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Chemicals on plant surfaces as a heretofore unrecognized, but ecologically informative, class for investigations into plant defence

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ABSTRACT

Plants produce and utilize a great diversity of chemicals for a variety of physiological and ecological purposes. Many of these chemicals defend plants against herbivores, pathogens and competitors. The location of these chemicals varies within the plant, some are located entirely within plant tissues, others exist in the air- (or water-) space around plants, and still others are secreted onto plant surfaces as exudates. I argue herein that the location of a given defensive chemical has profound implications for its ecological function; specifically, I focus on the characteristics of chemical defences secreted onto plant surfaces. Drawing from a broad literature encompassing ecology, evolution, taxonomy and physiology, I found that these external chemical defences (ECDs) are common and widespread in plants and algae; hundreds of examples have been detailed, yet they are not delineated as a separate class from internal chemical defences (ICDs). I propose a novel typology for ECDs and, using existing literature, explore the ecological consequences of the hypothesized unique characteristics of ECDs. The axis of total or proportional investment in ECDs *versus* ICDs should be considered as one axis of investment by a plant, in the same way as quantitative *versus* qualitative chemical defences or induced *versus* constitutive defences is considered. The ease of manipulating ECDs in many plant systems presents a powerful tool to help test plant defence theory (e.g. optimal defence). The framework outlined here integrates various disciplines of botany and ecology and suggests a need for further examinations of exudates in a variety of contexts, as well as recognition of the effects of within-plant localization of defences.

Key words: plant defence, exudates, herbivory, plant chemistry, chemical localization, pathogens, allelopathy.

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I. INTRODUCTION

> '*The location of a particular toxic chemical may be as important as the presence or absence of that chemical*.'
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> (Stipanovic, 1983)

Plants defend themselves physically and chemically against herbivores, pathogens and competitors. The study of these defences has defined much coevolutionary and evolutionary ecological thinking for the past half century (in terrestrial systems: Ehrlich & Raven, 1964; Thompson, 2005; Agrawal, 2011; in marine systems: Pohnert, Steinke & Tollrian, 2007; Hay, 2009). Plant defence theory includes several broad hypotheses attempting to explain the evolution and allocation of defensive traits (Stamp, 2003; Massad *et al.*, 2011). Plant investment in chemical defences can be defined along a number of axes including whether they are constitutive or induced (Karban & Baldwin, 1997); at what point during ontogeny they are produced or peak; whether they are present as potent toxins in small quantities (qualitative defences) or as less-potent toxins in larger quantities (quantitative defences) (Feeny, 1976) and how toxic they are to the plant itself (autotoxicity) (Schoonhoven, Van Loon & Dicke, 2005). Allocation patterns of defensive chemicals in relation to these axes can be driven by climatic and geographic patterns in terrestrial (Moreira *et al.*, 2014), freshwater (Morrison & Hay, 2012), and marine systems (Cetrulo & Hay, 2000). Many comparative studies find considerable variation across closely related plants on several of these axes (e.g. Pearse & Hipp, 2012), and congruities amongst plants in relation to these axes may show evolutionarily informative patterns.

Stipanovic (1983) recognized and highlighted the importance of defensive chemical location; yet despite advances in determining the localization of specific chemicals (e.g. Shroff *et al.*, 2008; Lane *et al.*, 2009) and a huge interest in various aspects of terrestrial and marine chemical ecology, there is no systematic exploration of the ecological implications of broad defensive chemical location. A whole suite of unrelated plants in the California coast range, where I conduct fieldwork, exhibit copious exudates. The convergence of this trait in ecologically similar but phylogenetically disparate plants, the shared herbivore and predator communities among these plants, and the fact that many of these exudates are defensive (e.g. LoPresti, 2014), made me question the broader consequences of the possession of defensive surface chemicals. Therefore, I focus this review on the questions: (*i*) are defensive exudates common enough to warrant attention; (*ii*) what are the basic ecological characteristics of a defensive exudate; and (*iii*) how do these characteristics influence the ecology of plants with defensive exudates?

II. EXUDATES ARE COMMON AND POTENTIALLY COSTLY

Secretion (i.e. non-waste removal) and excretion (e.g. waste removal: Fahn, 1979) of various compounds is ubiquitous in plants. Two books (Fahn, 1979; Roschina & Roschina, 1993) focus on the physiology of secretion, and many reviews highlight individual structures involved in secretion or exudate functions (e.g. Thomas, 1991; Barthlott *et al.*, 1998; Heil, 2008; Dennis, Miller & Hirsch, 2010). Exudates can serve many functions simultaneously including desiccation resistance (e.g. Paiva, 2009), excretion of excess ions (e.g. Osmond, Bjorkman & Anderson, 1980), maintenance of water pressure gradients (e.g. Fahn, 1979), ultraviolet (UV) protection (e.g. Stephanou & Manetas, 1997), structuring microbial communities (Dennis *et al.*, 2010) and plant defence (e.g. Krimmel & Pearse, 2013). Exudates exist broadly across plant phylogeny (Fahn, 1979; Roschina & Roschina, 1993; Shepherd & Wagner, 2007; Weber & Keeler, 2013; Table 1) including commonly in marine algae (Hay & Fenical, 1988) and have evolved many times independently. Certain secretory structures are confined to just one clade (e.g. 'salt' bladders of the former Chenopodiaceae: LoPresti, 2014), while many others are widespread. Root exudates are probably ubiquitous, but understudied (Dennis *et al.*, 2010). Shepherd & Wagner (2007) estimate that 30% of plant species possess the secretory form of glandular trichomes. Colleters – which secrete resins onto developing buds – occur in at least 60 families (Thomas, 1991) and new examples are discovered frequently (e.g. Paiva, 2009). Epicuticular waxes have been examined in over 13000 species (Barthlott *et al.*, 1998) and contain similar compounds, some defensive, in both higher plants and bryophytes, including many ferns (Wollenweber, 1978; Haas, 1982). Weber & Keeler (2013) estimate that the number of plants with extrafloral nectaries (EFNs), which produce specialized indirect defensive exudates, greatly exceeds the known 4000 species in over 100 families. Hydathodes, which secrete guttation water and defensive proteins (Grunwald *et al.*, 2003), occur in at least 100 families of angiosperms (Fahn, 1979), but also occur in more basal taxa (e.g. Sperry, 1983). While the presence of exudates does not imply a defensive function, the near-ubiquity of secretory capabilities suggests selection for these traits in both terrestrial and marine autotrophs.

