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Original Article

Defence syndromes in lodgepole – whitebark pine ecosystems relate to degree of historical exposure to mountain pine beetles

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ABSTRACT

Warming climate is allowing tree-killing bark beetles to expand their ranges and access naïve and semi-naïve conifers. Conifers respond to attack using complex mixtures of chemical defences that can impede beetle success, but beetles exploit some compounds for host location and communication. Outcomes of changing relationships will depend on concentrations and compositions of multiple host compounds, which are largely unknown. We analysed constitutive and induced chemistries of *Dendroctonus ponderosae*'s primary historical host, *Pinus contorta*, and *Pinus albicaulis*, a high-elevation species whose encounters with this beetle are transitioning from intermittent to continuous. We quantified multiple classes of terpenes, phenolics, carbohydrates and minerals. *Pinus contorta* had higher constitutive allocation to, and generally stronger inducibility of, compounds that resist these beetle–fungal complexes. *Pinus albicaulis* contained higher proportions of specific monoterpenes that enhance pheromone communication, and lower induction of pheromone inhibitors. Induced *P. contorta* increased insecticidal and fungicidal compounds simultaneously, whereas *P. albicaulis* responses against these agents were inverse. Induced terpene accumulation was accompanied by decreased non-structural carbohydrates, primarily sugars, in *P. contorta*, but not *P. albicaulis*, which contained primarily starches. These results show some host species with continuous exposure to bark beetles have more thoroughly integrated defence syndromes than less-continuously exposed host species.

Key-words: Bark beetles; carbohydrates; climate change; conifers; defence; fungi; induction; ophiostomatoid; phenolics; terpenes.

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INTRODUCTION

Herbivorous insects can rapidly expand geographic ranges with increasing temperatures, due to their exothermic physiology, short generation times and high mobility (Parmesan 2006). As insects enter new regions, or survive more frequently in intermittently accessed areas, relationships with newly encountered plant species and populations will provide either barriers or springboards. In some cases, lack of evolutionary relationships may preclude an insect's ability to locate a plant, or tolerate its chemistry, while in others, less-pronounced coevolved defences may yield widespread plant mortality (Erbilgin *et al.* 2014; Bentz *et al.* 2016; Burke & Carroll 2016). We currently lack a predictive framework for addressing these challenges, in part because empirical tests typically focus on one or two groups of compounds, or conversely on a very broad category of compounds within which bioactivities are highly variable (Raguso *et al.* 2015).

Plants often resist attack through integrated, multipartite defences (Agrawal & Fishbein 2006; Mithöfer & Boland 2012; Fürstenberg-Hägg *et al.* 2013). These mechanisms include both constitutive defences and induced traits elicited by the attacking agents (Karban *et al.* 1999; Underwood & Rausher 2002; Bonello *et al.* 2006; Heil & Bueno 2007; Pieterse *et al.* 2013). While some plants appear to rely on one or two defence compounds to resist attack, most species deploy mixtures of allelochemicals, which challenge the abilities of herbivores and their symbionts to tolerate or adapt to them (Whitehead & Bowers 2014, Raguso *et al.* 2015). Suites of traits that collectively minimize herbivory are termed 'plant defence syndromes' (Agrawal & Fishbein 2006). Within these syndromes, specific compounds can impede specific aspects of an herbivore's behaviour, development or symbioses. Plant defences are energetically and ecologically costly (Gershenzon 1994; Kessler 2015), so resources allocated to defence can detract from other important functions (Moreno *et al.* 2009). Over evolutionary time, plants appear to develop optimal strategies for balancing these trade-offs, based on their life history strategy, source–sink relationships, anatomical

architecture and herbivore pressure (Herms & Mattson 1992; Franceschi *et al.* 2005; Villari *et al.* 2014). We have little understanding, however, of how carbon allocation patterns, both between primary and secondary compound biosynthetic pathways and among diverse secondary compounds, that evolved under historical conditions (Strauss *et al.* 2002; Goodsman *et al.* 2013; Moreira *et al.* 2014), will protect plants as herbivores expand their geographic ranges with a warming climate (Erbilgin *et al.* 2017).

Bark beetles (Curculionidae, Scolytinae) are subcortically feeding herbivores and include some species whose successful development typically causes host death (Negron & Fettig 2014). Larvae feed in secondary phloem, a critical tissue for nutrient translocation. Adults emerge, disperse to locate and enter new trees, attract mates and oviposit. Beetles exploit some secondary chemicals as host-recognition cues, or as synergists and precursors of aggregation pheromones they employ to overwhelm tree defence by mass attack (Blomquist *et al.* 2010). Populations of some species undergo intermittent landscape-scale outbreaks, during which they kill millions of trees and alter key ecological processes (Kurz *et al.* 2008). During intervening endemic periods, these same species lack the critical population densities to overcome defences of healthy trees and instead restrict attacks to highly stressed individuals (Wallin & Raffa 2004; Bleiker *et al.* 2014). Stressed trees provide a marginal resource for reproduction, however, because they are relatively sparse, nutritionally suboptimal and laden with competing species (Powell *et al.* 2012). Bark beetles have close relationships with fungal symbionts, which can enhance larval nutrition or assist beetles in overcoming tree defence by functioning as cofactors (Klepzig & Six 2004; Hammerbacher *et al.* 2013).

Conifers respond to beetle attacks by exuding oleoresin and undergoing rapid induced responses at the attack site. Oleoresin contains multiple classes of compounds that can negatively affect beetle adults, brood and symbionts, and can also physically delay beetles while induced defences commence (Klepzig *et al.* 1996). Concentrations and relative proportions of various compounds change markedly in response to attack, reaching levels that can repel or kill beetles, and inhibit fungal growth and germination (Schiebe *et al.* 2012; Villari *et al.* 2012; Mason *et al.* 2015; Keefover-Ring *et al.* 2016). Various compounds have complementary activities, with each being particularly effective against different components of the beetle–microbial complex. Chemical defences of temperate conifers consist almost entirely of terpenes and phenolics. Among terpenes, monoterpenes have the strongest insecticidal activities, and high concentrations have been associated with increased tree survival (Zhao *et al.* 2010, 2011; Boone *et al.* 2011). Diterpenes have the strongest antifungal activity, while sesquiterpenes have no known activity against beetle–fungal complexes (Raffa *et al.* 2015a). Among phenolic groups, stilbenes typically have potent antifungal activity (Hart 1981; Evensen *et al.* 2000; Hammerbacher *et al.* 2013), and one phenylpropanoid inhibits beetle aggregation (Hayes & Strom 1994).

Mountain pine beetle, *Dendroctonus ponderosae* Hopkins, is a native North American species that undergoes some of the largest outbreaks of any forest insect (Bentz *et al.* 2010; Safranyik *et al.* 2010; Anderegg *et al.* 2015). This herbivore's host range includes approximately 11 of 16 pine species within its geographic range in the United States and Canada (and others in cut logs or late-stage outbreaks). (Wood 1982; Burns & Honkala 1990; Bentz *et al.* 2016). Its most common host is lodgepole pine, *Pinus contorta* Doug., which accounts for ~87% of areas affected (Meddens *et al.* 2012). Recent warming has allowed *D. ponderosae* to spread north and access and colonize *Pinus banksiana* Lamb. in Alberta, Canada (Cullingham *et al.* 2011; Erbilgin *et al.* 2014).

Rocky Mountain biomes show pronounced elevational gradients. Low- to mid-level elevations are dominated by *P. contorta*. High-elevation stands are dominated by five-needled pines, such as whitebark pine, *Pinus albicaulis* Engelm, a keystone species that plays critical roles in biodiversity, succession, soil quality and hydrology (Arno 1986; Tomback & Achuff 2010). *Pinus contorta* exhibits rapid growth and early reproduction, whereas *P. albicaulis* is relatively slow-growing, late-reproducing and long-lived (Hansen *et al.* 2016). Historically, *P. albicaulis* was only accessed by *D. ponderosae* during occasional, brief warm periods that permitted overwintering survival (Jewett *et al.* 2011, Dooley *et al.* 2015, Esch *et al.* 2016, Sidder *et al.* 2016). Beetle populations would diminish upon return to normal weather. In recent years, however, continuous warm temperatures have allowed successful reproduction, and shorter development times, over extended periods (Logan *et al.* 2003, 2010; Preisler *et al.* 2012; Lahr & Sala 2014). Models based on predicted temperature increases and beetle cold tolerance project most years will be environmentally suitable for overwintering survival across nearly all of the Greater Yellowstone Ecosystem by the end of this century (Buotte *et al.* 2016).

Our goals were to characterize and compare the phloem chemistries of *P. contorta* and *P. albicaulis* within the context of susceptibility to *D. ponderosae*. In particular, we aimed to (1) analyse the full range of secondary compounds present, including products of both terpene and phenolic pathways (McKay *et al.* 2003; Hamberger *et al.* 2011); (2) place special emphasis on secondary compound classes previously demonstrated to be toxic to *D. ponderosae* and its symbionts, and on allocation to specific compounds that influence beetle behaviour; (3) analyse both constitutive and induced tissues, to compare relative degrees of elicitation and its spatial scale; (4) quantify non-structural carbohydrates to compare energy storage strategies and evaluate potential allocation patterns and conversion to bioactive defence compounds; (5) quantify inorganic constituents in phloem to provide information on minerals that might influence tree defence capabilities and beetle nutrition; and (6) sample trees along an elevational gradient so elevation can be incorporated into interspecific comparisons.

METHODS

Description of system

Dendroctonus ponderosae is broadly distributed across western North America, from northern British Columbia to

northernmost Mexico. It undergoes one reproductive flight annually, usually within a two to three week period beginning in late July to late August, depending on region. Brood development is usually completed within one year, but requires two years at colder temperatures (Bentz *et al.* 1991). Its major symbiont is *Grosmannia clavigera* (Robinson-Jeffery and Davidson) Zipfel, de Beer, a moderately pathogenic ophiostomatoid fungus (Kim *et al.* 2008).

The chemical ecology of host–*D. ponderosae*–*G. clavigera* interactions has been studied in some detail, particularly for monoterpenes. Toxicity to beetles is influenced more by concentration than identity (Reid & Purcell 2011; Manning & Reid 2013; Reid *et al.* 2017), a pattern that occurs with other bark beetles such as *Ips pini* (Say) (Raffa & Smalley 1995). Limonene may be somewhat more toxic than other monoterpenes, but differences appear relatively minor and inconsistent. Several compounds have specific behavioural effects, and the functionality and relative benefits to either insect or host can vary markedly (Raffa *et al.* 2016). For example, adult *D. ponderosae* exploit β-phellandrene as a host recognition cue (Huber *et al.* 2000; Miller & Borden 2000). Beetles exploit (−)-α-pinene as a precursor to their aggregation pheromone (−)-*trans*-verbenol (Blomquist *et al.* 2010; Keeling 2016), and after defences are overcome, to verbenone, which prevents overcrowding (Pitman *et al.* 1968;). These conversions are primarily metabolic, but autoxidation can account for 0.8% of each (Hunt *et al.* 1989). Beetles also exploit myrcene, α-pinene and to a lesser extent δ-3-carene, as pheromone synergists (Billings *et al.* 1976; Miller & Borden 2000; Borden *et al.* 2008). The phenylpropanoid 4-allylanisole inhibits attraction of flying beetles to aggregation pheromones, with high concentrations increasing tree survival (Hayes & Strom 1994; Emerick *et al.* 2008). Diterpene acids are particularly strong inhibitors of *G. clavigera* (Boone *et al.* 2013).

Previous work conducted in Wyoming (~230 km from our study sites) found that *P. contorta* had higher total monoterpenes than *P. albicaulis* (Raffa *et al.* 2013). However, the extent to which this extends geographically or to other groups of defence compounds is unknown. Moreover, behavioural relationships are more complex, in that beetles are more likely to enter *P. contorta* in mixed stands, but this preference is relative in that it declines with increasing stand composition of *P. albicaulis* (Raffa *et al.* 2013; Bentz *et al.* 2015). Additionally, beetles that enter *P. albicaulis* are more likely to attract conspecifics and succeed in eliciting aggregation, than those that enter *P. contorta* (Bentz *et al.* 2015).

Site description

Sampling was conducted at six stands in the Gallatin National Forest near Cooke City, Montana, USA (45.05°N, −109.92°W) within the Greater Yellowstone Ecosystem. This region is characterized by a cold temperate climate (mean annual temperature 1 °C), with long, cold, snowy winters (average > 500 cm per year, and short, mild summers. Trees were sampled along an elevation gradient from 2662 to 2931 m (Supporting Information Table S1), along which tree species composition was characterized by decreasing *P. contorta* and increasing *P. albicaulis*. The non-hosts *Picea engelmannii* Parry and *Abies lasiocarpa* (Hook.) Nutt. intermixed with pines at the middle and lower elevations, and were predominant at intermediate elevations.

Experimental design

We sampled trees during July 2014. We collected phloem tissue 1.5 m above ground from trees showing no above ground signs of physical or biotic injury. This initial sample was designated 'constitutive'. We concurrently administered a mechanical wound, coupled with inoculation of *G. clavigera* (isolate # MT-1747), to simulate beetle attack, using a 6-mm-diameter cork borer and 5 mm plug of active mycelium. Inoculating trees with beetle-vectored fungi elicits defensive responses morphologically and chemically similar to those of natural attacks (Raffa & Berryman 1982; Solheim & Krokene 1998; Franceschi *et al.* 2005). Detailed methods are in Boone *et al.* (2011). Trees were re-sampled after 3 weeks. Resulting reaction zones, and phloem tissue from the opposite side, were removed with a scalpel, and designated local and systemic induction, respectively. Samples were shipped over dry ice for analysis of various chemical groups. A total of 132 trees were sampled (48 *P. contorta* and 84 *P. albicaulis*), but induced treatments of some had to be excluded due to anomalously sustained dormancy at the highest elevations during the extreme winter lows of the 2014 'polar vortex' (Cohen *et al.* 2014). Exact sample sizes for each analysis are reported in the corresponding figures.

Chemical analyses

Detailed methods of chemical analyses are in Supporting Information. Briefly, monoterpenes and sesquiterpenes were extracted in 1 mL 95% *n*-hexane with 0.2 μL mL^{-1} toluene and nonyl acetate as internal standards, and analysed by gas chromatography (GC) on an enantioselective column (Keefover-Ring *et al.* 2016). We converted diterpenes to methyl esters and analysed them by GC-FID as described previously (Keefover-Ring & Linhart 2010; Keefover-Ring *et al.* 2016). Compounds were identified by retention time matches to standards, mass spectra and relative retention times on polar and non-polar columns (Dethlefs *et al.* 1996; NIST 2008; Popova *et al.* 2010). We used dry weights to calculate compound levels (mg compound/g dry weight) with standard curves of authentic standards, when available.

Phenolics were extracted in ethanol and separated and identified using ultra high-pressure liquid chromatography–diode array detection–mass spectrometry (UHPLC-DAD-MS), using an acidified water–methanol gradient and an ethylene bridged hybrid C18 column (Chakraborty *et al.* 2014). Compounds were identified based on mass fragmentation patterns and UV spectral data, and quantified using UV spectral data. We produced five-point external standard curves ($R^2 > 0.99$) of identified phenolics, or their closest available equivalents, using authentic standards. Dry weights were used to calculate *in planta* levels of identified

phenolic compounds, as mg compound per g dry weight. We quantified unknown phenolics as internal standard-equivalent peak area per g dry weight.

Concentrations of water-soluble sugars and total starch were quantified as in Chow & Landhäusser (2004). Water-soluble sugar was extracted from ground oven-dried tissue in 80% hot ethanol and measured colorimetrically using a spectrophotometer at 490 nm after reaction with phenol-sulfuric acid. Starch in the remaining residue was solubilized by sodium hydroxide and enzymatically digested by a mixture of α-amylase (ICN 190151, from *Bacillus licheniformis*) and amyloglucosidase (Sigma A3514, from *Aspergillus niger*). The colouring reagent peroxidase-glucose oxidase/*o*-dianisidine was combined with the resultant glucose hydrolysate (Sigma Glucose Diagnostic Kit 510A). Total starch concentration was measured at 525 nm.

A 2.54 cm square section of phloem was separated from outer bark, excised, dried and weighed. Dried sample weights were multiplied by dried surface area and thickness to obtain g cm^{-3}. Dried phloem tissue was then ground in a coffee grinder to a fine particle size for nutrient analysis. Tissue N levels were analysed by micro-Kjeldahl procedure, and other elements were determined using an inductively coupled plasma emission spectrometer. Nutrient concentrations were multiplied by mean bark biomass of each tree sample (average of two reps) to obtain nutrient content.

Statistical analyses

Comparisons between tree species of quantities of various chemical groups in constitutive phloem, and of specific compounds known to affect key aspects of *D. ponderosae* behaviour from previously published work, were performed using a general linear model (PROC MIXED, SAS ver. 9.4; SAS Institute 2013) employing the Satterthwaite approximation for denominator degrees of freedom. Total quantities were natural log transformed, and proportions were arcsine square-root transformed. Firstly, we tested species as a function of constitutive chemistry, including elevation and tree diameter at breast height as covariates, to identify whether these influenced constitutive chemistry. Mixed models in SAS were also used to compare constitutive and induced phloem chemistry, testing for differences by species, treatment (constitutive, induced, systemic) and species × treatment, utilizing repeated-measures to account for lack of independence among treatments collected from the same tree. Least-squares differences in means were evaluated to quantitatively assess the significance of treatment effects among samples. As noted earlier, a subset of 'induced' samples was lost due to the 'polar vortex', in which unusually severe and long-lasting cold left trees in a semi-dormant state, and we did not see the characteristic necrotic lesions that always accompany fungal inoculation. Therefore, we used all trees to analyse constitutive chemicals, but only the plots where normal histological responses occurred for induced tissues. For the latter analyses, we only included constitutive samples from the same trees to facilitate within-tree comparisons in our repeated-measures modelling structure.

We evaluated within-tree correlations among chemical groups using Pearson product–moment correlation coefficients. Correlations were evaluated by species for constitutive samples (using all trees), and separately by species for locally and systemically induced samples.

We ordinated the data to visualize the multi-dimensional variation in phloem chemistry by species and treatment. We employed principle coordinates analysis, PCoA (Gower 1966), to concurrently evaluate distributions among all compounds. PCoA, that is, multi-dimensional scaling, uses a dissimilarity matrix of Bray–Curtis distance among samples for calculation rather than the covariance matrix on raw data as in PCA and maintains metric distances in contrast to rank-orders used in non-metric multidimensional scaling (NMDS). NMDS is less suitable for these analyses because the 'distances' in chemistry space are metric; also, our data lacked the large numbers of zeroes that often drive its use for species-level analyses. However, we recognize the advantages of NMDS for visual representation, so these analyses are provided in Supporting Information. We performed separate analyses for all known compounds, separated into two sets: constitutive-only and all treatments. The multivariate analyses were also conducted using the various groups of compounds within classes.

