g/mL}$, corresponding to 300–600 μM) in the zones of infection are greater than the glyceollin concentrations (25–215 μM) that inhibit *F. solani* in vitro. In conclusion, the levels of daidzein, genistein, and glyceollin in soy seedling tissue appear to be sufficient to offer resistance to phytopathogens.

It has been observed that the SM present in seeds occasionally are not sufficient to combat the attacks of phytopathogens, and it is therefore necessary to biosynthesise de novo other compounds that intervene in defence. This scenario appears to occur in *Annona diversifolia* in which the seeds accumulate considerable quantities of the acetogenins Laherradurine and Rollinastatin-2 (100 and 30 $\mu\text{g/g}$, respectively), which possess insecticidal activity and deterrent activity. Nevertheless, during the imbibition, these acetogenins do not inhibit the growth of the phytopathogens *Rhizopus stolonifer* and *Aspergillus flavus* until germination occurs, which is when the population of these fungi decreases. The decrease in the fungal population appears to be related to the production of the antimicrobial alkaloid liriodenine, which accumulates (up to 849 $\mu\text{g/g}$ dry tissue) to 100–300 times the amount necessary for its activity in vitro (de la Cruz Chacón et al. 2011; de la Cruz Chacón and González-Esquinca 2012).

In some legumes, phenolic compounds are also released rapidly from emerging roots during seed germination and seedling growth (Mandal et al. 2010). Particularly, the flavonoids and isoflavonoids are implicated as promoters of nodulation between the roots of *G. max* and *Medicago sativa* seedlings and nitrogen-fixing microorganisms (Graham 1991; Hartwig et al. 1991). This phenomenon occurs with alfalfa (*M. sativa*), in which the seeds possess

flavonoids but are not capable of inducing nodulation. Nevertheless, at 24 h after radicle emergence, the presence of conjugate isoflavonoids (glucosides of medicarpine-6''-O-malonate (MGM), glucoside of formononetin 7-O-malonate (FGM), glucosides of coumestrol (CG), luteolin 7-glucoside, and quercetin 3-galactoside) is detected at levels sufficient to induce the nodulation genes of *Rhizobium meliloti*. Graham (1991) monitored the germination of *G. max*, collecting the excretions of the seeds and seedling roots. The data from these experiments suggest that the conjugate flavonoids of daidzein and genistein are freed rapidly during seed imbibition until the plants have a developed radicle system, at which point the quantities detected in the excretions (1–10 μM) are sufficient to attract *Bradyrhizobium japonicum* and induce the appropriate nodulation genes (*nod*).

The constant presence of coloured flavonoids during the germination of various species (*Brassica* spp., *Vigna radiata*, *Lycopersicum esculentum*, *Sinapis alba*, *Z. mays*, *A. thaliana*, and *L. luteus*) has permitted speculation and investigation concerning the photoprotective role of these SM (Siegelman and Hendricks 1957; Dumortier and Vendrig 1982a; Rengel and Kordan 1988; Kubasek et al. 1992; Kubasek et al. 1998; Huub et al. 1997; Katagiri et al. 2002; Zhou et al. 2007; Poustka et al. 2007; Pourcel et al. 2010; Milkowski and Strack 2010). Huub et al. (1997) evaluated this hypothesis with 3-day-old *Lycopersicum esculentum* plants that were irradiated with red light (681 nm) at various intensities (0.0001 to 10 $\text{pmol/m}^2\text{s}$) after 24 h and with a darkness control. The authors observed a proportional positive relationship between the production of coloured anthocyanins and light intensity. Similar results were found with *V. radiata*, in which a relationship was found between seedling development and the presence of phytochromes for producing red anthocyanins. Importantly, the 36–48-hour-old seedlings overproduce anthocyanins after irradiation with red light. This expression contrasts with that of seedlings under normal conditions or at an earlier developmental stage (Dumortier and Vendrig 1982a, b).

Summary

Even where studies on SM in plants are scarce, it is evident that spatio-temporal programming depends on the biosynthesis of diverse SM. The SM produced de novo or from the mother plant, biosynthesised in roots,

stalks or leaves, or interchanged, utilised or excreted, all translate into constitutive or induced advantages for the new plant during development. This ability initially allows the plant to establish relationships with new environments. Studies on the presence of SM in early plant development may strengthen the different hypotheses that are trying to explain the assignment of energetic resources for the production of diverse SM (Stamp 2003; Hartmann 2007). Aspects regarding the level of development will perhaps provide insight into the basic plant production independent of environmental pressures, both biotic and abiotic. The variation of the temporal and spatial composition between the organs and the changes during early ontogeny may provide tests for theories regarding plants' chemical defences (Schaffner et al. 2003; Gregianini et al. 2004; Yamaji and Ichihara 2012).

The presence of terpenes, monoterpenes, and sesquiterpenes during germination is poorly documented, possibly because of the small number of studies or because the presence of these molecules has not been justified. It will also be important to know whether the observed behaviour in the species covered in this review extend to other species that produce SM. Several of the applications of these studies may be related to the optimal regulation of the production of certain SM that are produced in greater quantities in these stages or in the presence of toxic compounds that are consumed by germinated plants.

Moreover, germinating seeds and developing seedlings provide an experimental model that can be used to determine various aspects of secondary metabolism and that provides rapid answers, is economical in terms of physical space, and allows the precise control of the environmental conditions. For example, recently Poustka et al. (2007) and Pourcel et al. (2010), using wild-type *Arabidopsis* seedlings with 3–5 days germination and *tt5*, *5gt*, and *atg* mutant seedlings (transparent testa loci, mutants that fail to glycosylate anthocyanidins at the 5-O-position, mutants that interfere with the autophagic process, respectively) as a model to understand how anthocyanin are accumulated, they show that anthocyanins in *Arabidopsis* can be accumulated as part of sub-vacuolar pigment bodies, the anthocyanic vacuolar inclusions (AVIs). The results suggest novel mechanisms for the formation of sub-vacuolar compartments capable of accumulating secondary metabolites (Pourcel et al. 2012).

Finally, the early development in plant represents a “physiological time zero” to explore both primary metabolism and secondary metabolism.

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