These exudates often require significant investment by plants. Dell & McComb (1979) found that dry masses of resinous exudates composed 7–29% of the leaf mass of plants in nine families from western Australia; resins of creosote bush (*Larrea tridentata*: Zygophallaceae) of North American deserts can exceed those figures (Lira-Saldivar, Hernandez-Suarez & Hernandez-Castillo, 2006). Talley, Coley & Kursar (2002) estimated that sagebrush (*Artemisia tridentata*: Asteraceae) exudates comprised ~17% of dry leaf mass; tobacco (*Nicotania tabacum*: Solanaceae) contains a similar percentage (Shepherd *et al.*, 2005). Roots may secrete a variety of chemicals which comprise ~10% of a plant's carbon (Dennis *et al.*, 2010). The synthetic costs of the exudates, whatever mass they represent, may be minimal from a reduction in growth perspective under many circumstances (Herms & Mattson, 1992); yet their direction to the exterior of the plant may impose other costs

Table 1. A partial list of possible or known external chemical defence (ECD)-secreting structures, their taxonomic affiliations, chemicals involved and references which note resistance functions to herbivores, pathogens and competitors, potential environmental degradation or removal, and known autotoxicity

				Exudate resistance function to:					
Exudate-producing structure	Plant family	Genus	Known compounds in exudates (non-exhaustive)	Herbivores	Pathogens	Competitors	Environmentally removable?	Are exudate constituents known to be autotoxic?	General references
'Salt' bladders	Chenopodiaceae	*Atriplex*, *Chenopodium*, *Oxybasis*, *Blitum*	NaCl, K^{+}, betalains, oxalates, heavy metals	Kenagy (1973), Mares *et al*. (1997) and LoPresti (2014)	Simon *et al*. (1994)^{a}	Unknown	E. F. LoPresti, personal observation	Yes^{b}	Cromwell (1950), Osmond *et al*. (1980), De Vecchi & Gerola (1981) and Schirmer & Breckle (1982)
Salt glands	Verbenaceae	*Avicennia*	NaCl, heavy metals	Newbery (1980), Leuck *et al*. (1974)^{a} and Coleman *et al*. (2005)^{a}	Gilbert *et al*. (2002)	Unknown	E. F. LoPresti, personal observation	Yes^{b}	Macfarlane & Burchett (2000) and Flowers *et al*. (2010)
	Tamaricaceae	*Tamarix*	NaCl, heavy metals	Leuck *et al*. (1974)^{a} and Coleman *et al*. (2005)^{a}	Belkin & Qvit-Raz (2010)^{a}	Unknown	Unknown	Yes^{b}	—
	Poaceae	*Phragmites*, *Spartina*	NaCl, heavy metals	Leuck *et al*. (1974)^{a} and Coleman *et al*. (2005)^{a}	Unknown	Unknown	E. F. LoPresti, personal observation	Yes^{b}	Burke *et al*. (2000)
Chalk glands^{c}	Plumbagaceae	*Plumbago*	$MgCO_3$, $CaCO_3$, etc.	Unknown	Unknown	Unknown	Unknown	Yes^{b}	Sakai (1974) and Faraday & Thomson (1986)
Stalked glands	Polypodiaceae	*Cheilanthes*, *Pityrogramma*, *Notholaena*	Flavenoids, terpenes, chalcones	Wollenweber (1978)^{a}	Wollenweber (1978)^{a}	Unknown	Unknown	Unknown	Wollenweber (1978)
Glandular trichomes	Solanaceae	*Solanum*, *Petunia*, *Nicotiana*, *Datura*	Nicotenoids, sugar esters, proteins, terpenes	Gregory *et al*. (1986), Tingey & Laubengayer (1981), Flanders *et al*. (1992), Lin *et al*. (1987), van Dam & Hare (1998*a*,*b*), Elle *et al*. (1999), Hare *et al*. (2003), Roda *et al*. (2003) and Weinhold & Baldwin (2011)	Hill (1966), Cruickshank *et al*. (1977), Shepherd *et al*. 2005 and Shepherd & Wagner (2007)^{a}	Unknown	Hill (1966) and E. F. LoPresti, personal observation	Roda *et al*. (2003)^{a}	Wollenweber & Dietz (1981), Stipanovic (1983), Wagner (1991), Dayan & Duke (2003), Wagner, Wang & Sheperd (2004), Shepherd & Wagner (2007), Wink (2010), Jaime *et al*. (2013) and Wheeler & Krimmel (2015)
	Lamiaceae	*Salvia*	Terpenoids, aglycones, waxes	Unknown	Unknown	Bisio *et al*. (2010)	Unknown	Unknown	

Table 1. Continued

Exudate-producing structure	Plant family	Genus	Known compounds in exudates (non-exhaustive)	Exudate resistance function to: Herbivores	Pathogens	Competitors	Environmentally removable?	Are exudate constituents known to be autotoxic?	General references
	Cannabaceae	*Cannabis*	Cannabinoids	Sirikantaramas *et al*. (2005)	Appendino *et al*. (2008)[a]	Unknown	Unknown	Sirikantaramas *et al*. (2005)	
	Asteraceae	*Artemisia*, *Dittrichia*, *Madia*, *Psiadia*, *Helichrysum*	Alkaloids, terpenoids, flavenoids, coumarins	Juma *et al*. (2001)[a] and Krimmel & Pearse (2013)	Tomás-Barberán *et al*. (1988*a*) and Talley *et al*. (2002)	Funke (1943), Stephanou & Manetas (1995) and Stephanou & Manetas (1997)	Funke (1943), Stephanou & Manetas (1995) and Stephanou & Manetas (1997)	Unknown	—
	Fabaceae	*Medicago*, *Stylosanthes*, *Canajus*	Aldehydes, alkanes, esters	Shade *et al*. (1975), Sutherst *et al*. (1982)[a], Ranger & Hower (2002) and Sujana *et al*. (2012)	Unknown	Unknown	Unknown	Unknown	Juma *et al*. (2001) and Kelsey & Shafizadeh (1980)
	Geraniaceae	*Pelargonium*	Phenolics, flavenoids	Gerhold *et al*. (1984)	Unknown	Unknown	Unknown	Unknown	—
	Grossulariaceae	*Ribes*	Flavenoids	Unknown	Atkinson & Blakeman (1982)	Unknown	Unknown	Unknown	Williams *et al*. (1997)
	Betulaceae	*Betula*	Flavenoid aglycones	Valkama *et al*. (2004)	Valkama *et al*. (2004)	Unknown	Unknown	Unknown	—
Hydathodes	Widespread	Many	Proteins	Unknown	Grunwald *et al*. (2003)	Unknown	Likely	Unlikely	Samac & Shah (1991); Shepherd & Wagner (2007) and Singh (2014)
Extra-floral nectaries	Widespread	Many	Sugars, free amino acids	Janzen (1966*a*,*b*), Madden & Young (1992), Weber *et al*. (2012) and Koptur *et al*. (2013)	Weber *et al*. (2012)	Janzen (1972) and Davidson *et al*. (1988)	Likely	Unlikely	Bentley (1977); Heil (2008) and Weber & Keeler (2013)
Epicuticular waxes	Widespread	Many	Wax esters, alcohols, terpenoids, flavenoids	Eigenbrode & Espelie (1995) and Inyang *et al*. (1999)	Skoropad & Tewari (1977) and Barthlott & Neinhuis (1997)1	Unknown	Cape & Fowler (1981) and Baker & Hunt (1986)	Unlikely	Eigenbrode & Espelie (1995); Barthlott *et al*. (1998) and Müller & Riederer (2005)
Colleters/resin glands	Widespread	Many	—	—	—	—	—	—	Dell & McComb (1979); Wollenweber & Dietz (1981); Thomas (1991) and de Castro Miguel *et al*. (2006)