RESULTS

Allocation of constitutive primary and secondary compounds in phloem of *P. contorta* and *P. albicaulis*

Among the classes of compounds analysed, both species contained approximately 85% non-structural carbohydrates, and 15% secondary compounds (Fig. 1). However, the relative compositions of these compounds varied substantially, as described later.

Total numbers of compounds likewise were similar between species. Each contained 27 terpenes, including 16 monoterpenes, 6 diterpenes and 5 sesquiterpenes. The two species also contained similar numbers of phenolics, including 3 vanilloids, 10 flavonoids, 6 hydroxycinnamic acids, 2 phenylpropanoids, 7 lignans and 2 stilbenes in *P. albicaulis*, and 4 vanilloids, 10 flavonoids, 5 hydroxycinnamic acids, 1 phenylpropanoid, 7 lignans and 2 stilbenes in *P. contorta.* Unidentified compounds are not included in Fig. 1, and these were more frequent in the phenolic than terpene fractions. Tree diameter had no statistical effect on any differences among species (or treatments) and was omitted from all analyses.

Total quantities of organic compounds and minerals in constitutive phloem

Statistical comparisons of secondary compounds between *P. contorta* and *P. albicaulis* are in Table S2a. Total concentrations of all terpene groups were 26.4 mg g^{-1} dw in *P. contorta*, compared to 19.7 mg g^{-1} dw in *P. albicaulis* phloem. The most abundant terpenes were diterpenes, followed by monoterpenes

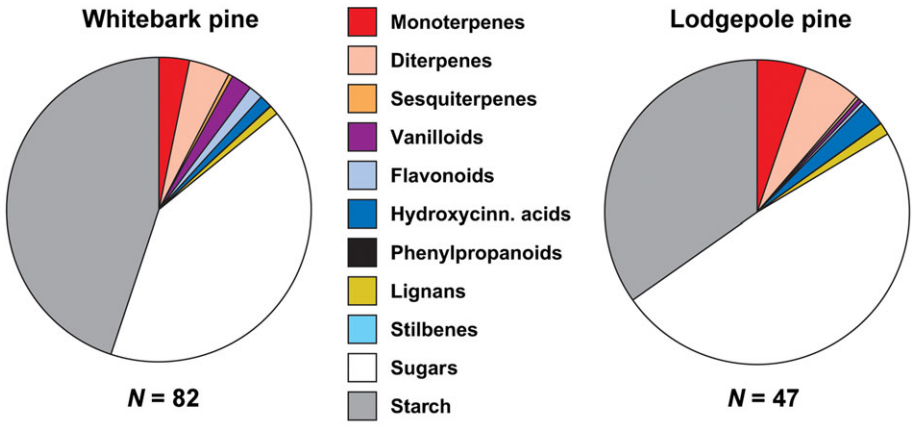

Figure 1. Allocation of carbon to primary and secondary compounds in *Pinus albicaulis* (whitebark pine) and *P. contorta* (lodgepole pine) constitutive phloem, in south-central Montana, USA, within the Greater Yellowstone Ecosystem. [Colour figure can be viewed at wileyonlinelibrary.com]

(Fig. 2). Only small quantities of sesquiterpenes were present. All three groups varied between tree species. Monoterpene and diterpene concentrations in *P. contorta* were 1.5× and 1.3× those in *P. albicaulis*, respectively. In contrast, sesquiterpene concentrations in *P. albicaulis* were 1.5× those in *P. contorta*. The quantities of individual compounds and their relative abundances are in Tables S3 and S4, respectively.

The most abundant phenolics were hydroxycinnamic acids and vanilloids, followed by lignans and flavonoids, then phenylpropanoids and stilbenes (Fig. 3). Total constitutive quantities of stilbenes and phenylpropanoids did not differ between tree species. Total concentrations of phenolic groups were higher in *P. albicaulis* than *P. contorta* (Table S2a). Distributions of phenolic fractions differed substantially between tree species (Table S2a). Vanilloids showed the greatest interspecific difference, with *P. albicaulis* concentrations being 5.5× those in *P. contorta*. Likewise, flavonoid concentrations in *P. albicaulis* were 4.4× those in

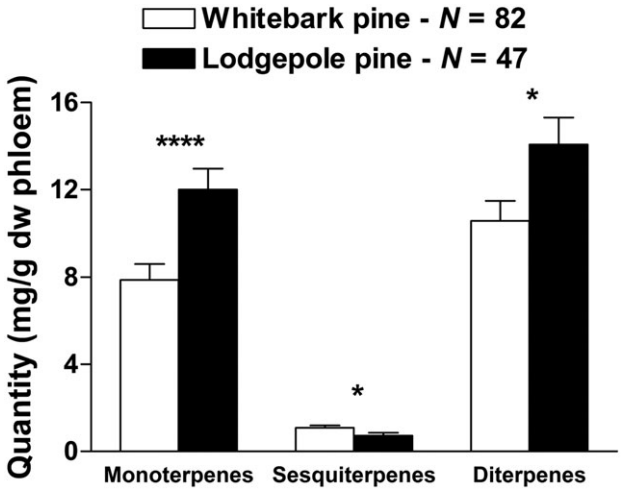

Figure 2. Quantities (mg g^{-1} dw phloem ± SE) of three terpene classes in constitutive phloem of *Pinus albicaulis* (whitebark pine) and *P. contorta* (lodgepole pine). * $P < 0.05$; ** $P < 0.01$; *** $P < 0.001$; **** $P < 0.0001$.

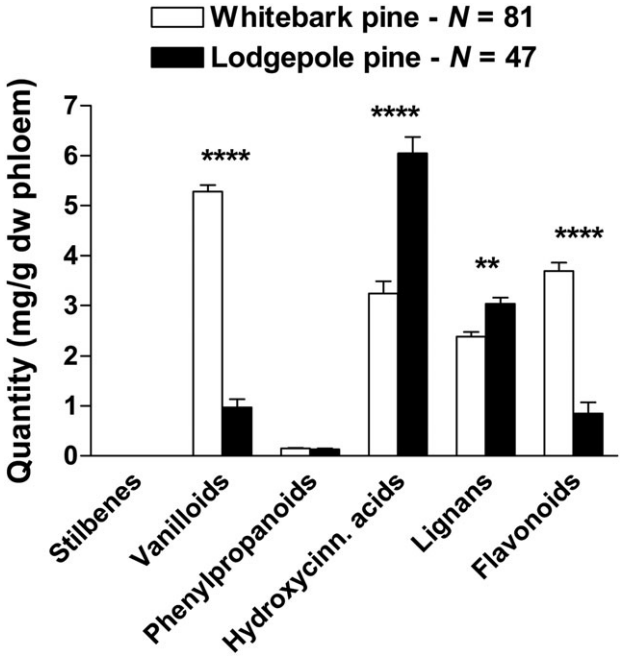

Figure 3. Quantities (mg g^{-1} dw phloem ± SE) of six phenolics classes in constitutive phloem of *Pinus albicaulis* (whitebark pine) and *P. contorta* (lodgepole pine). * $P < 0.05$; ** $P < 0.01$; *** $P < 0.001$; **** $P < 0.0001$.

P. contorta. Conversely, hydroxycinnamic acids in *P. contorta* were 1.8× those in *P. albicaulis*, and lignans were 1.3× those in *P. albicaulis*. Concentrations of individual phenolic compounds, including estimates for unidentified phenolics, are in Table S3. The chromatographic, UV and mass-spectral data are in Table S5.

Statistical comparisons of non-structural carbohydrates between *P. contorta* and *P. albicaulis* are shown in Table S2b. The two species had roughly equivalent concentrations of total non-structural carbohydrates. However, they showed contrasting patterns, with whitebark pine having higher concentrations of starch, and lodgepole pine having higher

concentrations of sugar (Fig. 4). *P. albicaulis* had a more even distribution of carbohydrates, with 50.11% starch and 49.89% sugar, whereas *P. contorta* had 40.99% starch and 59.01% sugar.

Statistical comparisons of minerals between *P. contorta* and *P. albicaulis* are shown in Table S2c. The most abundant minerals were Ca, N and K, followed by Mg, P and Al, and only trace amounts of Fe, B and Cu (Fig. 5). Ca and Al were 1.44× and 1.87× higher, respectively, in lodgepole pine. Cu was 1.03× higher in whitebark pine.

The overall effect of elevation on secondary chemistry was less pronounced than that of tree species (Table S2). Elevation affected total terpenes (weak increase with elevation) but none of their subclasses, total phenolics including four subclasses, no classes of primary compounds and three of twelve minerals. Statistically significant elevation effects were almost exclusively in *P. albicaulis*, with total phenolics increasing with elevation in constitutive samples. Vanilloids decreased with elevation in induced *P. albicaulis*, while flavonoids, phenylpropanoids and hydroxycinnamic acids increased with elevation in constitutive samples. Mn decreased with increasing elevation in both species, while Fe and Al increased with elevation in *P. albicaulis*.

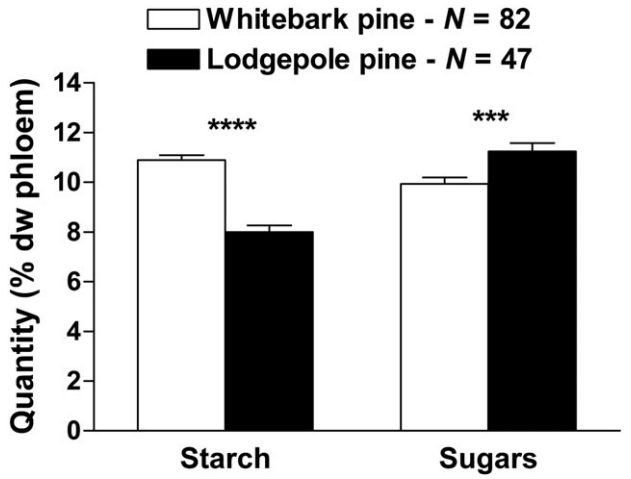

Figure 4. Quantities (% dw phloem ± SE) of carbohydrates in constitutive phloem of *Pinus albicaulis* (whitebark pine) and *P. contorta* (lodgepole pine). * $P < 0.05$; ** $P < 0.01$; *** $P < 0.001$; **** $P < 0.0001$.

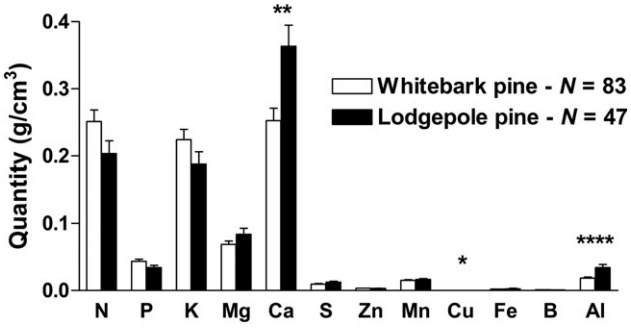

Figure 5. Quantities (g/cm^3 ± SE) of minerals in constitutive phloem of *Pinus albicaulis* (whitebark pine) and *P. contorta* (lodgepole pine). * $P < 0.05$; ** $P < 0.01$; *** $P < 0.001$; **** $P < 0.0001$.

Constitutive concentrations of individual compounds associated with performance of *D. ponderosae* and its fungal associates

Statistical comparisons between *P. contorta* and *P. albicaulis* of specific compounds known to affect *D. ponderosae* and its associates are in Table S6. *Pinus contorta* phloem had a much higher proportion (2.6×) of β-phellandrene than did *P. albicaulis* (Fig. 6). In contrast, the concentrations of (−)-α-pinene (2.4×), myrcene (1.6×), δ-3-carene (2.1×) and limonene (2.0×) were higher in *P. albicaulis* than *P. contorta* phloem. The concentration of the phenylpropanoid pheromone inhibitor 4-allylanisole (aka estragole) was 2.3× higher in *P. contorta* than *P. albicaulis* phloem (Fig. 6).

Total concentrations of induced terpenes, phenolics and non-structural carbohydrates in response to simulated *D. ponderosae* attack

Total concentrations of monoterpenes underwent strong localized induction (Table S7a), showing a 17.9× increase in *P. contorta* and a 15.2× increase in *P. albicaulis* (Fig. 7). There were no differences between constitutive and induced systemic concentrations, in either species. There were also no interspecific differences in constitutive concentrations within this smaller subset of trees, nor in induced total concentrations. Diterpenes likewise showed pronounced local induction (Table S7a) in both *P. albicaulis* (31.9×) and *P. contorta* (22.1×) (Fig. 7). As with monoterpenes, neither tree species showed different concentrations between constitutive and post-treatment systemic tissues. Sesquiterpenes were more abundant in *P. albicaulis* than *P. contorta* in all categories (Table S7a). Sesquiterpenes showed high local induction in *P. albicaulis* (33×) but not *P. contorta* (Fig. 7). They did not undergo systemic induction in either species.

Total concentrations of vanilloids (Table S7a) decreased from constitutive levels in locally induced tissue in both *P. albicaulis* (0.3×) and *P. contorta* (0.4×) (Fig. 8). There were no systemic changes in either species. Concentrations of vanilloids were higher in *P. albicaulis* than *P. contorta* in constitutive (7.1×), locally induced (5.7×) and systemic (7.3×) phloem. Flavonoids showed a generally similar pattern in that concentrations in *P. albicaulis* decreased in locally induced tissue (0.6×), did not show systemic induction in either species and were higher in *P. albicaulis* in constitutive, locally induced and systemic phloem (5.5×, 1.7×, 5.4×, respectively). Hydroxycinnamic acids followed the same general pattern, in that they decreased in locally induced tissue in both *P. albicaulis* (0.3×) and *P. contorta* (0.3×) and did not show systemic induction in either species. However, hydroxycinnamic acids were higher in *P. contorta* constitutive, locally induced and systemic phloem (1.8×, 2.1×, 1.7×, respectively). Phenylpropanoids decreased in locally induced

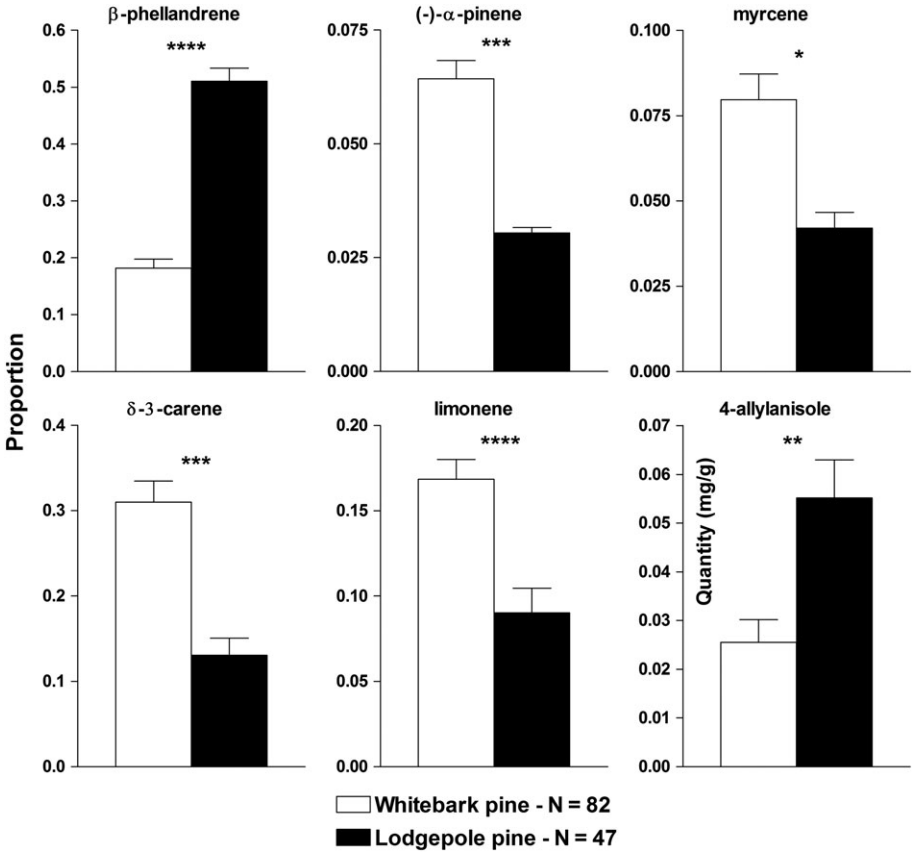

Figure 6. Secondary compounds (± SE) affecting key aspects of mountain pine beetle behaviour in constitutive phloem of *Pinus albicaulis* (whitebark pine) and *P. contorta* (lodgepole pine). * $P < 0.05$; ** $P < 0.01$; *** $P < 0.001$; **** $P < 0.0001$.

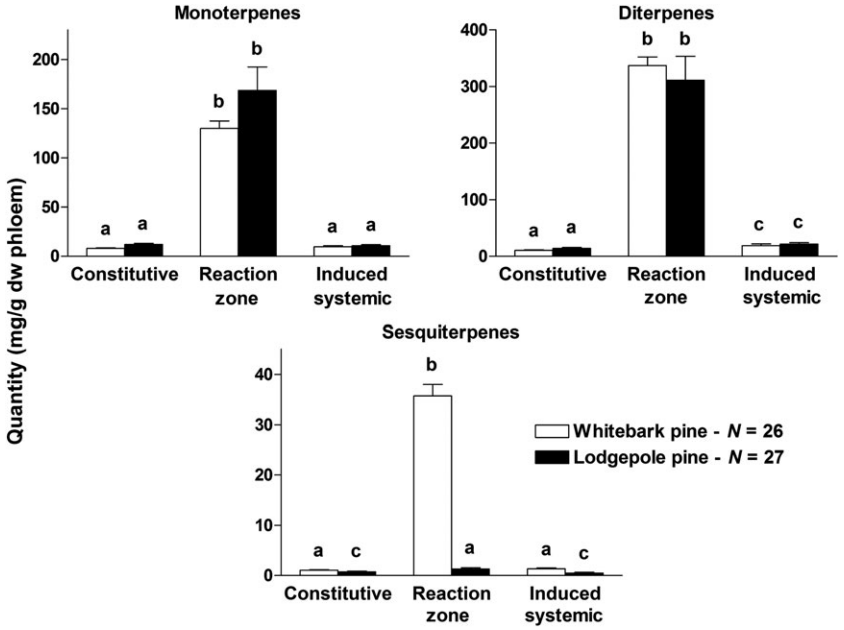

Figure 7. Induction patterns of three classes of terpenes (mg g^{-1} dw phloem ± SE) in *Pinus albicaulis* (whitebark pine) and *P. contorta* (lodgepole pine) phloem. Mean separations at $P < 0.05$.

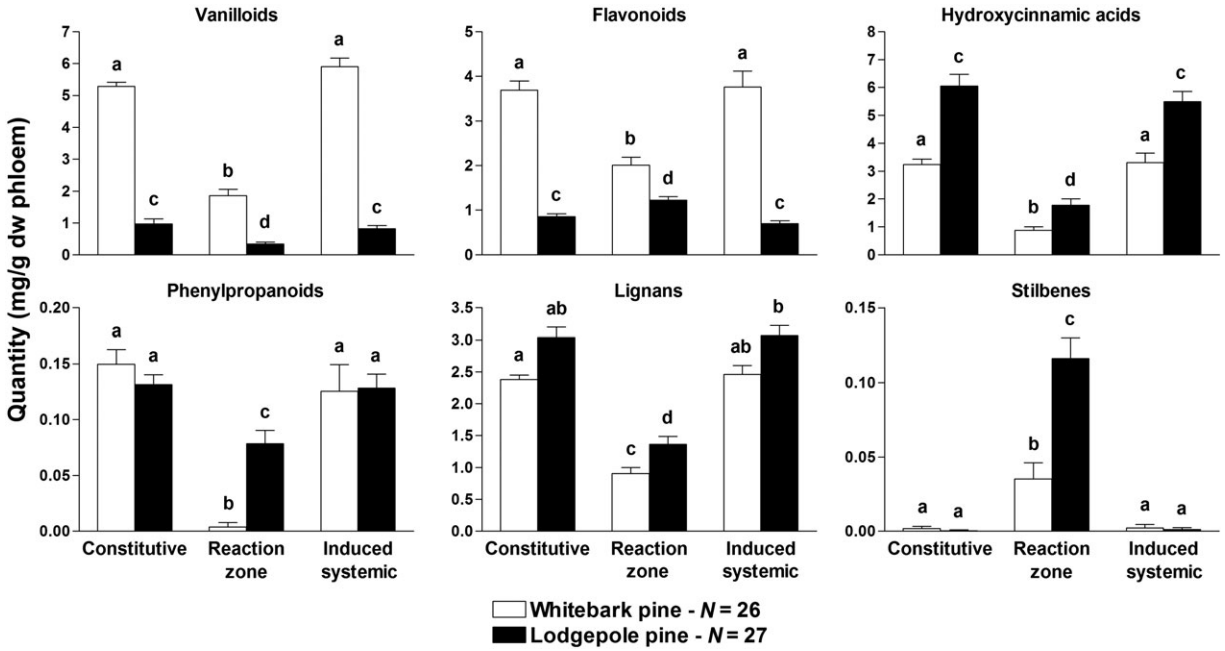

Figure 8. Induction patterns of six classes of phenolics (mg g^{-1} dw phloem ± SE) in *Pinus albicaulis* (whitebark pine) and *P. contorta* (lodgepole pine) phloem. Mean separations at $P < 0.05$.

tissue in *P. albicaulis* (0.03×) and to a lesser extent in *P. contorta* (0.64×). Neither tree showed systemic induction. Concentrations in locally induced tissue were much higher in *P. contorta* (18.6×) than *P. albicaulis*. Lignans showed the same general pattern as most phenolics, in that their concentrations within the locally induced tissues decreased in both *P. albicaulis* (0.40×) and *P. contorta* (0.46×), and neither species showed systemic induction. Lignans were higher in *P. contorta* than *P. albicaulis* in all tissue types (1.3× constitutive, 1.5× local, 1.2× systemic). Stilbene responses to simulated bark beetle attack were markedly different from those of other phenolics groups (Fig. 8). Specifically, stilbenes showed strong local induction, with increases of 137× in *P. contorta* and 22× in *P. albicaulis*. Additionally, concentrations in locally induced tissue of *P. contorta* were much higher (3.5×) than in *P. albicaulis*, even though they did not differ in constitutive phloem. As with the other phenolics, stilbenes did not show systemic induction.

Statistical analyses of non-structural carbohydrates are in Table S7b. Sugars decreased within the reaction zone, in both *P. albicaulis* (0.5×) and *P. contorta* (0.6×) (Fig. 9). There were no systemic changes. Starches also decreased within the reaction zone, but to a greater extent, declining to 0.4× that of constitutive phloem in *P. albicaulis* and 0.5× in *P. contorta*.

Treatment effects on relative concentrations of specific system-bioactive compounds

Sources of variation of compounds with key behavioural activities to *D. ponderosae* are reported in Table S8. The major differences between species occurred in myrcene and 4-allylanisole (Fig. 10). Myrcene underwent a significant decrease (0.56×) in its proportion of the monoterpene fraction in *P. contorta* following simulated attack, but was unchanged in *P. albicaulis*. Induced tissue in *P. albicaulis* had 2.7× higher concentrations of myrcene, than *P. contorta*. 4-Allylanisole showed much higher local induction in *P. contorta* (15×) than *P. albicaulis* (9×) following simulated attack. Induced quantities of 4-allylanisole were 3.8× higher in *P. contorta* than *P. albicaulis*.

Proportions of (−)-α-pinene and limonene did not differ among treatments in *P. albicaulis*, and there was only a minor increase (1.1×) in reaction zone δ-3-carene relative to constitutive phloem. The relative proportions of β-phellandrene, (−)-α-pinene and δ-3-carene did not differ among treatments in *P. contorta*, and there was a minor decrease (0.7×) in reaction zone limonene. Neither tree showed any differences between constitutive and post-treatment phloem distant from the inoculation, that is, systemic induction, for any compound. β-phellandrene and limonene showed minor local decreases in *P. albicaulis* and *P. contorta*, respectively.

Three of the monoterpenes showed two stereoisomers present, and their relative abundances sometimes change during induced local responses (Table S3). The ratios of (−) to (+)-limonene were 13 in *P. contorta* constitutive phloem and 0.7 in reaction zone phloem. In *P. albicaulis*, they were 58 and 55.3, respectively. The ratios of (−) to (+)-α-pinene were 2.4 in *P. contorta* constitutive phloem and 0.8 in reaction zone phloem. In *P. albicaulis*, they were 1.4 and 0.6, respectively. The ratios of (−) to (+)-β-pinene were 1.6 in *P. contorta* constitutive phloem and 116.9 in reaction zone phloem. In *P. albicaulis*, they were 3.5 and 47.9, respectively.

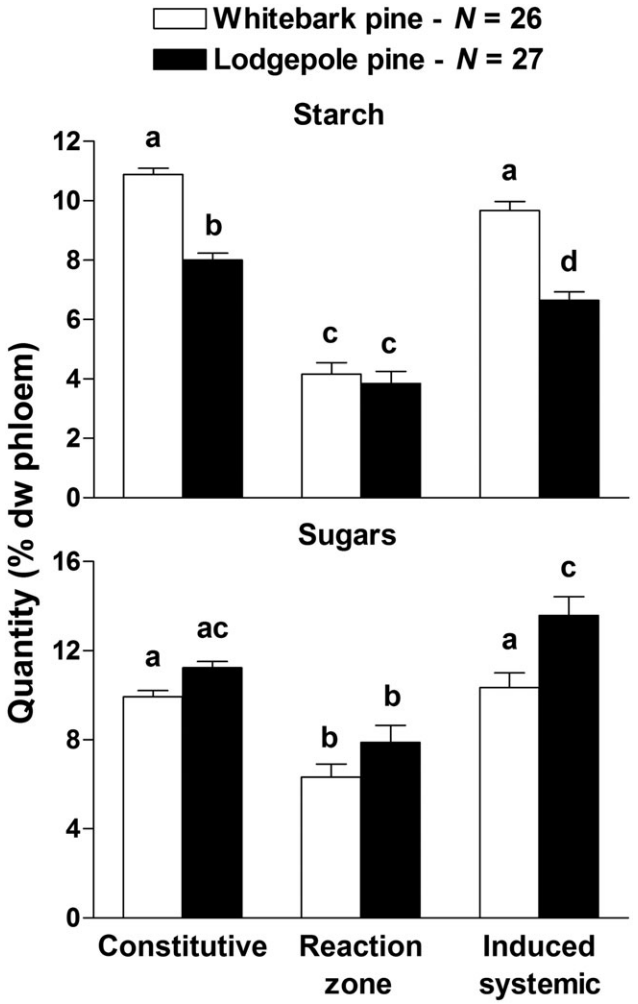

Figure 9. Induction patterns of carbohydrates (% dw phloem ± SE) in *Pinus albicaulis* (whitebark pine) and *P. contorta* (lodgepole pine) phloem. Mean separations at $P < 0.05$.

Relationships among phloem constituents

Correlations among the various chemical groups are shown for *P. contorta* and *P. albicaulis* in Table S9a and b, respectively. Levels of statistical significance are in Table S10a and b, respectively.

There were three major, comparable trends within *P. contorta* and *P. albicaulis*. Firstly, quantities of most compounds in constitutive tissue were either positively- or un-related, indicating there are few inherent trade-offs among pathways or carbon pools. For example, there was no relationship between total terpenes and phenolics. Further, relationships among terpene groups and among phenolic groups were either positive or absent. In both *P. albicaulis* and *P. contorta*, there were no relationships between total terpenes or phenolics with sugars, starches or total carbohydrates, with one exception. However, sugars and starches were inversely related in *P. contorta*. Secondly, pronounced inverse relationships emerged during induction. In *P. albicaulis*, these included total terpenes, monoterpenes and diterpenes versus total phenolics and multiple phenolics subgroups. However, in *P. contorta*, these tended to be among carbohydrates and terpenes, rather than between terpenes and phenolics. Third, inter-compound relationships among constitutive tissue and post-treatment tissue distant from simulated attack were nearly identical.

There were three major differences between tree species in relationships among secondary compounds. Firstly, 4-allylanisole became strongly related to monoterpenes and diterpenes during induction of *P. contorta* but not *P. albicaulis*. In constitutive tissue, the opposite relationship occurred, that is, allylanisole was related to these monoterpenes and diterpenes in *P. albicaulis* but not *P. contorta*. Secondly, during induction, stilbenes became inversely related to monoterpenes and total terpenes in *P. albicaulis*, but neither of these relationships arose in *P. contorta.* Third, monoterpenes, diterpenes and total terpenes became inversely related to phenolics during induction of *P. albicaulis*, but relationships were not significant in *P. contorta.*

Correlations among the various chemical groups with minerals differed between tree species (Tables S9c & S10c). In *P. albicaulis*, most relationships were among phenolics, with flavonoids and hydroxycinnamic acids being positively related to most minerals, and lignans being inversely related to all minerals. In contrast, most relationships with minerals in *P. contorta* involved monoterpenes, with all but three minerals showing positive trends. Total phenolics were inversely related to seven phloem minerals. Phenolics were unrelated to the other five minerals but always trended in a negative direction. Another interspecific difference is that sugars were related to seven minerals in *P. albicaulis*, but none in *P. contorta.* Starches and total carbohydrates were generally unrelated to minerals in both tree species.

PCO plots indicate differences among constitutive and induced chemical profiles of *P. contorta* and *P. albicaulis.* Among constitutive samples, there is clear separation in major chemical groups between *P. contorta* and *P. albicaulis* (Fig. 11a). Samples were separated on axis 1 primarily by monoterpenes and diterpenes, and axis 2 due to on starches, flavonoids, vanilloids and sesquiterpenes and sugars and hydroxycinnamic acids. When tree responses were included in the analysis, that is, locally (reaction zone) and tissue-wide, there was a large amount of separation between locally induced samples and constitutive and systemic samples (Fig. 11b). This was primarily along the axis 1 (76.6% of variation), with stilbenes, sesquiterpenes, monoterpenes and diterpenes correlated with induced samples. There was no clear separation between constitutive and systemically induced samples. In general, there was weak separation along axis 2 (10.1% of variation). The PCO plots of all chemicals with both trees combined show similar trends (Supporting Information Fig. S1). Likewise, the NMDS plots show clear distinctions by tree species, treatment (constitutive and systemic, versus locally induced) for all compounds (A), terpenes (B) and phenolics (C).

The spatial scale and direction of induction differed among chemical groups (Fig. 12), with the same general patterns holding for both tree species. Among terpenes, all classes showed localized increases in concentrations. However, systemic increases only occurred in diterpenes. Among

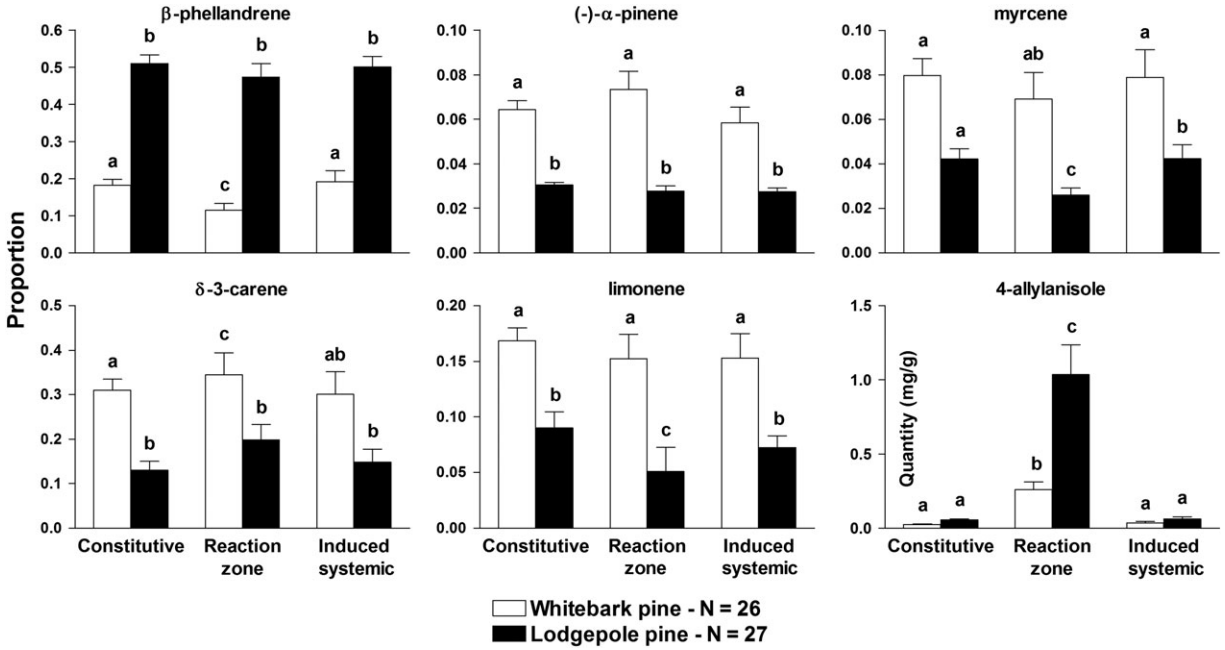

Figure 10. Induction patterns of secondary compounds (± SE) in *Pinus albicaulis* (whitebark pine) and *P. contorta* (lodgepole pine) phloem that affect key aspects of *Dendroctonus ponderosae* behaviour. Mean separations at $P < 0.05$.

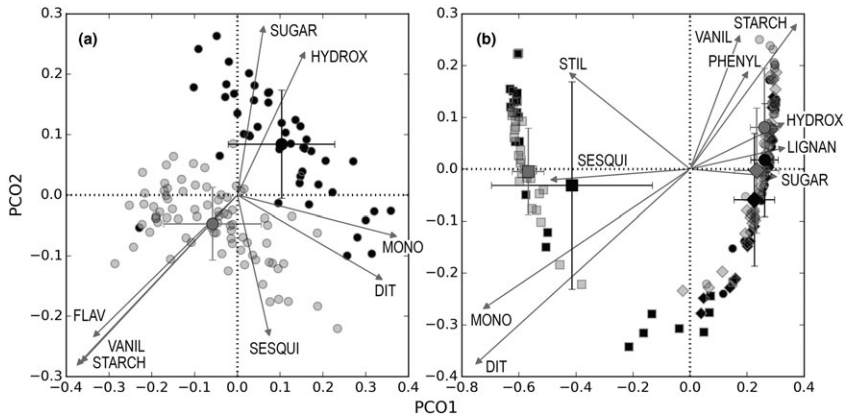

Figure 11. Principal coordinates analysis (PCO) of major chemical groups for *Pinus albicaulis* (light) and *P. contorta* (dark): (a) constitutive samples only; (b) constitutive (circle), locally induced (square) and systemic samples (diamond). Biplot vectors show direction and strength of significant correlations with major chemical groups. Vectors are scaled to data extent. MONO = monoterpenes, DIT = diterpenes, SESQUI = sesquiterpenes, VANIL = vanilloids, FLAV = flavonoids, HYDROX = hydroxycinnamic acids, PHENYL = phenylpropanoids, STIL = stilbenes.

phenolics, the most common response in local tissue was decreased concentrations. The major exception was in stilbenes, which showed pronounced increases in locally induced tissues, in both tree species. There were no systemic changes in phenolics. Non-structural carbohydrates always showed decreased concentrations in locally induced tissue. Systemic changes in carbohydrates were usually absent, with the exception of starches in lodgepole pine.

DISCUSSION

Pinus contorta and *P. albicaulis* were generally similar in overall allocations to primary and secondary compounds, but differed in how they allocate among the major compound classes, how various classes and specific compounds respond to simulated attack and how different classes of compounds relate during induced defence responses. Collectively, these differences suggest higher constitutive allocation by *P. contorta* to compounds that are known to increase resistance against *D. ponderosae–G. clavigera* complexes, higher inducibility of compounds inhibitory to beetles and symbiotic fungi and higher allocation by *P. albicaulis* to storage compounds that confer protection from environmental extremes. These patterns appear consistent with historically different selective pressures from biotic and abiotic stressors related to environmental niche (Kessler 2015).