Table 1. Continued

Exudate-producing structure	Plant family	Genus	Known compounds in exudates (non-exhaustive)	Exudate resistance function to: Herbivores	Pathogens	Competitors	Environmentally removable?	Are exudate constituents known to be autotoxic?	General references
	Zygophyllaceae	*Larrea*	Phenolics, lignans, flavones, saponins, wax esters	Rhoades (1977) and Gonzalez-Coloma *et al.* (1988)	Lira-Saldívar (2003) and Lira-Saldivar *et al.* (2006)	Elakovich & Stevens (1985)	Gonzalez-Coloma *et al.* (1988)	Likely; Elakovich & Stevens (1985)	—
	Betulaceae	*Betula*	Terpenes	Bryant & Kuropat (1980), Bryant (1981), McLean *et al.* (2009) and Forbey *et al.* (2011)	Unknown	Unknown	Unknown	Unknown	—
	Salicaceae	*Populus*	Chalcones, carboxylic acids, flavenoids.	Curtis & Lersten (1974)	Unknown	Unknown	Unknown	Unknown	Greenaway *et al.* (1987)
Root structures (e.g. root cap, border cells)	Widespread	—	Extremely varied	—	—	—	—	—	Walker *et al.* (2003); Bais *et al.* (2006); Badri *et al.* (2009); Dennis *et al.* (2010); Inderjit Wardle *et al.* (2011) and De-la-Peña & Loyola-Vargas (2014)
	Poaceae	*Oryza*, *Zea*, *Secale*, *Sorghum*	Terpenes, hydroxamic acids	Neal *et al.* (2012)	Park *et al.* (2004) and Kato-Noguchi *et al.* (2008)	Czarnota *et al.* (2001), Kato-Noguchi *et al.* (2002), Baerson *et al.* (2008) and Kato-Noguchi *et al.* (2008)	Macías *et al.* (2004) and Gimsing *et al.* (2009)	Unknown	Niemeyer (2009) and Baetz & Martinoia (2014)
	Fabaceae	*Vigna*	Proteins	Unknown	Nóbrega *et al.* (2005)	Unknown	Unknown	Unknown	—
Various structures or specialized cells in marine algae	Various	Many	Tannins, terpenes, phenolics, indoles	Hay *et al.* (1987)	Lane *et al.* (2009)	Johnson & Mann (1986), Keats *et al.* (1993), Dobretsov (1999), Smith *et al.* (2006), Rasher & Hay (2010), Rasher *et al.* (2011) and Andras *et al.* (2012)	Hay *et al.* (1987) and Jennings & Steinberg (1994)	Likely; Dworjanyn *et al.* (1999)	Hay & Fenical (1988); Steinberg *et al.* (1997); Targett & Arnold (1998) and Sieg & Kubanek (2013)

General references listed in the right-hand column include detailed reviews in which other references or syntheses of the known literature are included.

[a] Not experimentally demonstrated, but see reference.

[b] Heavy metals: e.g. Weis & Weis (2004).

[c] Often treated with/as salt glands.

(e.g. removal) that an internal chemical may not require. Additionally, certain secretory processes require energy, independent of the costs of exudate production (Fahn, 1979). Unsurprisingly, a high level of secretion comes with a fitness cost in some contexts. While exudates of *Datura wrightii* (Solanaceae) were toxic to several herbivores (van Dam & Hare, 1998*a,b*) and resulted in lower herbivory (Elle, van Dam & Hare, 1999), the secretory phenotype consistently had a lower reproductive output relative to the non-secretory phenotype, possibly due to high costs of exudate production (Hare, Elle & van Dam, 2003). Across the phylogeny, plants possess a variety of secretory structures and often invest heavily in exudates, whether for solely defensive functions, other functions entirely, or both.

III. DEFENSIVE ROLE OF EXUDATES

The exudates of many plants have proven chemically mediated resistance functions (Table 1). Ernst Stahl, in one of the first experimental tests of plant chemical defences, found that acid droplets secreted from trichomes of several genera of Onagraceae completely deterred snails (Hartmann, 2008), although later investigations on the same plants did not recognize this class of defenses (Johnson *et al.*, 2014). While the exact mode of action – and indeed the chemicals responsible – have not been identified in most systems, in some they have been characterized in fine detail.

Chemicals in exudates can act directly on a herbivore in various ways, including morbidity (e.g. van Dam & Hare, 1998*a*), mortality (e.g. Gerhold, Craig & Mumma, 1984), decreased settlement likelihood (e.g. Ranger & Hower, 2002), reduced feeding (e.g. Shade, Thompson & Campbell, 1975) and interference with digestion (e.g. McLean *et al.*, 2009). They can also act indirectly through a third organism. Exudates of tobacco eaten by caterpillars degrade during digestion and the resultant chemicals recruit predatory ants to the caterpillars (Weinhold & Baldwin, 2011). Similarly, epicuticular waxes of *Brassica* spp. (Brassicaceae) contain compounds that trigger germination of an entomopathogenic fungus that attacks a beetle herbivore (Inyang *et al.*, 1999). While most studied examples of defensive chemicals are constitutive, concentrations of several exuded flavonols in tobacco increased after insect feeding (Roda *et al.*, 2003), indicating an induced defence.

Chemicals in exudates directly reduce pathogen infection through a variety of mechanisms, including inhibiting germination of pathogenic spores (Shepherd *et al.*, 2005) and reducing mycelial growth (Lira-Saldivar *et al.*, 2006). Defence against pathogens can also occur from indirect interactions. For example EFNs on several *Viburnum* species (Adoxaceae) attract mycophagous mites (Weber *et al.*, 2012), which consume fungal pathogens (e.g. Norton *et al.*, 2000). Delgado *et al.* (2011) hypothesize that promotion of mutualistic fungi living on EFN exudates promotes competitive dominance of these species over pathogenic fungi also on the phylloplane. Inhibition of competitors occurs through the action of exudates as well, either directly as an allelochemical by reducing the growth or germination of neighbouring plants (e.g. Kato-Noguchi *et al.*, 2002) or indirectly through mutualistic partners (e.g. ants attracted to EFNs clip back neighbouring plants; Davidson, Longino & Snelling, 1988). An elegant experiment by Smith *et al.* (2006) demonstrated that chemicals secreted by algae indirectly caused mortality of corals (competitors for space in reefs) through microbial activity, as antibiotics eliminated these effects. Table 1 includes these and many other examples of resistance functions of exudates from widespread taxa such as ferns, angiosperms and algae.