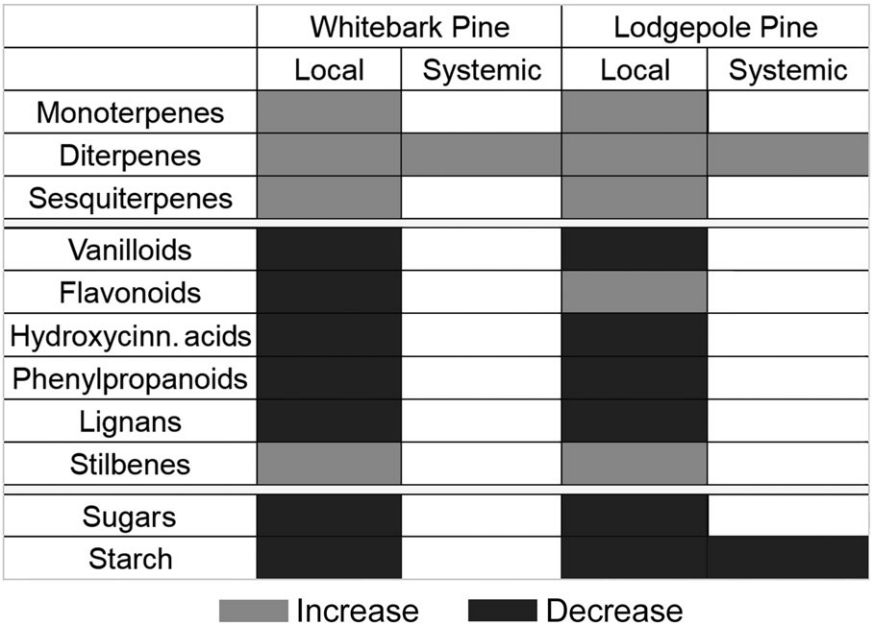

Figure 12. Spatial scale and direction of induced chemical reactions in *Pinus albicaulis* (whitebark pine) and *P. contorta* (lodgepole pine) phloem following simulated attack by *Dendroctonus ponderosae*. Local refers to within reaction zone; systemic refers to opposite side of tree. Light grey indicates increases; dark grey indicates decrease; open cell indicates no change.

Pinus contorta and *P. albicaulis* had similar pools of non-structural carbohydrates once elevation is accounted for, but differed in their relative allocation to starch and soluble sugar. Specifically, *P. albicaulis* had more starch, whereas *P. contorta* had more sugar. *Pinus contorta* likewise exhibited higher allocation to sugars than starch in Alberta (Goodsman *et al.* 2013), suggesting this occurs over a broad geographic pattern. Higher allocation to starch versus sugar in the slow-growing, long-lived *P. albicaulis* relative to the fast-growing, short-lived *P. contorta* is consistent with the roles these carbohydrates play in energy storage and drought tolerance, versus rapid energy conversion, respectively (Kaelke *et al.* 2001; Poorter & Kitajima 2007; Loehman *et al.* 2011; Lintunen *et al.* 2016).

Pinus contorta had higher concentrations of terpenes, particularly monoterpenes and diterpenes, than *P. albicaulis*, despite their equivalent carbohydrate reserves. This pattern may extend over a fairly large area, as monoterpenes were likewise more abundant in *P. contorta* than *P. albicaulis* phloem in western Wyoming (diterpenes not assayed) (Raffa *et al.* 2013). High monoterpene concentrations have been shown to repel and kill bark beetles, inhibit their fungal and bacterial associates and be correlated with reduced levels of tree mortality in multiple studies (reviewed in Raffa *et al.* 2015b). The higher monoterpene and diterpene concentrations cannot be explained on the basis of different soil nutrient availabilities, as mineral compositions were generally similar. Moreover, when selection factors are similar, slow-growing, long-lived plants such as *P. albicaulis* generally invest more in defence than fast-growing short-lived plants such as *P. contorta* (Herms & Mattson 1992; Kaelke *et al.* 2001), counter to what we observed. In cold high-elevation environments, there may be relatively higher allocation to environmental tolerance than either growth or defence. Induced monoterpenes in Montana followed the same trend as in Wyoming, that is, being higher in *P. contorta* than *P. albicaulis* (Raffa *et al.* 2013), but the differences were not statistically significant. This may reflect regional variation, the smaller sample size in the current study, or both. The only terpenes consistently higher in *P. albicaulis* than *P. contorta* phloem were sesquiterpenes, but it is unknown whether these have any bioactivity against bark beetles or their associates.

The observed differences in concentrations of behaviour-modifying compounds may explain some of the natural patterns occurring in the field. For example, *D. ponderosae* are more likely to succeed in initiating mass attacks and killing trees after entering *P. albicaulis* than *P. contorta.* This difference in beetles' ability to elicit aggregation is consistent with *P. albicaulis*' higher concentrations of the pheromone precursor (−)-α-pinene and pheromone enhancers myrcene and δ-3-carene, and lower quantity of the pheromone inhibitor 4-allylanisole. Further, *P. contorta* responded to simulated attack by undergoing pronounced increases in 4-allylanisole, and decreasing its proportion of myrcene, whereas *P. albicaulis* only had a moderate increase in 4-allylanisole, and myrcene proportions did not change. Thus, both the constitutive and induced chemistries of *P. albicaulis* appear less able than those of *P. contorta* to prevent mass attack once beetles discover a whitebark pine. However, the relative continuity of historical interactions also influences *D. ponderosae*'s host-finding behaviour. Specifically, beetles are more likely to enter *P. contorta* than *P. albicaulis* under natural conditions in mixed stands (Raffa *et al.* 2013; Bentz *et al.* 2015). This behavioural difference is consistent with *P. contorta*'s much higher concentrations of β-phellandrene, which *D. ponderosae* exploits in host recognition (Huber *et al.* 2000; Miller & Borden 2000).

Phenolics were more diverse but less abundant than terpenes in both tree species. For most phenolics, we lack evidence of effects on bark beetles or their symbionts, and also whether they represent stable phytochemicals or biosynthetic intermediaries. Unlike other phenolics that decreased in locally induced tissues, stilbenes increased following simulated attack. This increase was much more pronounced in *P. contorta* than *P. albicaulis*. Stilbenes have been reported to directly inhibit fungi associated with bark beetles (Hart 1981; Evensen *et al.* 2000; Bonello & Blodgett 2003; Hammerbacher *et al.* 2013). However, in some cases, they can contribute to autotoxicity or may be more related to symptom expression than actual resistance (Bonello *et al.* 1993). We do not know the extent to which decreases in other phenolic groups during induction represent degradation by inoculated fungi (Hammerbacher *et al.* 2013; Wadke *et al.* 2016), crosstalk among metabolic pathways (Thaler *et al.* 2012), unknown processes or combinations thereof. Similar trends have been observed in invasive insect–tree interactions, specifically *Fraxinus* spp. attacked by *Agrilus planipennis* Fairmaire, which is not known to vector phytopathogenic fungi (Chakraborty *et al.* 2014).

In addition to constitutive differences in total concentrations of defence compounds and in compounds particularly inhibitory to bark beetles and their symbionts, *P. contorta* appears to undergo more comprehensive induced defences. For example, *P. contorta* shows higher co-occurrence of monoterpenes with diterpenes, the most insecticidal and one of the two most fungicidal groups, respectively, in pine defence syndromes. Likewise, induced levels of the most repellent compound, 4-allylanisole, are correlated with monoterpenes and diterpenes in induced tissues of *P. contorta* but not *P. albicaulis.* Additionally, *P. albicaulis*, but not *P. contorta*, appears to face trade-offs between defence against insects versus fungi, which may reduce efficacy against beetle–fungal complexes. Specifically, induced defences of *P. albicaulis* show inverse relationships between stilbenes and monoterpenes, and inverse relationships between phenolics versus monoterpenes, diterpenes and total terpenes. In contrast, *P. contorta* shows none of these apparent metabolic trade-offs in defence specificity. *Pinus contorta*, but not *P. albicaulis*, shows strong negative relationships between both monoterpenes and diterpenes with both sugars and starches during induction, consistent with rapid conversion of carbohydrates to defence chemicals (Kozlowski 1992; Ögren *et al.* 1997; Goodsman *et al.* 2013; Dietze *et al.* 2014)**.** The greater extent to which secondary compounds with demonstrated activity against *D. ponderosae* and *G. clavigera* co-occur during the induced responses of *P. contorta*, and the stronger relationships between these increases and declines in non-structural carbohydrates during induction, appear to be an important difference in the overall defence syndromes between these two trees against this lethal complex.

In general, responses to simulated bark beetle attack did not extend around tree circumferences. This differs from systemic induction in pines to fungal pathogens, at least when the induced and systemically responding tissues are anatomically connected along the longitudinal stem axis (e.g. Blodgett *et al.* 2007; Sherwood & Bonello 2016). Similarly, only localized induction was observed within *P. ponderosa* to *G. clavigera* (Keefover-Ring *et al.* 2016). Responses to the initial attacking beetles can be particularly important in whether trees live or die (Erbilgin *et al.* 2007; Zhao *et al.* 2011). If beetles succeed in initiating aggregation, systemically protecting the entire circumference of mature trees with the high concentrations of defence chemicals needed to kill *D. ponderosae* (Reid & Purcell 2011; Manning & Reid 2013) may be physiologically unattainable. Instead, the optimal defence strategy may be to exert all available resources at the point of first attack. Anatomical impediments related to vascular architecture in large gymnosperms may further contribute to the low level of defence induction across stems.

Mineral contents were generally similar between species. The major difference was that *P. contorta* had higher Ca content. Ca is widely involved in the biosynthesis and signalling of plant defence chemicals (Schlink 2011) and induced strengthening of cell walls (Bonello *et al.* 1991). The stronger correlations of N and Ca with monoterpenes in *P. contorta* are noteworthy, because these minerals have been associated with plant signalling during defensive induction (Kiep *et al.* 2015; Ranty *et al.* 2016). Future research is needed to explore these potential roles in pines.

This study represents the first comprehensive analysis of the primary, secondary and mineral chemistry of *P. contorta* and *P. albicaulis* phloem. This information should prove useful as new toxicological, behavioural and synergistic activities of various secondary metabolites against *D. ponderosae* and other current or impending biotic agents become known, particularly within understudied chemical groups. In general, the secondary chemistry of *P. albicaulis* appears more amenable to the pheromone signalling that *D. ponderosae* uses to coordinate mass attacks, which places this tree at increased risk as warming climate increases beetle access. However, *P. contorta* has higher concentrations of compounds that *D. ponderosae* has evolved to exploit for locating hosts. The possibility that this combination of host chemistries could be manipulated at the stand scale to lessen impacts of *D. ponderosae* should be investigated within the context of associational resistance (Barbosa *et al.* 2009).

Future studies are needed to determine the potential roles of geographic variation, regional population pressure by *D. ponderosae* and other biotic agents such as the invasive alien pathogen *Cronartium ribicola* A. Dietr, and landscape factors affecting resource allocation to defence. For example, *P. contorta* occurs largely within a connected matrix, while *P. albicaulis* occurs largely on montane islands, which can substantially influence population genetic structure (Bruederle *et al.* 1998; García-Fernández *et al.* 2012). Additionally, certain groups of secondary compounds should be assayed for potential activity against *D. ponderosae* and its associates. In particular, sesquiterpenes and several classes of phenolics are abundant and dynamic, yet no bioassays on their potential defence functions, nor on other potential physiological functions, have been conducted. For example, the flavonoid naringenin from Chinese *Pinus tabuliformis* Carr. can inhibit an exotic beetle–fungal complex (Cheng *et al.* 2016) but was not detected in either of these two North American species.

The extent to which host tree species influences the abilities of microbial associates to metabolize defence compounds (DiGuistini *et al.* 2011; Boone *et al.* 2013; Hammerbacher *et al.* 2013; Wang *et al.* 2014) should also be investigated. Finally, other components of defence, including morphological structures, such as resin ducts that facilitate deployment of defence compounds, resin physical properties such as viscosity and indirect defences driven by interactions among tree chemicals, beetle pheromones and predators need investigation.

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AUTHOR CONTRIBUTIONS

K.F.R., P.A.T. and C.J.M. designed the experiment. P.A.T. supervised field sampling. C.J.M., P.B., S.C., N.E., K.K.R., J. G.K. and C.V. performed chemical analyses. P.A.T. and C.J. M. conducted statistical analyses and data inventory. All authors contributed to writing the manuscript. Two anonymous reviewers helped us improve the quality of our paper.

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SUPPORTING INFORMATION

Additional Supporting Information may be found online in the supporting information tab for this article.

Table S1. Locations and elevations of study sites for chemical analyses of *Pinus contorta* and *P. albicaulis* in south-central Montana, USA.
Table S2. Comparison of constitutive concentrations of chemicals in *Pinus contorta* vs. *Pinus albicaulis* phloem.
Table S3. Concentration (mg/g dw) of fully or partially characterized secondary metabolites in in *Pinus albicaulis* and *P. contorta* constitutive and induced phloem tissues. B.

Concentration of unknown phenolics expressed in absorbance units /mg of phloem. All numbers represent means ± std error. nd = not detected. C. Mean separations (P<0.05, within row) of absolute values of compounds known to affect *D. ponderosae* behavior. Nat. log(1+) normalized, elevation incorporated.

Table S4. Percent compositions of specific compounds within monoterpenes, sesquiterpenes, and diterpenes

Table S5. Chromatographic, UV, mass-spectral data, and assigned identities of phenolic compounds isolated from phloem of *Pinus albicaulis* (Pa) and *P. contorta* (Pc).

Table S6. Comparison of constitutive compounds known to be behavior-modifying to mountain pine beetle and associated microbes in *Pinus contorta* vs. *Pinus albicaulis* phloem

Table S7. Sources of variation (ANOVA) of total concentrations of compounds in *Pinus contorta vs. Pinus albicaulis* phloem

Table S8. Sources of variation (ANOVA) of total concentrations of compounds with known bioactivity to mountain pine beetle and associates

Table S9A. Correlations among compounds in Whitebark Pine. R values highlighted in green or yellow for significant (P<0.05) positive and negative relationships, respectively.

Table S9B. Correlations among compounds in Lodgepole Pine. R values highlighted in green or yellow for significant (P<0.05) positive and negative relationships, respectively.

Table S9C. Correlations among compounds in Lodgepole and Whitebark Pine. R values highlighted in green or yellow for significant (P<0.05) positive and negative relationships, respectively.

Table S10A. Statistical significance of relationships among compounds in Whitebark Pine. P values are highlighted in green or yellow for significant (P<0.05) positive and negative relationships, respectively.

Table S10B. Statistical significance of relationships among compounds in Lodgepole Pine. P values are highlighted in green or yellow for significant (P<0.05) positive and negative relationships, respectively.

Table S10C. Statistical significance of relationships among compounds in Whitebark Pine and Lodgepole pine. P values are highlighted in green or yellow for significant (P<0.05) positive and negative relationships, respectively. Abbreviations are described in xyz.

Figure S1. PCO plot of all chemicals *P. albicaulis* (red) and *P. contorta* (blue): constitutive (circle), induced (square) and systemic samples (diamond). Biplot vectors show direction and strength of significant correlations with major chemical groups. Vectors are scaled to data extent. Vectors are not labeled for all chemicals due to the large number of chemicals and significant relationships

Figure S2. NMDS of compounds in *P. contorta* and *P. albicaulis*.

SUPPLEMENTAL MATERIALS:

1. Details of Chemical Methods
2. Tables: 10
3. Figures: 2

Chemical Analyses

Terpenes

Samples were stored in a -30C freezer. We cut phloem into ~2-3 mm cubes, and divided them into two portions. For monoterpene and sesquiterpene extraction, we immediately submerged one portion in 1 ml of 95% *n*-hexane with 0.2 µl/ml of toluene and nonyl acetate, as internal standards, in 2 ml GC vials with PTFE screw caps. We used the second portion for diterpene extraction, submerging the tissue into 1 ml of 100% ethanol in 2 ml microcentrifuge tubes with sealed screw caps. We sonicated all vials and tubes in a water bath for 10 min, vortexed them briefly, and shook them overnight on an orbital mixer. We then decanted the solvent from the mono-/sesquiterpene samples into fresh GC vials. We centrifuged the diterpene samples at 14,000 rpm for 10 minutes and transferred the clear ethanol solution with a micropipette into fresh tubes. We diluted all samples from inoculation treatments 1 into 11 (1 part sample + 10 parts solvent) with their respective solvents prior to analysis, due to their much higher terpene concentrations.

We analyzed compositions of mono- and sesquiterpenes by gas chromatography (GC) on an enantioselective column. This system consisted of a Hewlett Packard 5890 GC equipped with a flame ionization detector (FID) and a Cyclodex-B capillary column, with 30 m × 0.25 mm I.D., film thickness 0.25 µm. (Agilent Technologies) with helium as carrier gas at 1.0 ml/min. We injected 2 µl of each sample directly, with a split flow ratio of 30:1. The oven program was 40 °C for 5 minutes, +3 °C /min to 200 °C, +25 °C /min to 220°C. Injector and detector temperatures were 260 °C and 250 °C, respectively.

We converted diterpenes to methyl esters by combing 75 µl of each sample with 50 µl of a 2.0 M (trimethylsilyl) diazomethane (TMS-DAM) solution in diethyl ether (Sigma-Aldrich, St. Louis, MO) (Robert *et al*. 2010); Keefover-Ring & Linhart (2010). After brief vortex mixing and 20 min incubation at ambient temperature, we vacuum-centrifuge dried samples and re-suspended them with 75 µl of methanol with 0.8 µl/ml of carvacrol as internal standard. GC conditions were as above, except for a DB-Wax capillary column, 30 m × 0.25 mm I.D., film

thickness 0.25 µm, (Agilent Technologies) and an oven program consisting of 160 °C, +2 °C /min to 250 °C, held for 20 min.

We conducted additional analyses using GC-MS with Shimadzu GC-2010 Plus gas chromatograph coupled with a QP-2010SE quadrupole mass spectrometer with an ion source of 70.0 eV at 230 °C, using helium carrier gas at 36 cm/sec (1.0 ml/min) and injector temperature of 250 °C. The oven program was 40 °C, +3 °C /min to 200 °C. We injected 1 µl of samples, available standards, and a continuous series of *n*-alkanes (C_8–C_{20}; Sigma-Aldrich) in splitless mode onto ZB-5 capillary column (30 m × 0.25 mm I.D., film thickness 0.25 µm; Phenomenex, Torrance, CA) and identified mono- and sesquiterpenes with retention time matches to pure standards, mass spectra, and/or linear retention indexes calculated with the alkane series (Adams 2007; NIST 2008; El-Sayed 2013). Diterpene samples were injected using the same conditions and compounds identified by retention time matches to standards, mass spectra, and their relative retention times on both polar and non-polar columns (Dethlefs et al. 1996; NIST 2008; Popova et al. 2010).

We dried phloem samples to a constant weight at 60 °C and used dry weight (dw) values to calculate compound concentrations (mg compound/g dw) with standard curves of authentic standards, when available, injected on the GC-FID. We obtained standards for all but two identified monoterpenes, longifolene, and 4-allylanisole from Sigma-Aldrich (St. Louis, MO). Purified β-phellandrene came from Glidco Organics (Jacksonville, FL) and α-thujene had no available standard. Abietic acid was obtained from Acros Organics (Thermo Fisher Scientific, Waltham, MA). The USDA Forest Service Forest Products Laboratory, Madison, WI, supplied the remaining diterpene standards, except for sandaracopimaric and isocupressic acids. We calculated concentrations of all unknowns and identified compounds for which we had no standards with the nearest eluting standard compound.

Phenolics

Phenolics were extracted in ethanol following the above-described procedure for diterpenes. Extracts were processed to exclude diterpene resin acids via precipitation by adding an equal volume of water containing 0.5 mg/mL resorcinol (Sigma-Aldrich) as an internal standard. Diterpene acids formed a white precipitate, which was separated from the supernatant

via centrifugation for 15 minutes at maximum speed. Before use, the aqueous supernatants were evaporated to dryness and resuspended in methanol.

We identified phenolics in pooled samples using ultra high pressure liquid chromatography - diode array detection-mass spectrometry (UHPLC- DAD-MS), with an Agilent 1290 Infinity UHPLC system (Agilent Technologies, Santa Clara, CA, USA). The injected volume was 0.5 µL. Separations were performed on an Acquity BEH C18 2.1×100 mm column, 1.7 µm particle diameter (Waters, Milford, MA, USA). The autosampler temperature was 24°C, and the column temperature was 50°C. The binary mobile phase, 0.1% acetic acid in water (solvent A), and 0.1% acetic acid in methanol (Solvent B), had a flow rate of 0.42 ml/min. The total run time was 21.0 min. The linear gradient was: 0.0, 93.0; 4.5, 85.0; 10.0, 70.0; 13.0, 10.0; 15.0, 0.0; 16.5, 0.0; 17.0, 93.0; 21.0, 93.0 [cumulative run time (min), % solvent A]. Detection of metabolites was performed with an Agilent 1260 DAD in line with a hybrid Triple Quadrupole/Ion trap mass spectrometer QTRAP 5500 from AB Sciex (Framingham, MA, USA), run in negative ionization mode. The UV spectral data were recorded from 210 to 400 nm, and compounds were detected at 280 nm. The MS parameters were: curtain gas, 30 psi; ionization, 4500 V; temperature, 550ºC; nebulizer gas, 60 psi; heating gas, 60 psi; declustering potential, 80 eV; and entrance potential, 10 eV. The enhanced full-scan (EMS) survey was conducted for masses ranging from 100 to 1000 *m/z* with a collision energy of 10 eV and a scan rate of 10,000 *m/z*/s. Information Dependent Acquisition (IDA) was used to obtain MS/MS spectra with a scan range from 100 to 1,000 *m/z*. IDA threshold was set at 500,000 cps, and a dynamic exclusion was set to 10 s after 2 appearances to permit detection of co-eluting compounds. AB Sciex Analyst 1.6.1 software was used to acquire and process both UV spectral and mass spectrometry data. Compounds were identified based on both fragmentation pattern and UV spectral data.

Compounds were quantified using a Waters Acquity H-class 1200 series UHPLC equipped with a DAD, using the same column, instrumental conditions and linear gradient as above. Data acquisition was performed using the Empower 3 software (Waters), and peak areas at 280 nm were integrated using the apex-track algorithm. We used a minimum detectable peak area of 12,500 peak area units, and we corrected the peak area of each compound by dividing it by the peak area of the internal standard. The retention times and DAD data of detected compounds were compared with the Agilent UHPLC chromatogram to match to the corresponding identified peaks. We produced five-point standard curves ($R^2 > 0.99$) of identified

phenolics, or their closest available equivalents, using authentic standards. Initial biomass dry weights (dw) were used to calculate the *in planta* levels of the identified phenolic compounds, as mg compound /g dw. We quantified unknown phenolic compounds as internal standard-equivalent peak area per g dw. A known concentration of pinosylvin was analyzed every 25 samples as a check standard (%RDS < 2). Caffeic acid, ferulic acid, trans-coumaric acid, quercetin, and vanillic acid were obtained from Sigma-Aldrich. Dihydro-coniferyl alcohol was obtained from MP Biomedicals (Illkirch, France). Catechin, isorhamnetine, pinocembrin, pinoresinol, pinosylvin, pinosylvin monomethyl ether, procyanidin B2 and taxifolin were obtained from Apin Chemicals (Abingdon, UK). HPLC grade methanol and acetic acid were obtained from Fisher Scientific (Pittsburg, PA, USA).

Non-Structural Carbohydrates

Concentrations of water-soluble sugars and total starch were quantified using protocols from Chow and Landhausser (2004). Ground tissues were oven-dried at 70 °C for 3 d. Water-soluble sugar was extracted from 50 mg tissue in 80% hot ethanol and measured colorimetrically using a spectrophotometer (Pharmacia LKB Ultrospec III, Sparta, NJ, USA) at a wavelength of 490 nm after reaction with phenol-sulfuric acid. Following sugar extraction, starch in the remaining residue was solubilized by sodium hydroxide and enzymatically digested by a mixture of α-amylase (ICN 190151, from *Bacillus lichenformis*) and amyloglucosidase (Sigma A3514, from *Aspergillus niger*). The coloring reagent peroxidase-glucose oxidase/*o*-dianisidine was combined with the resultant glucose hydrolysate (Sigma Glucose Diagnostic Kit 510A). Total starch concentration was measured at a wavelength of 525 nm.

Minerals

Tissues were slightly thawed to allow separation of cambium from outer-bark. A 2.54 cm square of cambium was excised, dried, weighed and its dimensions (dried thickness and area) recorded. Dried sample weights were multiplied by dried surface area and thickness to obtain g/cm^3. All dried cambium tissue was then ground in a coffee grinder to a fine particle size for nutrient analysis. Tissue N levels were analyzed using a standard micro-Kjeldahl procedure, and other elements were determined using an inductively-coupled plasma emission spectrometer (ICP). Nutrient concentrations (% or ppm values converted to %) were multiplied by the mean bark biomass of each tree sample (average of two reps) to obtain nutrient content.

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Suppl. Table 1: Locations and elevations of study sites for chemical analyses of *Pinus contorta* and *P. albicaulis* in south-central Montana, USA.

Site Name	Elevation (m) Plot Center	Elevation (m) Plot Minimum	Elevation (m) Plot Maximum	Latitude	Longitude
F	2679	2662	2693	45.048	109.909
D	2733	2719	2753	45.057	109.930
E	2767	2738	2808	45.056	109.918
G	2776	2737	2830	45.039	109.915
C	2785	2770	2800	45.061	109.940
B	2844	2806	2866	45.066	109.944
A	2913	2897	2931	45.069	109.944

Suppl. Table 2. Comparison of constitutive concentrations of chemicals in *Pinus contorta* vs. *Pinus albicaulis* phloem.

a. Secondary Compounds

Class	Group	F	P
Terpenes	Monoterpenes	-16.96	0.0001
	Diterpenes	-6.78	0.0104
	Sesquiterpenes	6.43	0.0125
	Total terpenes (***)	-12.24	0.0007
Phenolics	Vanilloids	65.26	0.0001
	Flavonoids (****)	136.47	0.0001
	Hydroxycinnamic acids (***)	-69.92	0.0001
	Phenylpropanoids (***)	1.50	0.2233
	Lignans	-10.67	0.0014
	Stilbenes	0.98	0.3240
	Total phenolics (**)	14.69	0.0002

b. Primary Compounds

Non-structural Carbohydrates	F	P
Starches	48.27	<0.001
Sugars	-2.44	<0.001
Total Non-structural Carbohydrates	2.71	0.103

c: Minerals

Mineral	F	P
Ca	-9.63	0.002
N	1.08	0.301
P	0.95	0.333
K	-1.19	0.278
Mg	-0.27	0.072
S	-2.69	0.103
Zn (*)	3.55	0.062
Mn (*)	-0.32	0.570
Cu	4.05	0.046
Fe (*)	0.17	0.680
B	2.18	0.143
Al (*)	-27.66	<0.001

Elevation Effect: * P<0.05, ** P<0.01, *** P<0.001, **** P<0.0001

Suppl. Table 3: Concentration (mg/g dw) of fully or partially characterized secondary metabolites in in *Pinus albicaulis* and *P. contorta* constitutive and induced phloem tissues. B. Concentration of unknown phenolics expressed in absorbance units / mg of phloem. All numbers represent means ± std error. nd = not detected. C. Mean separations (P<0.05, within row) of absolute values of compounds known to affect *D. ponderosae* behavior. Nat. log(1+) normalized, elevation incorporated.

A.	*P. contorta*			*P. albicaulis*		
	Constitutive	Systemic	Reaction Zone	Constitutive	Systemic	Reaction Zone
Monoterpenes						
α-Thujene	0.03 ± 0	0.03 ± 0	0.31 ± 0.05	0.01 ± 0	0.01 ± 0	0.11 ± 0.02
(-)-α-Pinene	0.31 ± 0.05	0.28 ± 0.04	4.63 ± 0.68	0.62 ± 0.15	0.59 ± 0.1	9.1 ± 0.99
(+)-α-Pinene	0.13 ± 0.03	0.15 ± 0.02	2.62 ± 0.43	0.45 ± 0.1	0.61 ± 0.11	15.13 ± 2.17
Tricyclene	0.02 ± 0	0.02 ± 0	0.19 ± 0.03	0 ± 0	0 ± 0	0.04 ± 0.02
UNK15	0 ± 0	0 ± 0	0.03 ± 0.02	0 ± 0	0 ± 0	0 ± 0
Camphene	0.02 ± 0	0.02 ± 0	0.29 ± 0.03	0.03 ± 0.01	0.04 ± 0.01	0.23 ± 0.04
Myrcene	0.45 ± 0.09	0.45 ± 0.1	3.67 ± 0.51	0.55 ± 0.1	0.77 ± 0.14	8.98 ± 1.49
UNK16_5	0.07 ± 0.01	0.1 ± 0.03	1.31 ± 0.22	0.18 ± 0.04	0.21 ± 0.05	2.21 ± 0.24
(+)-β-Pinene	0.54 ± 0.34	0.26 ± 0.17	0.16 ± 0.04	0.16 ± 0.15	0.1 ± 0.08	0.19 ± 0.04
(-)-β-Pinene	0.87 ± 0.12	0.84 ± 0.13	18.71 ± 3.3	0.56 ± 0.14	0.81 ± 0.2	9.11 ± 2.16
δ-3-Carene	1.28 ± 0.32	1.71 ± 0.49	47.12 ± 11.02	2.08 ± 0.42	2.93 ± 0.58	48.07 ± 7.88
UNK17-9	0.05 ± 0.01	0.12 ± 0.04	1.41 ± 0.22	0.01 ± 0	0.01 ± 0	0.12 ± 0.04
UNK18-03	0 ± 0	0.01 ± 0.01	0.15 ± 0.07	0 ± 0	0 ± 0	0.08 ± 0.03
(-)-Limonene	0.65 ± 0.11	0.67 ± 0.11	3.65 ± 1.2	1.16 ± 0.23	1.14 ± 0.2	18.26 ± 2.61
(+)-Limonene	0.05 ± 0.01	0.05 ± 0.01	5.36 ± 4.61	0.02 ± 0	0.02 ± 0	0.33 ± 0.02
ρ-Cymene	0.02 ± 0	0.02 ± 0	0.37 ± 0.08	0.02 ± 0	0.02 ± 0	0.31 ± 0.05
β-Phellandrene	4.95 ± 0.53	5.13 ± 0.62	75.15 ± 11.06	2.08 ± 0.69	2.03 ± 0.51	14.14 ± 2.22
γ-Terpinene	0.31 ± 0.07	0.33 ± 0.06	3.01 ± 0.62	0.17 ± 0.02	0.23 ± 0.04	2.85 ± 0.36
α-Terpinolene	0.03 ± 0.01	0.03 ± 0	0.09 ± 0.03	0.01 ± 0	0.01 ± 0	0.04 ± 0.02
UNK26-9	0.01 ± 0	0.01 ± 0	0.11 ± 0.06	0.02 ± 0.01	0.03 ± 0.01	0.57 ± 0.07
Bornyl acetate	0.07 ± 0.01	0.06 ± 0.01	1.04 ± 0.2	0.03 ± 0.01	0.04 ± 0.01	0.26 ± 0.05
Sesquiterpenes						
UNK32-7	0.02 ± 0.01	0.01 ± 0	0.02 ± 0.02	0.02 ± 0	0.02 ± 0	0.23 ± 0.04
α-Cubenene	0.01 ± 0.01	0.01 ± 0	0 ± 0	0.1 ± 0.02	0.12 ± 0.02	3.61 ± 0.24
UNK34-8	0.01 ± 0.01	0.01 ± 0	0.01 ± 0.01	0 ± 0	0 ± 0	0 ± 0
UNK37	0.05 ± 0.02	0.05 ± 0.01	0.03 ± 0.02	0.02 ± 0.01	0.02 ± 0.01	0.33 ± 0.04
UNK36	0.01 ± 0	0.01 ± 0	0 ± 0	0.03 ± 0.01	0.04 ± 0.01	0.37 ± 0.04
UNK37-46	0.13 ± 0.05	0.19 ± 0.07	0.03 ± 0.01	0.05 ± 0.01	0.06 ± 0.01	2.09 ± 0.15
β-Caryophellene	0.12 ± 0.06	0.06 ± 0.03	0.06 ± 0.03	0.03 ± 0.01	0.04 ± 0.01	0.93 ± 0.1
γ-Muurolene	0.01 ± 0	0.01 ± 0	0.04 ± 0.02	0.04 ± 0.01	0.05 ± 0.01	1.68 ± 0.11
α-Muurolene	0.02 ± 0.01	0.02 ± 0.01	0.01 ± 0.01	0.56 ± 0.1	0.66 ± 0.1	21 ± 1.46
UNK40-5	0.04 ± 0.01	0.04 ± 0.01	0.1 ± 0.03	0.13 ± 0.05	0.13 ± 0.03	2.35 ± 0.2

UNK40-61	0.02 ± 0.01	0.03 ± 0.01	0 ± 0	0.04 ± 0.01	0.05 ± 0.01	0.56 ± 0.08
δ-Cardinene	0.08 ± 0.04	0.07 ± 0.02	0.15 ± 0.09	0.02 ± 0	0.02 ± 0	0.39 ± 0.06
UNK44-33	0.02 ± 0.01	0.01 ± 0	0.87 ± 0.19	0.1 ± 0.01	0.12 ± 0.02	2.2 ± 0.22
Diterpene Acids						
Sandaracopimaric	0.48 ± 0.06	0.66 ± 0.07	14.92 ± 2.19	0.29 ± 0.05	0.41 ± 0.05	12.96 ± 1
Pimaric	0.2 ± 0.03	1.27 ± 0.97	4.2 ± 0.59	0.31 ± 0.04	0.48 ± 0.05	7.05 ± 0.37
Levopimaric	6.07 ± 0.74	8.64 ± 0.87	167.38 ± 23.96	2.09 ± 0.41	3.08 ± 0.33	64.43 ± 3.1
Isopimaric	3.04 ± 0.44	4.5 ± 0.53	35.69 ± 5.02	3.1 ± 0.42	4.81 ± 0.48	92.94 ± 4.42
Dehydroabietic/ abietic	2.65 ± 0.51	3.87 ± 0.5	40.87 ± 6.75	3.96 ± 0.65	9.03 ± 2.54	136.54 ± 6.58
Neoabietic	1.57 ± 0.25	2.49 ± 0.31	47.96 ± 6.86	0.66 ± 0.11	1.09 ± 0.13	23.38 ± 1.44
Vanilloids						
Hydroxypropiovanillone hexoside	0.57 ± 0.09	0.59 ± 0.1	0.28 ± 0.06	4.79 ± 0.22	5 ± 0.23	1.52 ± 0.17
Vanillic acid derivative	0.13 ± 0.01	0.13 ± 0.01	0.05 ± 0.01	0 ± 0	0 ± 0	0 ± 0
Vanillic acid hexoside	0.07 ± 0.01	0.08 ± 0.01	0.01 ± 0	0 ± 0	0 ± 0	0 ± 0
Vanillin derivative 1	0 ± 0	0 ± 0	0 ± 0	0.52 ± 0.03	0.58 ± 0.04	0.23 ± 0.02
Vanillin derivative 2	0.01 ± 0.01	0.02 ± 0.01	0 ± 0	0.23 ± 0.01	0.25 ± 0.01	0.09 ± 0.01
Vanillin derivative 3	0 ± 0	0 ± 0	0 ± 0	0.05 ± 0.01	0.06 ± 0.01	0.02 ± 0.01
Vanillin derivative 4	0 ± 0	0 ± 0	0 ± 0	0.01 ± 0.01	0.02 ± 0.01	0 ± 0
Flavonoids						
Epi/Catechin	0.17 ± 0.01	0.18 ± 0.01	0.07 ± 0.01	0.23 ± 0.01	0.23 ± 0.01	0.06 ± 0.01
Hyperoside	0.01 ± 0.01	0.01 ± 0.01	0 ± 0	0.1 ± 0.02	0.11 ± 0.01	0.03 ± 0.01
Isorhamnetin derivative	0 ± 0	0 ± 0	0.12 ± 0.02	0 ± 0	0 ± 0	0.14 ± 0.01
Pinocembrin	0 ± 0	0 ± 0	0.51 ± 0.06	0 ± 0	0 ± 0	0.05 ± 0.02
Procyanidin dimer 1	0.07 ± 0.01	0.08 ± 0.01	0.02 ± 0.01	0.4 ± 0.04	0.43 ± 0.04	0.12 ± 0.01
Procyanidin dimer 2	nd	nd	nd	0.06 ± 0.01	0.07 ± 0.01	0.01 ± 0
Procyanidin trimer	0.37 ± 0.04	0.4 ± 0.04	0.37 ± 0.04	1.09 ± 0.1	1.15 ± 0.1	0.63 ± 0.07
Quercetagetin dimethyl ether	0 ± 0	0 ± 0	0.08 ± 0.01	0 ± 0	0 ± 0	0.04 ± 0.01
Taxifolin	0 ± 0	0 ± 0	0.04 ± 0.02	0.01 ± 0.01	0.01 ± 0	0.25 ± 0.04
Taxifolin hexoside	0.02 ± 0.01	0.02 ± 0.01	0.01 ± 0	1.83 ± 0.28	1.75 ± 0.24	0.67 ± 0.11
Hydroxycinnamic acids						
Caffeic acid hexoside	0.04 ± 0.01	0.03 ± 0.01	0.02 ± 0.01	0.14 ± 0.02	0.18 ± 0.02	0.03 ± 0.01
Coumaric acid hexoside	0.44 ± 0.05	0.47 ± 0.05	0.14 ± 0.03	1.56 ± 0.17	1.62 ± 0.16	0.41 ± 0.07
Ferulic acid	0.01 ± 0	0 ± 0	0.05 ± 0.01	0 ± 0	0 ± 0	0 ± 0
Ferulic acid derivative	0 ± 0	0 ± 0	0 ± 0	0.07 ± 0.02	0.09 ± 0.02	0.06 ± 0.01
Ferulic acid hexoside 1	4.7 ± 0.46	4.66 ± 0.32	1.4 ± 0.2	1.32 ± 0.17	1.42 ± 0.19	0.38 ± 0.06
Ferulic acid hexoside 2	0.3 ± 0.04	0.33 ± 0.04	0.16 ± 0.02	0 ± 0	0 ± 0	0 ± 0
Phenylpropanoids						
Dihydroconiferin 1	0 ± 0	0 ± 0	0 ± 0	0.08 ± 0.01	0.07 ± 0.01	0 ± 0

Dihydroconiferin 2	0.12 ± 0.01	0.13 ± 0.01	0.08 ± 0.01	0.06 ± 0.02	0.05 ± 0.01	0 ± 0
Stilbenes						
Pinosylvin	0 ± 0	0 ± 0	0.11 ± 0.01	0 ± 0	0 ± 0	0.01 ± 0
Pinosylvin monomethyl ether	0 ± 0	0 ± 0	0.01 ± 0	0 ± 0	0 ± 0	0.03 ± 0.01
Lignans						
Lignan coumaroyl glucoside derivative	0.02 ± 0.01	0.02 ± 0.01	0 ± 0	0.23 ± 0.02	0.26 ± 0.02	0.1 ± 0.01
Lignan deoxyhexoside	0.65 ± 0.05	0.65 ± 0.05	0.33 ± 0.03	0.75 ± 0.04	0.8 ± 0.06	0.36 ± 0.03
Lignan hexoside 1	0.65 ± 0.07	0.69 ± 0.05	0.3 ± 0.03	0.81 ± 0.05	0.84 ± 0.05	0.25 ± 0.03
Lignan hexoside 2	0.42 ± 0.04	0.41 ± 0.04	0.18 ± 0.03	0.06 ± 0.02	0.06 ± 0.02	0.01 ± 0.01
Lignan xyloside 1	0.18 ± 0.01	0.19 ± 0.01	0.07 ± 0.01	0 ± 0	0 ± 0	0 ± 0
Lignan xyloside 2	1.06 ± 0.07	1.1 ± 0.06	0.45 ± 0.05	0.25 ± 0.02	0.29 ± 0.02	0.1 ± 0.02
Oligoligon	0.01 ± 0	0.01 ± 0	0.01 ± 0	0.18 ± 0.02	0.21 ± 0.02	0.09 ± 0.01
Pinoresinol	0.00	0.00	0.00	nd	nd	nd

B.