IV. WHY DIFFERENTIATE INTERNAL AND EXTERNAL CHEMICAL DEFENCES?

Chemical defences secreted onto plant surfaces as liquids or solids (external chemical defences – ECDs) may have different characteristics than those inside plant tissues (internal chemical defences – ICDs) and volatiles released into the environment. Volatiles are already treated separately in the literature and several comprehensive, informative reviews are available (e.g. Dudareva *et al.*, 2006), therefore, they are not included herein. Defences retained in plant tissues differ in specific location as well. For instance the same chemical in a root and a leaf will have different interactions with other organisms and the environment. At a finer scale, chemicals in intercellular spaces likely differ characteristically from those in vacuoles and other locations. A systematic review of ICD location and ecological and evolutionary consequences is beyond the scope of this paper. Instead, herein I will focus on the ecological characteristics of ECDs, using ICDs (the broad group) as a comparison when necessary, as the two have not been separated previously. A set of five fundamental characteristics differentiates ECDs from ICDs: (1) they are in direct contact with the abiotic environment; (2) they are not in direct contact with plant tissues apart from the cuticle; (3) they are first contacted by the vast majority of interacting organisms; (4) they may contact more than just the feeding and digestive parts of interacting organisms; (5) they are secreted from specialized structures or cells (or derived from a secretion thereof).

ECDs and ICDs may differ at the scale of a single compound(s) secreted – i.e. its physiological or ecological activity may differ depending on whether it is outside or inside a plant. Certain chemicals may fall completely on one end of this spectrum. For instance, some glandular trichomes synthesize certain defensive chemicals just prior to secretion (e.g. Shepherd *et al.*, 2005); others are retained completely in vacuoles, intracellular spaces or a myriad of other intra-tissue locations. For chemicals solely on either end of the spectrum, the difference in activity might be ecologically irrelevant, yet the location is still extremely important in these systems in order properly to consider ecological relationships and to design informative experiments. Other chemicals may be intermediate between these extremes, synthesized in or

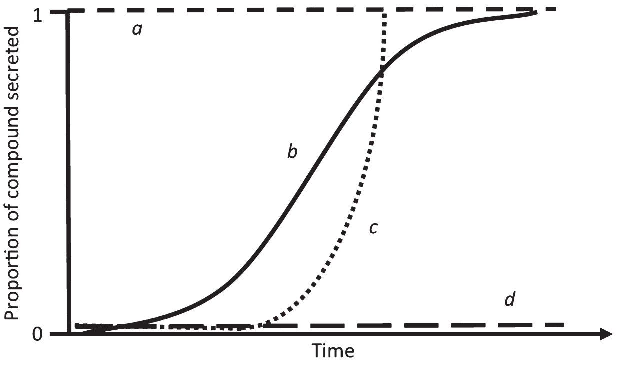

Fig. 1. Hypothesized allocation patterns of compounds externally over time. Line *a* represents a compound synthesized at the point of secretion; *b* is a compound synthesized internally, then moved into secretory structures and secreted; *c* is a pseudo-external chemical defence (ECD), secreted following a mechanical (or other) stimulus; and *d* is an internally synthesized and sequestered compound.

taken up by leaf, root or stem tissues then transported partially or completely by secretory structures to aerial or belowground plant surfaces (e.g. NaCl; Newbery, 1980). For these examples, only the compound outside the plant cuticle fulfills criterion 2 and thus can be considered an ECD. Comparisons of activity at both locations for these chemicals could be extremely informative; the plant may balance the costs and benefits of the chemical at each location given the available environmental information (abiotic conditions, herbivore cues, etc.).

At a broader level, with knowledge of ECD–ICD activity differences, patterns of investment at a leaf or plant level can be informative physiologically, evolutionarily and ecologically, especially with comparative methods. ‘Investment’ can be measured in different ways, i.e. allocation patterns of a single compound, a suite of compounds in a medium (e.g. resins), or total exudate production. Allocation may change over time, ontogeny, or space (e.g. an environmental or biotic gradient) producing shapes characteristic of different ECD strategies (Fig. 1), which may be ecologically informative. This distinction may be entirely binary – i.e. a chemical is either an ECD or an ICD (Fig. 1: lines *a*, *d*) – or exhibit a gradient of ‘externality’ (Fig. 1: *b*, *c*). In those cases, whether the compound is in tissues or on surfaces will result in different physiological roles, costs and interactions with other organisms because of the characteristics listed above.

The definition of an ECD as ‘a defensive chemical on a plant surface’ has potential pitfalls. Differentiating ECDs from external physical (mechanical) defences may be difficult. For instance, a glandular trichome could itself physically deter feeding and additionally deter feeding as a result of its distasteful or toxic exudates. Further, through emergent chemical properties (e.g. stickiness) an exudate may physically impede insects (e.g. Krimmel & Pearse, 2013). Where does the internal environment end and the external begin? Plant cuticular waxes lie outside the cell walls of epidermal cells, yet they form the leaf surface as we, and most other organisms, perceive it. Therefore, I here consider epicuticular waxes and all other epicuticular compounds as ECDs (if defensive), but cuticular waxes and compounds within and beneath the cuticle as internal. Lending support to this dichotomy, new methods allow independent study of these two classes, which often differ substantially in chemical and physical properties (Müller & Riederer, 2005). The outside of a root may be difficult to define as well; root exudates contain a diversity of chemicals as well as sloughed-off cells and mucilage (Dennis *et al.*, 2010) and while new techniques now allow detailed study of rhizodeposits, further methodological developments are needed (Bais *et al.*, 2006).

Certain glands or ducts accumulate compounds internally, then rupture and spread compounds on the plant surface when triggered (e.g. latex: Hagel, Yeung & Facchini, 2008; Agrawal & Konno, 2009; Konno, 2011). Prior to rupture, these exudates violate characteristics 1 (not in contact with abiotic environment), 3 (not in contact with interacting organisms), 4 (again, not in contact with interacting organisms), and sometimes 2 (in contact with plant tissues), although after rupture they meet all criteria of an ECD. I term this group ‘pseudo-ECDs’ as after secretion they are functionally and ecologically equivalent to ‘true’ ECDs (*c* in Fig. 1).

This review considers solely the defensive functions of exudates (Table 1); their many other well-known functions are referenced here sparingly. Herein, rather than using the narrow sense of Karban & Myers (1989), where a positive fitness benefit differentiates a defensive from a resistance trait, I consider defensive traits in a broad sense as those that reduce damage from herbivores (e.g. insects, mammals), infection by pathogens (e.g. fungi, bacteria), or negative effects of competitors (allelopathy) (Wink, 2010); a fitness benefit to the plant need not occur or be measured. Many excellent and illustrative studies on ECDs include no measurements of plant fitness.