	P. albicaulis			*P. contorta*		
	Constitutive	Systemic	Reaction Zone	Constitutive	Systemic	Reaction Zone
unk1	1.12 ± 0.24	1.04 ± 0.12	0.36 ± 0.12	nd	nd	nd
unk2	0.04 ± 0.02	0.02 ± 0	0 ± 0	0.1 ± 0.02	0.12 ± 0.02	0.02 ± 0.02
unk3	nd	nd	nd	0.02 ± 0	0.02 ± 0	0.1 ± 0.02
unk4	nd	nd	nd	0.08 ± 0.02	0.08 ± 0.02	0.02 ± 0
unk5	0.1 ± 0.02	0.1 ± 0.02	0 ± 0	0.14 ± 0.02	0.14 ± 0.02	0.04 ± 0.02
unk6	0 ± 0	0 ± 0	0 ± 0	0.04 ± 0.02	0.04 ± 0.02	0 ± 0
unk7	0 ± 0	0 ± 0	0 ± 0	0.02 ± 0	0.02 ± 0	0 ± 0
unk8	0.32 ± 0.02	0.34 ± 0.02	0.1 ± 0.02	0 ± 0	0 ± 0	0 ± 0
unk9	nd ±	nd ±	nd ±	0.42 ± 0.06	0.42 ± 0.06	0.22 ± 0.02
unk10	0.02 ± 0.02	0.04 ± 0.02	0.02 ± 0	0.02 ± 0	0 ± 0	0.02 ± 0.02
unk11	0 ± 0	0 ± 0	0 ± 0	0.08 ± 0.02	0.08 ± 0.02	0.12 ± 0.02
unk12	0 ± 0	0 ± 0	0 ± 0	0.04 ± 0.02	0.04 ± 0.02	0 ± 0
unk13	0.02 ± 0.02	0.04 ± 0.02	0.06 ± 0.02	0 ± 0	0 ± 0	0 ± 0
unk14	0.02 ± 0.02	0.04 ± 0.02	0 ± 0	0.14 ± 0.04	0.1 ± 0.04	0.12 ± 0.02
unk15	0.38 ± 0.04	0.38 ± 0.04	0.08 ± 0.02	0.32 ± 0.04	0.36 ± 0.04	0.06 ± 0.02
unk16	0.4 ± 0.04	0.42 ± 0.04	0.18 ± 0.02	0.16 ± 0.02	0.18 ± 0.02	0.06 ± 0.02
unk17	nd	nd	nd	0.04 ± 0	0.02 ± 0	0 ± 0
unk18	0.2 ± 0.02	0.22 ± 0.02	0.06 ± 0.02	0.08 ± 0	0.08 ± 0	0.04 ± 0
unk19	0.18 ± 0.02	0.2 ± 0.02	0.1 ± 0.02	0.02 ± 0	0.02 ± 0	0.02 ± 0
unk20	0.18 ± 0.02	0.22 ± 0.04	0.08 ± 0.02	0.12 ± 0.02	0.12 ± 0.02	0.06 ± 0.02

unk21	0 ± 0	0 ± 0	0.14 ± 0.02	0 ± 0	0 ± 0	0 ± 0
unk22	0.12 ± 0.02	0.16 ± 0.02	0.1 ± 0.02	0.14 ± 0.02	0.16 ± 0.02	0.12 ± 0.02
unk23	0.48 ± 0.1	0.48 ± 0.06	0.12 ± 0.06	nd	nd	nd
unk24	0 ± 0	0 ± 0	0 ± 0	0 ± 0	0 ± 0	0.06 ± 0.02
unk25	0 ± 0	0 ± 0	0.14 ± 0.02	0 ± 0	0 ± 0	0 ± 0
unk26	0 ± 0	0 ± 0	0.1 ± 0.02	0 ± 0	0 ± 0	0 ± 0
unk27	0 ± 0	0 ± 0	0 ± 0	0 ± 0	0 ± 0	0.44 ± 0.04
unk28	0 ± 0	0 ± 0	0 ± 0	0.02 ± 0	0.04 ± 0	0 ± 0
unk29	0 ± 0	0 ± 0	0.06 ± 0.02	0 ± 0	0 ± 0	0 ± 0
unk30	0.02 ± 0	0.02 ± 0	0 ± 0	0 ± 0	0 ± 0	0 ± 0
unk31	0 ± 0	0 ± 0	0.12 ± 0.02	0 ± 0	0 ± 0	0 ± 0
unk32	0 ± 0	0 ± 0	0 ± 0	0.02 ± 0	0.02 ± 0	0 ± 0
unk33	0 ± 0	0 ± 0	0 ± 0	0.04 ± 0	0.04 ± 0	0.04 ± 0.02
unk34	0 ± 0	0 ± 0	0 ± 0	0.02 ± 0	0.02 ± 0	0 ± 0
unk35	0 ± 0	0 ± 0	0 ± 0	0 ± 0	0.02 ± 0	0.04 ± 0
unk36	nd	nd	nd	0 ± 0	0.02 ± 0	0.08 ± 0
unk37	0.32 ± 0.1	0.28 ± 0.08	0.08 ± 0.04	0.12 ± 0.02	0.16 ± 0.04	0.02 ± 0.02
unk38	0.02 ± 0	0.02 ± 0	1.28 ± 0.14	0 ± 0	0 ± 0	0 ± 0
unk39	0.06 ± 0.02	0.06 ± 0.02	0.12 ± 0.04	0 ± 0	0 ± 0	0 ± 0
unk40	0.04 ± 0.02	0.06 ± 0.02	0.02 ± 0.02	0 ± 0	0 ± 0	0 ± 0
unk41	nd	nd	nd	0.2 ± 0.02	0.2 ± 0.02	0.08 ± 0.02

C.

	P. contorta			*P. albicaulis*		
	Constitutive	Systemic	Reaction Zone	Constitutive	Systemic	Reaction Zone
(-)-α-Pinene	a	a	b	a	a	c
Myrcene	a	a	b	a	a	c
δ-3-Carene	a	a	b	a	a	b
Limonene	a	a	b	a	a	c
β-Phellandrene	b	bc	d	a	a	c

Suppl. Table 4: Percent compositions of specific compounds within monoterpenes, sesquiterpenes, and diterpenes

	P. contorta			*P. albicaulis*		
	Constitutive	Systemic	Reaction Zone	Constitutive	Systemic	Reaction Zone
Monoterpenes						
α-Thujene	0.3 ± 0	0.2 ± 0	0.2 ± 0.1	0.1 ± 0	0.2 ± 0	0.1 ± 0
(-)-α-Pinene	2.9 ± 0.2	2.7 ± 0.2	2.8 ± 0.2	6.1 ± 0.7	5.8 ± 0.7	7.3 ± 0.8
(+)-α-Pinene	1.3 ± 0.1	1.4 ± 0.1	1.8 ± 0.2	7 ± 1	7.6 ± 1.4	12.8 ± 1.9
Tricyclene	0.1 ± 0	0.1 ± 0	0.1 ± 0	0 ± 0	0 ± 0	0 ± 0
UNK15	0 ± 0	0 ± 0	0 ± 0	0 ± 0	0 ± 0	0 ± 0
Camphene	0.2 ± 0	0.2 ± 0	0.2 ± 0	0.4 ± 0.1	0.4 ± 0.1	0.2 ± 0
Myrcene	4.5 ± 0.6	4.2 ± 0.6	2.6 ± 0.3	8.6 ± 1.1	7.9 ± 1.2	6.9 ± 1.2
UNK16_5	0.7 ± 0	0.9 ± 0.2	0.7 ± 0.1	2 ± 0.3	2.3 ± 0.3	1.8 ± 0.2
(+)-β-Pinene	2.5 ± 1.4	1.5 ± 1	0.2 ± 0.1	0.5 ± 0.3	0.8 ± 0.6	0.1 ± 0
(-)-β-Pinene	9.4 ± 1.3	8.9 ± 1.3	12.2 ± 1.2	6.1 ± 0.8	7.1 ± 1.2	6.5 ± 1.3
δ-3-carene	14.1 ± 3	14.8 ± 3	19.9 ± 3.2	33.8 ± 3.8	30.1 ± 5	34.5 ± 5
UNK17-9	0.6 ± 0.1	1.2 ± 0.3	4.4 ± 1.7	0.1 ± 0	0.1 ± 0	0.1 ± 0
UNK18-03	0 ± 0	0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0	0 ± 0.	0.1 ± 0
(-)-Limonene	6.7 ± 1.1	6.8 ± 1.1	2.2 ± 0.9	14.2 ± 1.6	15 ± 2.2	15 ± 2.2
(+)-Limonene	0.5 ± 0	0.5 ± 0	3 ± 1.9	0.2 ± 0	0.3 ± 0	0.3 ± 0
ρ-Cymene	0.1 ± 0	2.7 ± 2.7	0 ± 0	0.1 ± 0	0.1 ± 0	0 ± 0
β-phellandrene	52.4 ± 2.4	50.1 ± 2.9	47.3 ± 3.3	17.9 ± 2.3	19.1 ± 3.1	11.4 ± 1.8
γ-terpinene	0.2 ± 0	0.1 ± 0	0.2 ± 0.1	0.2 ± 0.1	0.2 ± 0	0.2 ± 0
α-terpinolene	3.1 ± 0.5	3.1 ± 0.5	1.9 ± 0.3	2.3 ± 0.2	2.4 ± 0.2	2.1 ± 0.2
UNK26-9	0.2 ± 0	0.2 ± 0	0.1 ± 0	0.1 ± 0	0.2 ± 0.1	0 ± 0
Bornyl acetate	0.1 ± 0	0.1 ± 0	0 ± 0	0.3 ± 0.1	0.3 ± 0.1	0.5 ± 0.1
Sesquiterpenes						
UNK32-7	4.6 ± 1.7	3.9 ± 1.5	2.4 ± 2.1	1.2 ± 0.3	1.8 ± 0.4	0.7 ± 0.2
α-Cubenene	0.8 ± 0.4	1.6 ± 0.7	0.3 ± 0.2	9.1 ± 0.5	9.3 ± 0.8	10.1 ± 0.1
UNK34-8	1.6 ± 0.9	3 ± 1.3	0.3 ± 0.8	0 ± 0	0.3 ± 0.2	0 ± 0
UNK37	16.5 ± 5.2	12.6 ± 3.6	4.8 ± 2.9	1 ± 0.3	1.2 ± 0.3	1 ± 0.2
UNK36	0.9 ± 0.5	1 ± 0.4	0 ± 0.1	3.3 ± 0.9	3.7 ± 1	1.1 ± 0.1
UNK37-46	26 ± 5.1	37.3 ± 6.6	2.7 ± 5.3	3.5 ± 0.3	4.1 ± 0.3	5.8 ± 0.2
β-Caryophellene	11.7 ± 4.6	5.4 ± 2.8	13.8 ± 5.7	2.8 ± 0.4	2.8 ± 0.3	2.6 ± 0.2
γ-Muurolene	1.7 ± 0.6	2.4 ± 0.8	2.7 ± 1.2	3 ± 0.3	3.3 ± 0.3	4.7 ± 0.1
α-Muurolene	4.3 ± 1.4	2.8 ± 1.2	1 ± 0.9	48.8 ± 1.8	46.3 ± 2.3	58.3 ± 0.7
UNK40-5	7.9 ± 1.7	7 ± 1.9	10.6 ± 3.6	9.7 ± 1	9.6 ± 0.9	6.4 ± 0.3
UNK40-61	6.3 ± 1.4	4.8 ± 1	0 ± 0.1	3.7 ± 0.6	4.4 ± 0.7	1.6 ± 0.2
δ-Cardinene	13.9 ± 2.2	16.2 ± 3.3	5.6 ± 2.4	1.5 ± 0.3	2.2 ± 0.7	1.1 ± 0.2
UNK44-33	3.8 ± 1.7	2.1 ± 0.7	55.9 ± 7.4	12.4 ± 1.4	10.9 ± 1.6	6.6 ± 0.7
Diterpene acids						
Sandaracopimaric	3.6 ± 0.2	3.4 ± 0.2	4.7 ± 0.3	3.1 ± 0.2	2.5 ± 0.3	3.8 ± 0.3
Pimaric	1.5 ± 0	3 ± 1.5	1.4 ± 1.4	3.2 ± 0.2	2.9 ± 0.2	2.2 ± 0.1
Levopimaric	45.2 ± 1.2	42.3 ± 1.3	51.9 ± 1.7	18.7 ± 0.6	17.8 ± 0.8	19.1 ± 0.3
Isopimaric	21.5 ± 0.7	20.9 ± 0.7	11.9 ± 0.6	30.2 ± 0.8	28.6 ± 1.0	27.6 ± 0.5
Dehydroabietic/ abietic	16.8 ± 1.5	17.7 ± 1.1	14.9 ± 1.2	38.3 ± 1.3	41.9 ± 1.9	40.4 ± 0.5
Neoabietic	11.5 ± 0.8	12.7 ± 0.9	15.2 ± 0.7	6.4 ± 0.5	6.3 ± 0.3	6.9 ± 0.3

Suppl. Table 5. Chromatographic, UV, mass-spectral data, and assigned identities of phenolic compounds isolated from phloem of *Pinus albicaulis* (Pa) and *P. contorta* (Pc).

Compound number	PDA RT	$[M-H]^-$	Main fragments by ESI-MS[b]	λ_{max} (nm)	Assigned identity	Standard equivalent	Species	References
1	1.72	343	163, 135, 93	220, 284	Unknown 1	-	Pa	
2	1.81	353	207, 161	224, 276	Unknown 2	-	Pc	
3	1.83	ND	ND	282	Unknown 3	-	Pa	
4	1.87	329	167, 108, 152	214, 253, 290 (sh)	Vanillic acid hexoside	Vanillic acid	Pc	(10)
5	2.11	167	108, 152	213, 253, 289 (sh)	Vanillic acid derivative	Vanillic acid	Pc	(7, 10)
6	2.33	ND	ND	230, 280, 308 (sh)	Vanillin derivative 1	Vanillic acid	Pa	(3)
7	2.55	ND	ND	230, 280, 308 (sh)	Vanillin derivative 2	Vanillic acid	Pa, Pc	(3)
8	2.62	577	407, 289, 161, 125, 425	278	Procyanidin dimer 1	Procyanidin B2	Pa, Pc	(4)
9	2.80	325	163, 119	219, 294	Coumaric acid hexoside	Trans-coumaric acid	Pa, Pc	(5)
10	3.08	865	407, 577, 125, 289	278	Procyanidin trimer	Procyanidin B2	Pa, Pc	(4)
11	3.18	343	181, 328, 165	279	Dihydroconiferin 1	Dihydro-coniferyl alcohol	Pa	(5)
12	3.44	289	245, 203	226, 281	Epi/Catechin	Catechin	Pa, Pc	(10)
13	3.63	ND	ND	284	Unknown 4	-	Pc	
14	3.88	327	147	219, 277	Unknown 5	-	Pa, Pc	
15	3.99	355	193	216, 290, 320 (sh)	Ferulic acid hexoside 1	Ferulic acid	Pa, Pc	(3)
16	4.24	341	179, 119, 161	212, 257, 295 (sh)	Caffeic acid hexoside	Caffeic acid	Pa, Pc	(1)
17	4.30	355	193	216, 290, 320 (sh)	Ferulic acid hexoside 2	Ferulic acid	Pc	(3)
18	5.02	ND	ND	229, 276, 304 (sh)	Unknown 6	-	Pa	
19	5.04	343	181, 161, 166	276	Dihydroconiferin 2	Dihydro-coniferyl alcohol	Pa, Pc	(5)
20	5.22	357	177, 162	229, 276, 304 (sh)	Hydroxypropiovanillone hexoside	Vanillic acid	Pa, Pc	(3, 10)
21	5.40	ND	ND	278	Unknown 7	-	Pa	
22	5.63	ND	ND	231, 284, 318 (sh)	Unknown 8	-	Pa	
23	5.92	ND	ND	291	Unknown 9	-	Pa, Pc	

24	5.94	577	285, 407	279	Procyanidin dimer 2	Procyanidin B2	Pa, Pc	(4)
25	6.21	311	149	213, 264	Unknown 10	-	Pa, Pc	
26	6.63	381	235, 161, 299	265, 300 (sh)	Unknown 11	-	Pa, Pc	
27	6.68	417	181, 166	278	Unknown 12	-	Pa, Pc	
28	6.80	417	181, 166, 121, 235	225, 279	Unknown 13	-	Pa, Pc	
29	6.94	525	389, 307	277	Unknown 14	-	Pc	
30	7.09	507	315, 327, 300, 345	280	Lignan hexoside 1	Pinoresinol	Pa, Pc	(3, 10)
31	7.35	507	315, 327, 300, 345	280	Lignan hexoside 2	Pinoresinol	Pa, Pc	(3, 10)
32	7.43	381	249, 161	284 (sh), 322	Unknown 15	-	Pc	
33	7.44	465	285, 303	289	Taxifolin hexoside	Taxifolin	Pa, Pc	(3)
34	7.51	357	195, 180	224, 267, 301 (sh)	Vanillin derivative 3	Vanillic acid	Pa	(10)
35	7.60	193	134	287 (sh), 321	Ferulic acid	Ferulic acid	Pc	(7, 9)
36	7.63	303	137, 285	289	Taxifolin	Taxifolin	Pa, Pc	(3, 9)
37	7.74	387	195, 180	224, 267, 301 (sh)	Vanillin derivative 4	Vanillic acid	Pa	(10)
38	7.88	495	363, 167, 179, 327	227, 278	Lignan xyloside 1	Pinoresinol	Pc	(3, 10)
39	8.05	495	363, 167, 149, 179	227, 278	Lignan xyloside 2	Pinoresinol	Pa, Pc	(3, 10)
40	8.62	ND	ND	279	Unknown 16	-	Pa	
41	9.09	509	377, 341, 179, 161	278	Unknown 17	-	Pa, Pc	
42	9.22	509	449, 377, 329, 195, 165	278	Unknown 18	-	Pa, Pc	
43	9.33	433	345, 221	278	Unknown 19	-	Pc	
44	9.35	363	167, 179	284	Unknown 20	-	Pa	
45	9.63	491	315, 354, 327	280	Lignan deoxyhexoside	Pinoresinol	Pa, Pc	(3, 10)
46	9.86	315	300, 255, 269, 121	281	Isorhamnetin derivative	Isorhamnetin	Pa, Pc	(6)
47	10.40	ND	ND	281	Unknown 21	-	Pa, Pc	
48	10.44	441	330, 397	240 (sh), 262	Unknown 22	-	Pa, Pc	
49	10.72	463	301, 271, 255	229, 278	Hyperoside	Quercetin	Pa, Pc	(7)
50	11.34	695	555, 549, 387	280	Lignan derivative 1	Pinoresinol	Pa, Pc	(2)
51	11.51	523	229, 123	281	Unknown 23	-	Pa, Pc	
52	11.63	ND	ND	279	Unknown 24	-	Pa, Pc	
53	11.68	ND	ND	279	Unknown 25	-	Pa, Pc	
54	11.80	ND	ND	281	Unknown 26	-	Pa, Pc	
55	11.83	ND	ND	230, 279	Unknown 27	-	Pa, Pc	

56	11.90	565	403, 241	304, 318 (sh)	Unknown 28	-	Pa	
57	11.94	557	555, 509, 165, 361	281	Lignan derivative 2	Pinoresinol	Pa, Pc	(2)
58	12.10	ND	ND	281	Unknown 29	-	Pa, Pc	
59	12.28	357	ND	229, 280	Pinoresinol	Pinoresinol	Pa, Pc	(2)
60	12.43	ND	ND	291	Unknown 30	-	Pc	
61	12.49	ND	ND	286	Unknown 31	-	Pa, Pc	
62	12.86	ND	ND	274	Unknown 32	-	Pa	
63	12.95	211	ND	299, 312 (sh)	Pinosylvin	Pinosylvin	Pa, Pc	(9)
64	13.24	255	213	290	Pinocembrin	Pinocembrin	Pa, Pc	(9)
65	13.25	193	134, 178	290 (sh), 325	Ferulic acid derivative	Ferulic acid	Pa	(7)
66	13.28	ND	ND	268, 293 (sh)	Unknown 33	-	Pc	
67	13.29	ND	ND	266, 303 (sh)	Unknown 34	-	Pc	
68	13.33	ND	ND	286	Unknown 35	-	Pa	
69	13.40	ND	ND	290 (sh), 325	Unknown 36	-	Pa	
70	13.56	ND	ND	274	Unknown 37	-	Pa	
71	13.57	ND	ND	260, 303 (sh)	Unknown 38	-	Pc	
72	13.60	225	210	299, 312 (sh)	Pinosylvin monomethyl ether	Pinosylvin monomethyl ether	Pa, Pc	(9)
73	13.77	345	330, 133	275, 300 (sh)	Quercetagetin dimethyl ether	Quercetin	Pa, Pc	(8)
74	13.80	ND	ND	219, 268, 303 (sh)	Unknown 39	-	Pc	
75	14.00	ND	ND		Unknown 40	-	Pc	
76	14.42	321	277	248, 290 (sh), 324	Unknown 41	-	Pa, Pc	

[a]Main fragments are reported in order of decreasing abundance; RT = Retention time; (sh) = Shoulder; ND = Not detected;

Suppl. Table 6. Comparison of constitutive compounds known to be behavior-modifying to mountain pine beetle and associated microbes in *Pinus contorta* vs. *Pinus albicaulis* phloem

Class	Group	F	P
Monoterpenes	β -phellandrene	-90.96	<0.001
	(-)-α pinene	71.86	<0.001
	Myrcene	6.35	0.013
	3-Carene	16.21	<0.001
	Limonene	20.57	<0.001
Phenylpropanoids	4-Allylanisole	-6.98	0.009

No Elevation Effect

Suppl. Table 7. Sources of variation (ANOVA) of total concentrations of compounds in *Pinus contorta* vs. *Pinus albicaulis* phloem

a. Secondary Compounds

Class	Group	Source	F	P
Terpenes	Monoterpenes	Species	0.55	0.461
		Treatment	265.78	<0.001
		Species X Treatment	1.20	0.307
	Diterpenes	Species	0.15	0.696
		Treatment	384.21	<0.001
		Species X Treatment	3.99	0.021
	Sesquiterpenes	Species	125.05	<0.001
		Treatment	418.62	<0.001
		Species X Treatment	249.65	<0.001
	Total terpenes	Species	0.16	0.695
		Treatment	385.78	<0.001
		Species X Treatment	2.52	0.086
Phenolics	Vanilloids (*)	Species	362.41	<0.001
		Treatment	173.71	<0.001
		Species X Treatment	46.85	<0.001
	Flavonoids (*)	Species	73.39	<0.001
		Treatment	2.16	0.121
		Species X Treatment	51.68	<0.001
	Hydroxycinnamic acids	Species	30.45	<0.001
		Treatment	213.66	<0.001

	Species X Treatment	0.64	0.532
Phenylpropanoids (*)	Species	10.01	0.003
	Treatment	31.11	<0.001
	Species X Treatment	6.82	0.002
Lignans	Species	5.06	0.029
	Treatment	156.21	<0.001
	Species X Treatment	0.22	0.804
Stilbenes	Species	8.64	0.005
	Treatment	73.55	<0.001
	Species X Treatment	24.13	<0.001
Total phenolics	Species	13.99	0.001
	Treatment	156.84	<0.001
	Species X Treatment	4.76	0.011

b. Primary Compounds

Non-structural carbohydrates	**Source**	**F**	**P**
Starches	Species	14.54	<0.001
	Treatment	127.61	<0.001
	Species X Treatment	2.63	0.077
Sugars (*)	Species	14.22	<0.001
	Treatment	37.52	<0.001
	Species X Treatment	1.10	0.338
Total non-structural carbohydrates	Species	0.31	0.581
	Treatment	98.06	<0.001

	Species X Treatment	0.88	0.419

Elevation Effect: * $P < 0.05$

Suppl. Table 8. Sources of variation (ANOVA) of total concentrations of compounds with known bioactivity to mountain pine beetle and associates

Class	Group	Source	F	P
Terpenes	β -phellandrene	Species	59.07	<0.001
		Treatment	6.69	0.002
		Species X Treatment	1.40	0.251
	(-)-α pinene	Species	20.84	<0.001
		Treatment	1.95	0.147
		Species X Treatment	1.82	0.168
	Myrcene	Species	3.08	0.086
		Treatment	16.23	<0.001
		Species X Treatment	6.11	0.003
	3-Carene	Species	4.26	0.045
		Treatment	5.43	0.006
		Species X Treatment	0.31	0.737
	Limonene	Species	12.29	0.001
		Treatment	2.91	0.059
		Species X Treatment	3.18	0.046
Phenylpropanoids	4-allylanisole	Species	10.79	0.002
		Treatment	53.73	<0.001
		Species X Treatment	12.80	<0.001

Suppl. Table 9A: Correlations among compounds in Whitebark Pine. R values highlighted in green or yellow for significant (P<0.05) positive and negative relationships, respectively.

	Monoter	4-AA	Sesquiter	Van	Flav	Hydroxy	Phenyl	Stilbene	Ligand	Sugar	Starch	Carbohy	Terpenes	Phenolics
Constitutive														
Diterp	0.75	0.47	0.61	0.00	-0.02	0.27	0.05	0.06	-0.01	0.06	0.01	0.04	0.93	0.12
Monoter		0.56	0.84	0.06	-0.03	0.21	-0.09	-0.01	-0.10	0.15	-0.11	0.03	0.94	0.07
4-AA			0.52	-0.08	0.03	0.08	0.03	-0.10	-0.01	0.22	-0.09	0.13	0.54	0.03
Sesquiter				0.03	-0.22	0.09	-0.20	-0.07	-0.16	0.00	-0.13	-0.09	0.79	-0.09
Van					0.15	0.10	0.12	-0.03	0.57	-0.11	0.21	0.04	0.02	0.56
Flav						0.42	0.66	0.00	0.18	0.25	0.11	0.30	-0.06	0.78
Hydroxy							0.32	-0.07	-0.07	0.15	0.00	0.14	0.23	0.69
Phenyl								-0.07	0.32	0.14	0.16	0.22	-0.06	0.60
Stilbene									-0.02	-0.11	0.20	0.08	0.02	-0.06
Ligand										-0.14	0.24	0.03	-0.09	0.44
Sugar											-0.13	0.74	0.12	0.15
Starch												0.55	-0.06	0.16
Carbohy													0.04	0.25
Terpenes														0.06
Reaction Zone														
Diterp	0.64	0.14	0.64	-0.62	-0.52	-0.70	-0.48	-0.15	-0.49	0.04	0.07	0.06	0.95	-0.67
Monoter		0.09	0.75	-0.43	-0.49	-0.58	-0.59	-0.44	-0.39	-0.03	-0.15	-0.08	0.83	-0.54
4-AA			0.13	-0.13	0.15	-0.07	-0.20	-0.19	-0.21	-0.14	-0.13	-0.15	0.14	-0.06
Sesquiter				-0.38	-0.22	-0.33	-0.36	-0.37	-0.28	-0.03	0.01	-0.01	0.78	-0.34
Van					0.59	0.55	0.24	0.19	0.90	-0.20	0.16	-0.05	-0.60	0.89
Flav						0.74	0.30	0.09	0.54	0.00	0.21	0.10	-0.55	0.86
Hydroxy							0.27	-0.06	0.45	0.02	0.23	0.12	-0.70	0.79
Phenyl								0.33	0.32	0.04	0.07	0.05	-0.55	0.30
Stilbene									0.17	0.12	0.05	0.09	-0.39	0.15
Ligand										-0.21	0.24	-0.01	-0.51	0.83
Sugar											0.63	0.93	0.03	-0.08
Starch												0.87	-0.01	0.24
Carbohy													0.01	0.06
Terpenes														-0.67

							Induced Systemic							
Diterp	0.72	0.48	0.61	0.20	0.08	-0.03	0.11	-0.34	-0.08	0.00	-0.03	-0.03	0.97	0.09
Monoter		0.57	0.71	0.36	0.21	-0.01	0.33	-0.41	0.26	-0.19	0.20	-0.11	0.87	0.28
4-AA			0.37	0.21	0.50	0.22	0.29	-0.15	0.20	-0.18	0.24	-0.08	0.53	0.45
Sesquiter				0.16	0.11	0.04	0.18	-0.31	-0.06	0.05	0.12	0.11	0.70	0.10
Van					0.15	-0.07	0.23	-0.07	0.69	-0.26	0.13	-0.24	0.27	0.55
Flav						0.67	0.76	0.02	0.25	-0.01	0.19	0.10	0.11	0.86
Hydroxy							0.46	-0.07	-0.04	0.25	0.02	0.29	-0.03	0.69
Phenyl								0.10	0.38	0.02	0.26	0.17	0.19	0.70
Stilbene									0.11	0.15	0.06	0.20	-0.40	-0.03
Ligand										-0.37	0.37	-0.27	0.03	0.55
Sugar											-0.54	0.90	-0.07	-0.09
Starch												-0.14	0.05	0.22
Carbohy													-0.06	0.00
Terpenes														0.15

Abbreviations: Diterp: Diterpenes; Monoter: Monoterpenes; 4-AA: 4-allyanisole; Sesquiter: Sesquiterpenes; Van: Vanilloids; Flav: Flavonoids; Hydroxy: Hydroxycinnamic Acids; Phenyl: Phenylpropanoids; Stilbene: Stilbenes; Ligand: Ligands; Sugar: Sugars; Starch: Starches; Carbohy: Carbohydrates: Terpenes: Total Terpenes; Phenolics: Total Phenolics

Suppl. Table 9B: Correlations among compounds in Lodgepole Pine. R values highlighted in green or yellow for significant (P<0.05) positive and negative relationships, respectively.

	Monoter	4-AA	Sesquiter	Van	Flav	Hydroxy	Phenyl	Stilbene	Ligand	Sugar	Starch	Carbohy	Terpenes	Phenolics
Constitutive														
Diterp	0.46	0.02	0.14	-0.19	0.17	-0.03	0.23	-0.12	0.04	-0.16	-0.08	-0.22	0.84	-0.08
Monoter		0.07	0.56	-0.25	0.11	-0.02	0.12	-0.11	-0.22	-0.05	-0.18	-0.20	0.85	-0.20
4-AA			0.01	-0.11	-0.20	-0.13	0.08	-0.16	-0.21	-0.03	-0.17	-0.15	0.07	-0.24
Sesquiter				0.03	-0.04	-0.10	-0.23	0.06	-0.20	-0.24	-0.04	-0.23	0.48	-0.18
Van					0.32	-0.07	-0.05	0.03	0.36	-0.28	0.35	0.07	-0.22	0.44
Flav						0.25	0.40	-0.12	0.39	-0.08	0.30	0.15	0.17	0.58
Hydroxy							0.43	-0.02	0.41	0.13	-0.26	-0.14	-0.04	0.78
Phenyl								-0.20	0.56	0.15	-0.32	-0.14	0.17	0.46
Stilbene									-0.13	0.02	-0.05	-0.03	-0.13	-0.07
Ligand										0.11	-0.15	-0.01	-0.11	0.74
Sugar											-0.32	0.66	-0.14	0.01
Starch												0.49	-0.13	-0.02
Carbohy													-0.25	-0.02
Terpenes														-0.17
Reaction Zone														
Diterp	0.90	0.55	0.54	-0.35	0.32	-0.17	0.09	0.02	-0.37	-0.72	-0.67	-0.73	0.99	-0.19
Monoter		0.54	0.56	-0.48	0.14	-0.28	-0.02	-0.09	-0.48	-0.61	-0.71	-0.68	0.96	-0.36
4-AA			0.31	-0.12	0.28	-0.31	-0.08	-0.36	-0.37	-0.30	-0.31	-0.32	0.56	-0.26
Sesquiter				-0.33	-0.11	-0.09	0.17	0.08	-0.27	-0.41	-0.40	-0.42	0.56	-0.24
Van					-0.19	0.42	0.28	-0.17	0.47	0.28	0.22	0.28	-0.47	0.52
Flav						0.10	0.09	0.30	0.07	-0.09	0.10	-0.02	0.27	0.31
Hydroxy							0.13	0.19	0.76	0.25	0.33	0.29	-0.21	0.92
Phenyl								-0.01	0.16	-0.27	-0.10	-0.20	0.00	0.23
Stilbene									0.20	0.21	0.29	0.24	0.00	0.24
Ligand										0.45	0.47	0.48	-0.47	0.87
Sugar											0.84	0.98	-0.69	0.32
Starch												0.94	-0.68	0.41
Carbohy													-0.72	0.37
Terpenes														-0.29

							Induced	**Systemic**						
Diterp	0.80	0.13	0.48	0.22	0.56	0.05	0.17	0.11	0.26	0.00	0.15	0.06	0.98	0.22
Monoter		0.16	0.47	0.21	0.47	0.04	0.25	0.12	0.31	-0.09	0.17	0.01	0.91	0.21
4-AA			0.06	0.23	0.19	0.17	0.44	-0.18	0.24	0.15	-0.17	0.14	0.15	0.27
Sesquiter				-0.04	0.06	-0.20	-0.24	0.39	-0.23	-0.10	0.11	-0.08	0.52	-0.21
Van					0.34	0.21	0.06	0.18	0.16	0.17	0.02	0.19	0.22	0.42
Flav						0.23	0.60	-0.12	0.56	0.39	0.27	0.57	0.55	0.51
Hydroxy							0.19	-0.01	0.41	-0.27	0.19	-0.20	0.04	0.91
Phenyl								-0.42	0.69	0.31	-0.15	0.34	0.20	0.44
Stilbene									-0.30	-0.31	0.21	-0.24	0.12	-0.08
Ligand										0.02	0.13	0.12	0.28	0.69
Sugar											-0.41	0.90	-0.04	-0.10
Starch												-0.01	0.18	0.21
Carbohy													0.04	0.00
Terpenes														0.21

Suppl. Table 9C: Correlations among compounds in Lodgepole and Whitebark Pine. R values highlighted in green or yellow for significant (P<0.05) positive and negative relationships, respectively.