Few, if any, plants solely possess ECDs or ICDs; most have both. This hypothesis does not preclude or replace existing plant defence theories, it merely suggests an under-studied – and sometimes informative – trait to consider in testing theory both experimentally and observationally. The defensive traits of plants have evolved against herbivores, pathogens, and competitors across time and space. No one of these factors acts in isolation (Berenbaum, 1995; Agrawal, 2007, 2011). Thus, it is unsurprising that some plants have more than one type of ECD (e.g. *Chaemaecrista dentata*: Meira, Francino & Ascensão, 2014; *Betula* spp.: several references in Table 1). Because of hard-to-predict antagonistic and synergistic effects of chemicals in defence (and physiological) functions there is little *a priori* reason to assume that ECDs directly trade-off with ICDs in any system (see Agrawal, 2011). Although many compounds are both internal and external within the same plant, to the best of my knowledge activity differences between these two locations have never been tested explicitly in any system. Therefore, this synthesis focuses on the activity of ECDs in light of these hypothesized characteristics, which have predicted costs and benefits as detailed in Table 2. Below, I detail the ecological and evolutionary consequences of each characteristic, briefly discuss the evolution of defensive secretions and conclude by suggesting ways to integrate this axis into current plant defence theory.

(1) Characteristic 1: ECDs are in direct contact with the environment

Chemicals on aerial plant surfaces lack the protection that a cuticular layer and other tissues provide; a parallel case occurs belowground around roots. The external location may make them more vulnerable to removal or degradation, either lessening their effectiveness due to reducing concentrations or increasing their effectiveness through chemical reactions or removal to other locations. Water is the most obvious ECD-removal agent; many exudates dissolve in water and wash off plants. This may have consequences for the plant; simulated rain on the ECD-producing *Atriplex rosea* (Chenopodiaceae) increased chewing herbivory compared to control plants that received the same amount of water at the base and controls that received no water (E. F. LoPresti, unpublished data). Rainfall may physically break down non-soluble exudates; hydrophobic epicuticular waxes degraded with small amounts of simulated rain (Baker & Hunt, 1986). Perhaps intuitively, seaweeds with external chemicals have evolved methods of retaining them on their surfaces despite submersion and water movement (e.g. Lane *et al.*, 2009). Root exudates are liable to breakdown by microorganisms that use them as an energy source (e.g. Gimsing *et al.*, 2009), a situation that may also occur on aboveground plant surfaces. Natural or anthropogenically elevated atmospheric chemicals may chemically alter exudates (e.g. sulfur dioxide; Cape & Fowler, 1981). Gonzalez-Coloma, Wisdom & Rundel (1988) demonstrated that a defensive phenolic in creosote bush (*Larrea tridentata*) resins is degraded by ozone and the resulting lower concentrations of this compound increased plant palatability to insect herbivores.

By contrast, removal of chemicals can also stimulate plant defences. Several studies have found that rainfall moves exudates from leaf surfaces to the soil where they inhibit germination of competitors (Funke, 1943; Star, 1980; Tanrisever, Fischer & Williamson, 1988; Stephanou & Manetas, 1995). These forms of degradation or removal, whether positive or negative for the plant, probably do not affect ICDs, which, given their cellular location (e.g. in vacuoles, intracellular spaces, etc.), are at least partially protected from these forces by the plant cuticle.

The external environment differs both at a microscale (e.g. driven by boundary flow), macroscale (e.g. regional climates) and all scales in between. Regional differences in climate may create patterns in ECDs, either by selecting for or against certain ECDs (resulting in local adaptation) or filtering the species which can occur in a specific region. Many workers have noted the prevalence of exudates in arid areas (e.g. Dell & McComb, 1979). Williams *et al.* (1997) surveyed the genus *Pelargonium* (Geraniaceae) and found flavonoid exudates only in species inhabiting dry areas. Whether exudates are produced as readily, but removed and thus not noted, in wetter areas remains an open question. However, several tarweed species (Asteraceae) of California have two phenologically distinct phenotypes, a mostly eglandular phenotype with little exudate production, which grows during the spring season (when rains are occasional), and a glandular phenotype producing copious defensive exudates, which grows during the dry summer (Carlquist, Baldwin & Carr, 2003; Krimmel & Pearse, 2013, 2014). These phenotypes from the same population differ in exudate production when grown under common conditions (W. Krimmel & I. Pearse, personal communication) and exudates wash off partially with water (E. F. LoPresti & W. Krimmel, personal observations). Therefore, this phenotypic dimorphism may be environmentally driven through selection on defensive function; experiments on this hypothesis are in progress. Susceptibility to degradation or removal by external forces may be the most important difference between ECDs and ICDs. More work is needed to determine the role of the interaction between ECDs and the environment in shaping plant distributions, allocation strategies of exudates, and life-history evolution.

(2) Characteristic 2: ECDs are not in direct contact with plant tissues apart from the cuticle

Chemicals external to the plant may no longer be directly involved in metabolic processes, yet they also may not harm the plant. Autotoxicity – the toxicity of a compound to the plant producing it (Schoonhoven *et al.*, 2005) – may force localization to particular areas or limit production of defensive chemicals (e.g. the within-tissue separation of precursors to hydrogen cyanide: Gleadow & Woodrow, 2002). Certain defences may be particularly costly because of this limitation (Baldwin & Callahan, 1993; Agrawal, Gorski & Tallamy, 1999), although synthesis away from photosynthetic or otherwise physiologically important tissues may minimize these costs (Wagner, 1991; Duke, 1994). In a well-characterized example, Sirikantaramas *et al.* (2005) demonstrated that cannabinoids were toxic both to herbivores and to *Cannabis sativa* (Cannabaceae) itself. However, the synthesis of these compounds in glandular trichomes and their subsequent secretion minimized or eliminated contact between vulnerable tissues and the compounds, a result also found in *Artemisia annua* (Asteraceae) (Duke, Paul & Elsohly, 1994). Other compounds present in exudates may reduce osmotic balance or interfere with cellular activities. Inorganic defensive compounds such as salts and heavy metals are not technically ‘autotoxic’, as they are not synthesized in the plant, yet can be toxic to plants and are common in exudates (see Table 1). By avoiding autotoxicity through secretion of an ECD, a plant may bypass this cost, yet increase the potential for degradation or removal of the chemical as an exudate, a potential trade-off.

Table 2. Potential advantages and disadvantages of external (ECDs) and internal chemical defences (ICDs) stemming from the five characteristics of ECDs and ICDs defined in this review. This list is not exhaustive but is intended to be a starting point for future explorations and hypotheses. Few, if any of these hypothesized differences have been rigorously tested across taxa

	Comparison with the same compound as an ICD	
ECD characteristic	Hypothesized benefits	Hypothesized costs
(1) In direct contact with the environment	Movement of chemical to surrounding areas	Removal or degradation of a defencive compound by water, wind, atmospheric chemicals, etc., lessening the effectiveness of defence
	No dilution effect of volume of plant tissues; less compound necessary for a given deterrent or allelopathic concentration	
	Unavoidable by surface-feeding herbivore, even if all tissue layers not consumed	Increased susceptibility to herbivores which do not feed at plant surface (e.g. homoptera or leaf miners)
(2) Not in direct contact with plant tissues apart from the cuticle	Avoidance of autotoxicity	Loss of simultaneous physiological functions
	Decoupling of tissue defences from external defences; potentially allowing ordered synergy between ECDs and ICDs	—
(3) First contacted by the vast majority of interacting organisms	Repellence of herbivores without damage to plant	Repellence of non-herbivores (e.g. natural enemies)
	Immediate repellence	—
(4) May contact more than just the feeding and digestive parts of interacting organisms	Broader activity (e.g. action on feet, spiracles or antennae, not just digestive tract or mouthparts)	The defence may not reach highest activity areas, especially in selective feeders
		May deter non-herbivores (e.g. beneficial natural enemies)
(5) Secreted from specialized structures or cells (or derived from a secretion thereof)	Ability to localize chemical externally	Active secretion can be costly
		Evolutionarily constrained within or amongst lineages
		Ontogenetically constrained
		Localization of chemical constrained
		Upkeep of construction costly

The role of autotoxicity in localization of chemical defences merits further attention, as it could be a potent selective force in the evolution of ECDs and secretory structures in general.

(3) Characteristics 3 and 4: ECDs are first contacted by the vast majority of interacting organisms and in contact with more than just their feeding and digestive parts

Compounds on plant surfaces are contacted by nearly every organism interacting with the plant; these compounds may mediate interactions before any feeding or other physical damage to the plant can occur. This relationship has been investigated thoroughly in two classes of ECDs – sticky compounds secreted from glandular trichomes and epicuticular waxes. Sticky compounds on plant surfaces can directly act on organisms, either herbivores or their predators, with toxic effects (e.g. Sutherst, Jones & Schnitzerling, 1982). This can, in some contexts, prevent potential herbivory; sticky morphs of *Datura wrightii* (Solanaceae) received less damage from generalist herbivores (Elle *et al.*, 1999), but certain sticky-plant-specialist herbivores caused higher damage to sticky morphs (e.g. Hare *et al.*, 2003). The role of epicuticular waxes in interactions with insect herbivores was reviewed by Eigenbrode & Espelie (1995), who found that the benefit of epicuticular waxes (comparing waxy to ‘glossy’ phenotypes within a species) was context dependent; some studies found a defensive function of epicuticular waxes, others found the opposite. Importantly, the literature on both epicuticular waxes and stickiness has shown that immediate contact and contact with all species, not just antagonists, can be either beneficial or detrimental to the plant (see also a parallel case in Eisner, Eisner & Hoebeke, 1998). These ECD characteristics and the community of interacting organisms involved determine whether the plant incurs a benefit or cost in a given context.

(4) Characteristic 5: secreted from specialized structures or cells (or derived from a secretion thereof)

Exudates are not secreted by every cell within a plant; the cell must be located on the outside of a plant and must have some secretory capacity – either being specialized (e.g. root cap cell) or part of a specialized structure (e.g. a salt gland) (see Section II and Table 1). The location of these cells in time and space determines the distribution of exudates on a plant. This distribution may be shaped by (*i*) selection for functional utility, (*ii*) developmental constraints on secretory structures or (*iii*) movement or degradation of exudates (see characteristic 1). Many exudates are more prevalent on the undersides of leaves, consistent with avoidance of environmental removal or degradation or developmental constraints. Examples include defensive salt bladders in chenopods (LoPresti, 2014), EFNs in *Viburnum* and other taxa (Weber *et al.*, 2012; Weber & Keeler, 2013), herbivore-deterring salt deposits in *Avicennia marina* mangroves (Acanthaceae/Verbenaceae) (Newbery, 1980; Gilbert, Mejía-Chang & Rojas, 2002) and antimicrobial or toxic exudates of ferns (Wollenweber, 1978; Stipanovic, 1983; Wollenweber *et al.*, 1998). Colleters of many families are usually located on uppersides of leaves, however during the bud phase, when most colleters are secretory, these surfaces are on the interior of the bud (Thomas, 1991).

Ontogenetically, exudates are often expressed most prominently on young leaves and other plant parts (e.g. Bentley, 1977; Osmond *et al.*, 1980; Bryant, 1981; Schirmer & Breckle, 1982; Tomás-Barberán *et al.*, 1988; Thomas, 1991; Hare *et al.*, 2003; LoPresti, 2014). Rhoades (1977) detailed insect attacks on older creosotebush (*Larrea* spp.: Zygophyllaceae) leaves; leaf expansion reduced the resinous coating per unit area during leaf ageing and increased palatability to herbivores (later work also highlighted the importance of environmental degradation of resins: see Gonzalez-Coloma *et al.*, 1988). By contrast, secretion from some structures, such as salt glands and hydathodes, is likely under stronger environmental than ontogenetic or temporal control and continues throughout leaf life (Fahn, 1979). These patterns could be investigated in ECD systems to determine whether this pattern of secretion is adaptive in light of the phenology of natural enemies and other selective forces or whether it is environmentally, spatially, ontogenetically or phenologically constrained. Although separation of these factors may be difficult, some approaches could differentiate the cause of an observed pattern. Reciprocal transplants and common garden experiments, long staples of comparative plant biology, could begin to answer whether environmental factors account for differences in exudate production among populations. Developmental studies of structures producing exudates or investigations into the production pathways of specific secondary metabolites have potential to elucidate constraints on production; especially when used in a comparative phylogenetic study (Agrawal, 2011). Independent convergent examples of ECD production or localization correlating with a given environmental agent could support a role for exudate removal as a selective force on ECD production. Conversely, if environmental removal and herbivore, pathogen and competitor phenology do not explain patterns of allocation, constraints – or other pleitropic functions of the exudate – may drive the observed patterns.