	Whitebark Pine														
Mineral:	Diterp	Monoter	4-AA	Sesquiter	Van	Flav	Hydroxy	Phenyl	Stilbene	Ligand	Sugar	Starch	Carbohy	Terpenes	Phenolics
N	0.19	0.22	0.17	0.07	-0.02	0.33	0.32	0.20	-0.10	-0.34	0.28	-0.11	0.14	0.22	0.22
P	0.15	0.18	0.14	0.04	-0.03	0.35	0.32	0.19	-0.11	-0.35	0.26	-0.11	0.13	0.17	0.22
K	0.20	0.23	0.16	0.08	0.01	0.32	0.29	0.18	-0.09	-0.29	0.25	-0.09	0.13	0.22	0.22
Mg	0.19	0.20	0.15	0.06	-0.01	0.29	0.31	0.17	-0.07	-0.29	0.24	-0.10	0.12	0.19	0.21
Ca	0.17	0.14	0.15	0.02	0.01	0.21	0.20	0.10	-0.03	-0.25	0.16	-0.12	0.05	0.15	0.13
S	0.10	0.19	0.13	0.05	0.03	0.25	0.22	0.18	-0.11	-0.28	0.30	-0.22	0.10	0.16	0.17
Zn	0.12	0.10	0.07	0.01	-0.05	0.08	0.12	-0.01	0.15	-0.31	0.18	-0.12	0.07	0.11	0.00
Mn	0.20	0.16	0.11	0.05	-0.05	0.09	0.15	0.05	-0.06	-0.29	0.18	-0.19	0.01	0.17	0.02
Cu	0.04	0.15	0.20	0.16	-0.02	0.08	0.06	-0.02	T0.01	-0.24	0.21	-0.14	0.07	0.10	0.00
Fe	0.23	0.23	0.16	0.09	0.01	0.25	0.32	0.17	-0.06	-0.28	0.23	-0.09	0.12	0.23	0.20
B	0.22	0.18	0.10	0.06	-0.01	0.27	0.30	0.18	-0.12	-0.31	0.21	-0.05	0.12	0.21	0.19
Al	0.16	0.13	0.10	0.00	-0.05	0.28	0.28	0.16	0.01	-0.37	0.19	-0.12	0.06	0.14	0.14

	Lodgepole Pine														
Mineral:	Diterp	Monoter	4-AA	Sesquiter	Van	Flav	Hydroxy	Phenyl	Stilbene	Ligand	Sugar	Starch	Carbohy	Terpenes	Phenolics
N	0.16	0.45	-0.20	0.25	-0.21	-0.08	-0.20	-0.21	0.17	-0.28	0.11	0.05	0.13	0.31	-0.29
P	0.34	0.56	-0.15	0.30	-0.29	-0.03	-0.19	-0.13	0.11	-0.30	0.04	0.03	0.05	0.49	-0.33
K	0.22	0.43	-0.15	0.19	-0.26	-0.13	-0.24	-0.19	0.13	-0.27	0.09	0.03	0.10	0.34	-0.35
Mg	0.16	0.42	-0.20	0.25	-0.25	-0.08	-0.06	-0.16	0.14	-0.19	0.13	-0.04	0.08	0.31	-0.19
Ca	0.11	0.37	-0.01	0.23	-0.31	-0.26	0.03	0.04	0.05	-0.05	0.16	-0.09	0.06	0.27	-0.18
S	0.33	0.41	-0.12	0.15	-0.29	-0.17	-0.20	-0.23	0.15	-0.29	0.04	0.03	0.04	0.37	-0.36
Zn	0.06	0.24	0.03	0.23	-0.23	-0.46	-0.34	-0.26	0.07	-0.21	0.08	-0.13	-0.01	0.12	-0.42
Mn	-0.01	0.04	0.29	-0.13	-0.21	-0.42	-0.24	-0.01	-0.18	-0.03	0.19	-0.24	0.00	0.00	-0.32
Cu	-0.11	0.14	-0.28	0.23	-0.25	-0.10	0.11	-0.18	0.16	-0.19	0.11	-0.11	0.00	0.00	-0.10
Fe	0.00	0.46	-0.21	0.25	-0.18	-0.03	-0.16	-0.19	-0.07	-0.28	0.04	0.06	0.07	0.26	-0.25
B	0.14	0.30	-0.05	0.12	-0.16	-0.23	-0.30	-0.27	0.09	-0.22	0.02	0.01	0.04	0.23	-0.34
Al	0.20	0.49	-0.25	0.24	-0.29	-0.04	-0.09	-0.09	0.08	-0.24	0.20	0.01	0.16	0.37	-0.26

Suppl. Table 10A: Statistical significance of relationships among compounds in Whitebark Pine. P values are highlighted in green or yellow for significant (P<0.05) positive and negative relationships, respectively.

	Monoter	4-AA	Sesquiter	Van	Flav	Hydroxy	Phenyl	Stilbene	Ligand	Sugar	Starch	Carbohy	Terpenes	Phenolics
Constitutive														
Diterp	0.00	0.00	0.00	0.99	0.89	0.02	0.65	0.62	0.91	0.59	0.92	0.69	0.00	0.30
Monoter		0.00	0.00	0.62	0.77	0.05	0.42	0.94	0.36	0.18	0.32	0.76	0.00	0.52
4-AA			0.00	0.48	0.80	0.49	0.77	0.35	0.96	0.05	0.40	0.25	0.00	0.79
Sesquiter				0.79	0.05	0.43	0.07	0.56	0.16	0.97	0.23	0.43	0.00	0.41
Van					0.18	0.35	0.29	0.80	0.00	0.32	0.06	0.71	0.85	0.00
Flav						0.00	0.00	0.98	0.11	0.02	0.33	0.01	0.59	0.00
Hydroxy							0.00	0.51	0.54	0.17	0.99	0.20	0.04	0.00
Phenyl								0.55	0.00	0.21	0.16	0.05	0.58	0.00
Stilbene									0.88	0.33	0.07	0.48	0.86	0.61
Ligand										0.22	0.03	0.77	0.41	0.00
Sugar											0.23	0.00	0.28	0.17
Starch												0.00	0.57	0.15
Carbohy													0.72	0.03
Terpenes														0.58
Induced Local														
Diterp	0.00	0.47	0.00	0.00	0.00	0.00	0.01	0.43	0.01	0.84	0.74	0.77	0.00	0.00
Monoter		0.64	0.00	0.03	0.01	0.00	0.00	0.02	0.05	0.90	0.45	0.68	0.00	0.00
4-AA			0.52	0.52	0.45	0.74	0.31	0.34	0.29	0.50	0.51	0.46	0.50	0.78
Sesquiter				0.05	0.26	0.09	0.07	0.06	0.15	0.89	0.97	0.96	0.00	0.08
Van					0.00	0.00	0.23	0.33	0.00	0.30	0.41	0.80	0.00	0.00
Flav						0.00	0.12	0.65	0.00	0.98	0.28	0.61	0.00	0.00
Hydroxy							0.16	0.78	0.02	0.93	0.24	0.54	0.00	0.00
Phenyl								0.08	0.10	0.85	0.74	0.80	0.00	0.12
Stilbene									0.38	0.56	0.80	0.66	0.05	0.46
Ligand										0.28	0.21	0.95	0.01	0.00
Sugar											0.00	0.00	0.90	0.67
Starch												0.00	0.95	0.21
Carbohy													0.95	0.75
Terpenes														0.00
Induced Systemic														
Diterp	0.00	0.01	0.00	0.32	0.68	0.87	0.60	0.08	0.69	1.00	0.87	0.89	0.00	0.66
Monoter		0.00	0.00	0.07	0.29	0.95	0.09	0.03	0.19	0.34	0.32	0.58	0.00	0.15
4-AA			0.06	0.29	0.01	0.28	0.14	0.46	0.31	0.36	0.23	0.71	0.00	0.02
Sesquiter				0.43	0.59	0.84	0.36	0.12	0.77	0.80	0.55	0.58	0.00	0.61
Van					0.45	0.74	0.26	0.74	0.00	0.20	0.53	0.23	0.18	0.00
Flav						0.00	0.00	0.94	0.21	0.97	0.34	0.63	0.58	0.00
Hydroxy							0.01	0.74	0.84	0.21	0.92	0.14	0.87	0.00
Phenyl								0.60	0.05	0.94	0.18	0.39	0.35	0.00
Stilbene									0.57	0.45	0.77	0.32	0.04	0.87
Ligand										0.06	0.06	0.17	0.87	0.00
Sugar											0.00	0.00	0.73	0.66
Starch												0.47	0.81	0.27
Carbohy													0.76	0.98
Terpenes														0.46

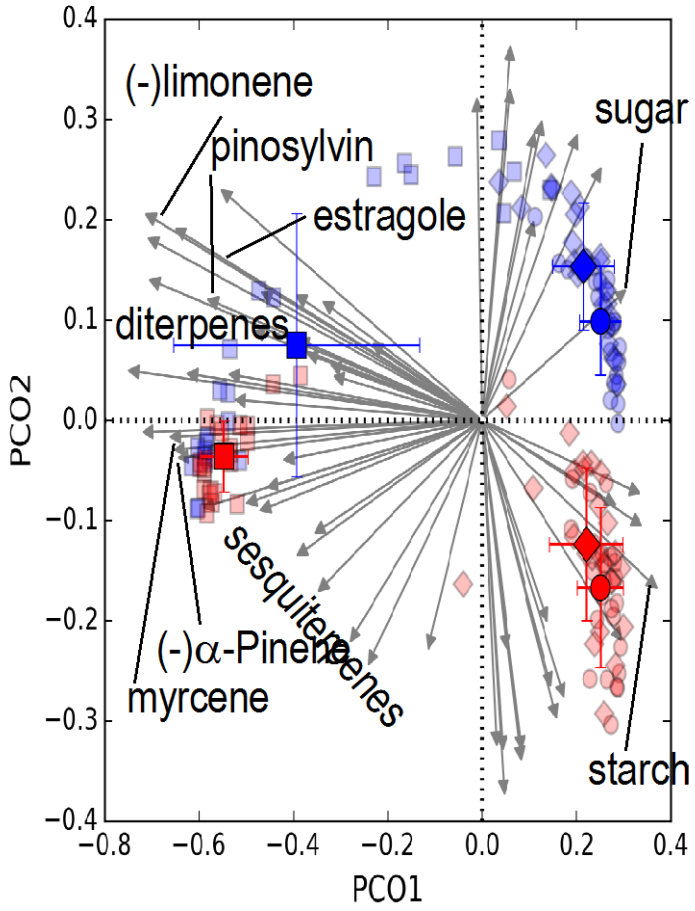
Suppl. Table 10B: Statistical significance of relationships among compounds in Lodgepole Pine. P values are highlighted in green or yellow for significant (P<0.05) positive and negative relationships, respectively.

	Monoter	4-AA	Sesquiter	Van	Flav	Hydroxy	Phenyl	Stilbene	Ligand	Sugar	Starch	Carbohy	Terpenes	Phenolics
Constitutive														
Diterp	0.00	0.92	0.37	0.20	0.26	0.83	0.13	0.45	0.81	0.30	0.59	0.15	0.00	0.59
Monoter		0.65	0.00	0.10	0.48	0.88	0.43	0.48	0.14	0.74	0.23	0.18	0.00	0.19
4-AA			0.94	0.44	0.18	0.39	0.60	0.28	0.16	0.83	0.26	0.33	0.64	0.10
Sesquiter				0.83	0.79	0.48	0.12	0.69	0.17	0.10	0.81	0.12	0.00	0.23
Van					0.03	0.62	0.72	0.82	0.01	0.06	0.02	0.63	0.14	0.00
Flav						0.09	0.01	0.43	0.01	0.57	0.04	0.31	0.28	0.00
Hydroxy							0.00	0.92	0.00	0.39	0.08	0.35	0.77	0.00
Phenyl								0.18	0.00	0.31	0.03	0.35	0.26	0.00
Stilbene									0.39	0.88	0.75	0.86	0.40	0.65
Ligand										0.47	0.33	0.96	0.47	0.00
Sugar											0.03	0.00	0.35	0.93
Starch												0.00	0.39	0.88
Carbohy													0.10	0.91
Terpenes														0.26
Induced														
Diterp	0.00	0.00	0.00	0.08	0.10	0.39	0.67	0.92	0.06	0.00	0.00	0.00	0.00	0.34
Monoter		0.00	0.00	0.01	0.50	0.17	0.92	0.68	0.02	0.00	0.00	0.00	0.00	0.08
4-AA			0.13	0.57	0.18	0.13	0.71	0.07	0.07	0.14	0.13	0.12	0.00	0.21
Sesquiter				0.10	0.61	0.65	0.40	0.70	0.17	0.04	0.04	0.03	0.00	0.24
Van					0.35	0.03	0.15	0.39	0.01	0.16	0.27	0.16	0.02	0.01
Flav						0.61	0.67	0.13	0.73	0.67	0.62	0.92	0.20	0.12
Hydroxy							0.51	0.34	0.00	0.22	0.10	0.14	0.30	0.00
Phenyl								0.95	0.42	0.18	0.63	0.31	0.99	0.25
Stilbene									0.32	0.29	0.14	0.24	1.00	0.23
Ligand										0.02	0.01	0.01	0.02	0.00
Sugar											0.00	0.00	0.00	0.10
Starch												0.00	0.00	0.04
Carbohy													0.00	0.06
Terpenes														0.17
Induced Systemic														
Diterp	0.00	0.52	0.01	0.28	0.00	0.80	0.40	0.60	0.19	0.99	0.45	0.75	0.00	0.28
Monoter		0.42	0.01	0.29	0.01	0.84	0.20	0.55	0.12	0.67	0.41	0.94	0.00	0.29
4-AA			0.78	0.24	0.33	0.38	0.02	0.37	0.22	0.46	0.40	0.48	0.47	0.17
Sesquiter				0.86	0.76	0.33	0.23	0.05	0.26	0.61	0.60	0.71	0.01	0.30
Van					0.09	0.30	0.76	0.37	0.42	0.39	0.91	0.33	0.27	0.03
Flav						0.26	0.00	0.54	0.00	0.04	0.18	0.00	0.00	0.01
Hydroxy							0.33	0.97	0.03	0.18	0.34	0.33	0.85	0.00
Phenyl								0.03	0.00	0.12	0.45	0.08	0.33	0.02
Stilbene									0.12	0.12	0.30	0.23	0.55	0.69
Ligand										0.93	0.53	0.54	0.16	0.00
Sugar											0.03	0.00	0.83	0.61
Starch												0.94	0.36	0.30
Carbohy													0.85	0.98
Terpenes														0.29

Suppl. Table 10C: Statistical significance of relationships among compounds in Whitebark Pine and Lodgepole pine. P values are highlighted in green or yellow for significant (P<0.05) positive and negative relationships, respectively. Abbreviations are described in xyz.

	Whitebark Pine														
Mineral:	Diterp	Monoter	4-AA	Sesquiter	Van	Flav	Hydroxy	Phenyl	Stilbene	Ligand	Sugar	Starch	Carbohy	Terpenes	Phenolics
N	0.08	0.05	0.13	0.54	0.83	0	0	0.07	0.39	0	0.01	0.33	0.19	0.05	0.05
P	0.19	0.1	0.22	0.74	0.79	0	0	0.08	0.31	0	0.02	0.34	0.24	0.14	0.05
K	0.07	0.04	0.14	0.46	0.9	0	0.01	0.11	0.41	0.01	0.02	0.42	0.26	0.05	0.04
Mg	0.09	0.07	0.17	0.6	0.95	0.01	0	0.13	0.55	0.01	0.03	0.37	0.28	0.08	0.06
Ca	0.14	0.2	0.17	0.86	0.92	0.06	0.08	0.38	0.8	0.02	0.14	0.28	0.65	0.17	0.25
S	0.35	0.09	0.26	0.63	0.77	0.02	0.04	0.11	0.33	0.01	0.01	0.05	0.36	0.16	0.13
Zn	0.29	0.37	0.55	0.9	0.63	0.48	0.27	0.94	0.18	0	0.09	0.27	0.55	0.31	0.97
Mn	0.08	0.16	0.32	0.65	0.67	0.42	0.18	0.63	0.6	0.01	0.1	0.08	0.91	0.12	0.86
Cu	0.73	0.19	0.07	0.14	0.83	0.46	0.62	0.85	0.91	0.03	0.05	0.2	0.53	0.39	0.98
Fe	0.03	0.04	0.15	0.43	0.96	0.02	0	0.12	0.6	0.01	0.03	0.42	0.3	0.04	0.07
B	0.04	0.11	0.37	0.58	0.95	0.01	0.01	0.1	0.29	0	0.06	0.63	0.27	0.06	0.08
Al	0.16	0.23	0.36	0.97	0.63	0.01	0.01	0.14	0.93	0	0.09	0.3	0.57	0.21	0.2
	Lodgepole Pine														
Mineral:	Diterp	Monoter	4-AA	Sesquiter	Van	Flav	Hydroxy	Phenyl	Stilbene	Ligand	Sugar	Starch	Carbohy	Terpenes	Phenolics
N	0.3	0	0.17	0.09	0.16	0.6	0.19	0.16	0.26	0.06	0.46	0.76	0.37	0.04	0.05
P	0.02	0	0.31	0.04	0.05	0.82	0.2	0.37	0.48	0.04	0.8	0.82	0.76	0	0.02
K	0.15	0	0.32	0.19	0.08	0.39	0.1	0.2	0.37	0.06	0.55	0.84	0.5	0.02	0.02
Mg	0.29	0	0.17	0.1	0.09	0.6	0.71	0.28	0.36	0.19	0.38	0.8	0.62	0.04	0.21
Ca	0.49	0.01	0.92	0.13	0.03	0.08	0.86	0.79	0.76	0.74	0.29	0.56	0.7	0.07	0.23
S	0.03	0	0.41	0.3	0.04	0.24	0.17	0.12	0.33	0.05	0.77	0.86	0.77	0.01	0.01
Zn	0.67	0.1	0.85	0.12	0.13	0	0.02	0.08	0.66	0.15	0.61	0.39	0.94	0.44	0
Mn	0.94	0.8	0.05	0.38	0.16	0	0.1	0.96	0.22	0.83	0.2	0.11	0.99	0.98	0.03
Cu	0.46	0.34	0.05	0.12	0.09	0.52	0.48	0.23	0.28	0.21	0.45	0.46	0.98	0.98	0.49
Fe	0.98	0	0.15	0.09	0.22	0.82	0.29	0.2	0.64	0.06	0.78	0.69	0.64	0.08	0.09
B	0.35	0.04	0.72	0.43	0.28	0.12	0.04	0.07	0.53	0.14	0.87	0.92	0.77	0.13	0.02
Al	0.19	0	0.09	0.11	0.05	0.78	0.53	0.53	0.6	0.11	0.18	0.95	0.27	0.01	0.08

Supplemental Figure 1. PCO plot of all chemicals *P. albicaulis* (red) and *P. contorta* (blue): constitutive (circle), induced (square) and systemic samples (diamond). Biplot vectors show direction and strength of significant correlations with major chemical groups. Vectors are scaled to data extent. Vectors are not labeled for all chemicals due to the large number of chemicals and significant relationships



Supplemental Figure 2: NMDS of compounds in *P. contorta* and *P. albicaulis*.