V. THE EVOLUTION OF DEFENSIVE CHEMICAL SECRETION

Many secretory structures in plants may have evolved for physiological functions and later been coopted or exapted to defence. Secretion usually has at least one energy-requiring step including synthesis of the exudate, construction and maintenance of secretory structures, or secretion itself (Fahn, 1979). Autotoxicity of metabolic byproducts may have selected for the excretion of any phytotoxic or more broadly biotoxic compounds; because of intrinsic phytotoxic or biotoxic effects, these might be immediately suited for a defensive function and could be further selected upon [suggested for the evolution of allelopathy by Leflaive & Ten-Hage (2007)]. Plants that secrete heavy metals provide a similar case. Salt marsh grasses *Spartina alterniflora* and *Phragmites australis* secrete Na, Cl, Cu, Pb, Cr and Zn through salt glands (Burke, Weis & Weis, 2000), lactifers of *Sebertia accuminata* (Sapotaceae) accumulate defensive Ni, colleters of several plants secrete Zn, Cu and Fe (Thomas & Dave, 1989), and *Avicennia marina* mangroves secrete Na, Zn and Cu (MacFarlane & Burchett, 2000). Most of these compounds can be toxic to plants at high concentrations (e.g. Weis & Weis, 2004) and are toxic (e.g. Coleman, Boyd & Eubanks, 2005) or deterrent to insect herbivores (e.g. Leuck, Wiseman & McMillan, 1974; Sagner *et al.*, 1998). It is also possible for plants to secrete compounds deleterious to herbivores together with non-toxic compounds that the plant needs to secrete to maintain osmotic or ionic balance (e.g. oxylates as cations for Na^+ in salt bladders of *Atriplex* spp.: Osmond *et al.*, 1980). In this case, the selective environment likely changes because selection by herbivores, pathogens, or competitors promotes evolution of the defensive properties of the exudate. This form of 'incidental' defence, co-opted from a physiological process, may be common in the defensive function and evolution of such structures as salt glands, hydathodes, colleters and salt bladders.

Other secretory structures probably evolved for defence, such as glandular trichomes (Duke, 1994), lactifers and resin glands (Farrell, Dussourd & Mitter, 1991) and possibly EFNs as well (see Weber & Keeler, 2013). Functional pleiotropy may also create a suite of benefits that outweigh structural, synthesis or secretory costs of external chemicals. Structures that evolved for secreting compounds useful in protection from UV radiation, reducing leaf water loss or leaf temperature, maintaining osmotic balance or water potential and that are immediately beneficial for defence might provide examples. The evolution of these unique defensive characteristics may enhance lineage diversification rates; Farrell *et al.* (1991) provide compelling evidence for increased diversification after independent evolution of lactifers and resin glands (functionally identical) in 13 out of 16 sister-group comparisons. Using this phylogenetic approach has the potential to elucidate evolutionary patterns in structures secreting ECDs and compounds involved in ECDs.

VI. INTEGRATION WITH PLANT DEFENCE THEORY

Researchers have long sought to explain the diversity, effectiveness and patterns of investment in secondary metabolites (and other defences) at several levels of organization (cell, tissue, plant, community). This approach has been hindered by hypotheses without clearly testable predictions and misinterpretations of existing hypotheses (Stamp, 2003). Plant defence depends on a complex combination of chemical, morphological, life-history (e.g. phenology, apparency) and physiological traits that can be difficult to untangle (although meta-analyses hold promise to parse these out broadly, e.g. Carmona, Lajeunesse & Johnson, 2011). We already consider chemical defences along at least three trait axes: qualitative *versus* quantitative (Feeny, 1976), induced *versus* constitutive (Karban & Baldwin, 1997) and when they are produced, ontogenetically or seasonally. The location of the compound, external or internal, represents another ecologically important axis (either as presence/absence or proportional investment). This axis can be incorporated into plant defence theory and may be useful in testing predictions of existing theory.

Optimal defence theory posits that plants will allocate defences to balance benefits and costs of defence and maximize fitness (Rhoades & Cates, 1976; Stamp, 2003). This hypothesis assumes a cost to the plant of creating any defence; expressed as a trade-off between growth or reproduction and defences. Costs of defence are often difficult to assess and fraught with confounding factors, for example recycling of nutrients (Stamp, 2003); in the case of exudates, certain costs are known (for instance active secretion), others can be quantified (loss of exudates over time) and others can be assumed to be minimal (e.g. autotoxicity). Furthermore, benefits of the chemical are easily assessed experimentally as many ECDs can be washed off without damage to the plant; this manipulation also allows assessment of any ecological costs such as pollinator or predator deterrence (e.g. Eisner *et al.*, 1998). Manipulation of concentrations of defensive chemicals without having to use genotypes that differ in these concentrations (and may also differ in other important traits) is very difficult in most terrestrial plants, although well established in marine algae (e.g. Hay, Fenical & Gustafson, 1987). A thin coating of commercial gelatin does not deter the generalist herbivores *Diabrotica undecimpunctata* (Coleoptera: Chrysomelidae) or *Heliothis virescens* (Lepidoptera: Noctuidae) and can be applied experimentally to create 'exudates' with chemicals in varying concentrations (LoPresti, personal observation). Supplementing or removing these chemicals from plant surfaces across different genotypes, species, populations, environmental gradients and different herbivores will allow extremely powerful comparisons of specific activity levels in conjunction with other varying defensive traits; furthermore it can be done in the field *in situ* on naturally occurring populations [as demonstrated in marine algae by Hay *et al.* (1987)].

Rhoades & Cates (1976) original formulation of the optimal defence hypothesis carefully detailed the costs of autotoxicity, including increased susceptibility of growing tissues to broad-spectrum (digestability-reducing) toxins (e.g. quantitative defences; Feeny, 1976). They contrast this with specialized toxins, qualitative defences, which often have modes of action that are insect or animal specific. Despite their compelling case, this specific prediction is rarely mentioned in later literature on the optimal defence hypothesis (e.g. not mentioned as a potential cost in Stamp, 2003) and remains untested. Many buds and young leaves of long-lived species have defensive resins that are probably digestibility-reducing and likely autotoxic [e.g. *Larrea* spp. (Rhoades & Cates, 1976; Rhoades, 1977); *Betula* spp. (Table 1)]; manipulation of plants with ECDs may be ideally suited to investigate this rarely tested prediction.

Plant apparency to herbivores may also determine investment and type of defences (Feeny, 1976; Rhoades & Cates, 1976), and is often considered as part of the optimal defence hypothesis (e.g. Stamp, 2003). Specifically, Rhoades & Cates (1976) predict that plants that are easily located by herbivores should invest in broadly effective defences (quantitative: Feeny, 1976), whereas less-easily found plants should invest in more specialized defences (qualitative: Feeny, 1976). Strauss *et al.* (in press) assessed apparency of herbaceous vegetation in barren areas, thus avoiding the confounding life-history correlates of woody and herbaceous vegetation, a past problem in testing this hypothesis (Stamp, 2003). They found that most unpalatable species in the suite of apparent plants in California grasslands and serpentine barrens have exudates. The authors focused on the volatile aspects of these exudates (and potential chemical aposematism), but exudates of several of these species (e.g. *Trichostema* spp., *Madia* spp.) are ECDs as well (E. F. LoPresti & B. A. Krimmel, unpublished data). Whether ECD plants are generally more apparent – or whether this is simply a function of the particular system studied – and whether defences within ECDs are generally quantitative should be examined in more depth.

At a within-plant level, allocation to defences also should be adaptive; 'within an organism, defenses are allocated in proportion to risk of the plant part and value of it to plant fitness, and in inverse proportion to cost of defense' (Stamp, 2003, p. 26). While intuitively appealing, testing this hypothesis presents many problems. Most plants show extreme differences in secondary metabolite chemistry among tissues (e.g. humans can eat tubers, but not the poisonous leaves, of the potato plant); yet because it is difficult to quantify costs and probability of attack is an elusive and often variable quantity across time and space, explicit tests of this hypothesis are elusive. Despite their non-uniform distribution on plants, and the ease with which they can be manipulated, ECDs may require specialized structures which are often constrained in location, thus the assumption as stated by Stamp (2003) that defences can occur anywhere that the plant needs them is contravened.

Herms & Mattson (1992) formalized the growth–differentiation balance hypothesis (GBDH), which posits that plants will allocate resources to either growth or differentiated tissue (i.e. not new tissue; all defensive secondary metabolism is differentiation), and that this balance is driven by abiotic factors. Specifically, they note that active growth requires more nutrients and water than differentiation processes, whereas differentiation processes, especially secondary metabolite production, are often not limited by nutrients and water, and thus excess photosynthate can be directed towards the production of these compounds when nutrients are limiting. As plants in natural environments are usually more limited by nutrients, water or temperature than by CO_2, differentiation processes, especially secondary metabolite production, will utilize the available photosynthate. Therefore, when a resource is low enough to slow growth but not photosynthesis, differentiation processes will predominate and when nutrients and water are in abundance, growth will predominate. Thus, a peak in defensive compound levels would be expected at intermediate nutrient levels (Herms & Mattson, 1992; Stamp, 2003). All differentiated tissue in a plant includes cell specialization after enlargement (Herms & Mattson, 1992); thus any test of this hypothesis must employ a proxy for this investment. Examples in Stamp's (2003) review focus on single secondary metabolites (e.g. terpenes), but exudates may be a better proxy for such defensively differentiated investment. Indeed, Herms & Mattson (1992) detail the functional pleiotropy of many secondary metabolites; not focusing exclusively on defence, and thus the predictions of their original formulation may be especially applicable to pleiotropic exudates.

The physiological and ecological factors outlined in the GDBH predict a continuum of correlated life-history traits along an axis from complete investment in growth to complete investment in differentiation (Herms & Mattson, 1992). Obviously the extremes do not exist commonly (except perhaps in senescing annual plants), but in theory each plant has a position on this axis that can be quantified (relative to other plants) and thus can be assigned as a 'growth-dominated' or 'differentiation-dominated' strategy. The ruderal and competitive strategies in Grime's (1977) classification of plant life histories correspond to a growth-dominated strategy; whereas his 'stress-tolerant' strategy corresponds to a differentiation-dominated strategy. Given that exudates are secondary metabolites, they should be an indicator of a differentiation-dominated or stress-tolerant strategy. This prediction agrees with the life-history dichotomy within populations of California tarweeds (Section IV.1); the fast-growing ruderal early-season phenotype produces almost no exudates, whereas the slow-growing late-season – when water is limiting – phenotype produces copious exudates. Harsh serpentine soils, both water and nutrient limited, have a preponderance of slow-growing plants with copious exudates (LoPresti, personal observation; Strauss *et al.*, in press).

Agrawal & Fishbein (2006) suggest that convergent defensive syndromes exist in plants and quantify variation in a psuedo-ECD as a relevant trait. They found high variation in latex production between species of milkweeds (*Asclepias*: Apocyanaceae). They termed the defensive syndrome of species that converged upon high levels of latex and trichome production 'nutrition and defence'; by contrast their 'tolerance/escape' and 'low nutritional quality' strategies did not invest heavily in latex. We cannot directly compare these syndromes to the life-history strategies of Grime (1977) or Herms & Mattson (1992) as their phenotype in a common garden experiment in Canada may differ from the phenotype expressed in their natural range. But their findings do support the prediction that investment in exudates correlates with other defensive strategies (e.g. trichomes) and likely does not occur in either fast-growing or extremely slow-growing species. The ease of quantification and manipulation of ECDs means that they represent a potentially useful tool to test predictions of a wide variety of plant defence theory.

VII. FUTURE DIRECTIONS

In any particular system, work should be directed to understanding the full functions of exudates physiologically and ecologically [as exudates can be functionally pleiotropic (see Section V), with defence only one of the possible functions]. Understanding the trait in question and the selection shaping this one function (external defence) requires examination of a suite of traits, including localization of chemicals, ontogeny, development, physiology and natural interactions with other organisms and its specific abiotic environment. Some exudates with defensive functions (ECDs) have been tested on herbivores, others on pathogens and others on competitors; none to my knowledge has been tested on all three – a necessity to truly understand the selective forces acting on the defensive traits associated with an ECD (e.g. exudate composition, phenology, investment). Certain exudates have been tested for degradation due to abiotic and biotic factors. Very few have been tested for autotoxicity; there are no comparisons of ECDs and ICDs in this respect. Exudates can serve many functions that internal chemicals cannot, including UV blocking, changing the wetness potential of plant surfaces, changing reflectance of light and decreasing water loss through surfaces. Similarly, ICDs may serve internal metabolic roles that ECDs cannot; this is increasingly recognized for 'secondary' metabolites (see Hartmann, 2007).

Future work using a comparative approach (Agrawal, 2007, 2011) to examine ECDs could focus on several questions. Does this strategy arise repeatedly in specific environments or clades? Does it speed up diversification rate and allow radiation of plants? *Atriplex* and *Chenopodium* are the most speciose genera of Chenopodiaceae; was their 'salt' bladder system (an ECD secretory tissue) a key innovation in these worldwide radiations? Are specific ECD constituent chemicals evolutionarily labile or fixed? Do herbivores, especially specialized insects, adapt to and radiate on plants with ECDs? Do certain ECDs act synergistically with other traits and evolve together (e.g. mite domatia and EFNs; Weber *et al.*, 2012)? The recognition of ECDs and their unique characteristics may allow new tests of plant defence theory and reinforce the pleas of Stipanovic (1983) and Shroff *et al.* (2008) to pay attention to within-plant localization of defences.

VIII. CONCLUSIONS

(1) Exudates are common across plants: epicuticular waxes, glandular trichomes, root exudates and extra-floral nectaries are found in thousands of plant species.

(2) Many exudates are defensive, directly and indirectly, against herbivores, pathogens and competitors; these are termed external chemical defences (ECDs) to separate them from internal chemical defences (ICDs).

(3) Two axes of ECDs and ICDs are informative: (*i*) activity of a compound within or outside of plant tissues, and (*ii*) relative investment in internal and external compounds.

(4) Many ECDs are removed or degraded by a variety of biotic and abiotic forces because of their external location.

(5) Many plants with exudates are found in regions with low potential for environmental removal and ECDs are often found in protected locations on the plant.

(6) Many ECDs are ontogenetically useful or ontogenetically constrained, often expressed most highly in young plants or tissues.

(7) The ease of manipulating ECDs may allow powerful tests of plant defence theory and activity of individual chemicals *in situ*.

(8) Future work should examine patterns in evolution, distribution and within-plant localization of ECDs.

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