

Article

Comparative Analysis of VOC Profiles in *Populus deltoides* cv. Harvard I-63/51 and *P. × canadensis* cv. Conti 12 Poplars Attacked by *Megaplatypus mutatus*

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Abstract

Megaplatypus mutatus, a major poplar pest in South America, tunnels into the xylem, weakening trunks and reducing wood quality. Volatile organic compounds (VOCs) are key mediators of plant–insect interactions and may reflect genotype-specific defence strategies. This study analysed VOC profiles of young and adult *Populus deltoides* cv. Harvard and *P. × canadensis* cv. Conti 12 under natural *M. mutatus* infestation. Gas chromatography–mass spectrometry putatively annotated 31 VOCs, including green leaf volatiles (GLVs), pentyl leaf volatiles (PLVs), terpenes, alcohols, aromatics and phenolics, 12 of which, to our knowledge, have not been previously reported in *Populus* VOC profiles. Harvard trees showed ~14.5-fold higher total VOC abundance than Conti trees. In Conti, constitutive VOC emissions remained stable regardless of infestation status or age. In contrast, under infestation, Harvard trees emitted 10-fold higher constitutive VOCs than non-infested Harvard trees and ~52-fold higher than Conti, a pattern consistent with increased defensive activity. GLVs and PLVs relatively dominated both genotypes, although Harvard showed higher emissions. Terpenes were not detected in young Conti trees under our analytical conditions but were abundant and diverse in infested Harvard trees, which may indicate a stronger terpene-associated response in this clone. Several compounds were detected only under specific genotype–condition combinations in our dataset and therefore represent candidate volatiles for future behavioural and functional studies. These results are consistent with differences in VOC emission patterns between

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genotypes and age classes, improve our understanding of putative chemical cues in the interaction between *Populus* and *M. mutatus*, and provide a basis for future work towards sustainable pest management strategies.

Keywords: pest resistance; volatile organic compounds; ambrosia beetle; plant defence; plant herbivory

1. Introduction

The interaction between plants and insects is crucial to ecological and evolutionary dynamics. Although many interactions are mutually beneficial, such as pollination and zoochory, plants, due to their sessile nature, are vulnerable to negative interactions such as herbivory [1]. Volatile organic compounds (VOCs) have emerged as an adaptive trait in the evolutionary history of plants, playing significant roles in attracting pollinators, natural enemies, and seed dispersers, as well as in plant defence against herbivores and pathogens [1]. Comprising approximately 1% of plant secondary metabolites, VOCs primarily consist of lipophilic molecules with low molecular weight and high vapor pressure, allowing them to cross biological membranes and diffuse into the environment [2].

Among VOCs, the largest group of emitted compounds comprises terpenes, including monoterpenes, sesquiterpenes, and isoprene, the structural precursor of these compounds [3]. To date, approximately 40,000 terpenes have been identified in plants [4]. Some of these terpenes exhibit repellent or attractant activities for herbivores and other animals. Another group of VOCs, known as green leaf volatiles (GLVs), consists of compounds such as six-carbon aldehydes, alcohols, and their acyl esters, all derived from fatty acids via the lipoxygenase (LOX) pathway [5]. GLVs are primarily associated with defence against herbivory and, to a lesser extent, defence against pathogens [5]. These compounds are emitted immediately after damage [6], acting both as direct agents by deterring herbivores and pathogens, and as indirect agents by attracting natural enemies [5].

Pentyl leaf volatiles (PLVs), another group of VOCs that are co-emitted with GLVs, are also derived from LOX activity and share structural similarities [7]. Although their biological role is less clear, recent studies suggest they may contribute to tolerance against pests such as aphids and enhance pathogen resistance through oxylipin production [7,8].

Besides the action of individual VOCs, their simultaneous emission can generate synergistic effects [9]. VOCs may act constitutively or be induced under stress [1,10], and their type and rate of emission vary by species and even plant age [11–14].

In addition to their ecological significance, understanding the role of VOCs and their influence on agroecosystems, including forestry, is crucial for pest control. Harnessing this knowledge could enhance forest health and productivity while contributing to the sustainability and economic viability of regional economies.

In the Argentinian Cuyo region, *Populus* spp. (Salicaceae) are central to forestry activities, serving as the main resource for the local wood industry. However, poplars are frequently attacked by their main pest, *Megaplatypus mutatus* (Chapuis) (Platypodidae; Coleoptera), leading to substantial economic losses [15]. This native South American ambrosia beetle is not only widespread in Argentina but is also found in Brazil, Uruguay, Paraguay, Venezuela, Bolivia, Peru, French Guiana, and even Italy [16]. Given its extensive distribution, there are concerns about its potential to become a global invader, particularly targeting *Populus* spp. [17].

Unlike most ambrosia beetles, *M. mutatus* attacks living trees, boring horizontal xylem galleries that appear externally as holes with sawdust [17]. These galleries reduce usable wood volume by causing wind breakage and lowering the quality of timber destined for sawing or veneer production [15]. Males initiate the attack by excavating a short “nuptial” gallery to attract females for mating. This gallery is later extended to shelter their brood. The presence of these galleries and associated fungal communities impacts the wood, darkening the cavities. These communities include species such as the symbiotic ambrosia fungus *Raffaelea* spp. as well as *Graphium basitruncatum*, *Fusarium solani*, *F. oxysporum* species complexes, and *Coprinellus radians*, among others, found in *Populus deltoides* [18]. Such diverse communities underscore the presence of complex multitrophic interactions [18]. The beetle usually prefers larger diameter trees, probably due to the greater space for brood development [19]. Differences in clone susceptibility are mainly attributed to trunk diameter, linked to growth rate, rather than to the genotype itself [19].

In Argentina, observational reports indicate that cultivars such as Harvard (I-63/51) and Conti 12 are among the poplar clones considered comparatively more susceptible to *M. mutatus* in the Cuyo region, whereas some comparative trials in other clone panels have failed to detect significant differences in attack intensity among genotypes [20].

Poplar species are known to emit VOCs in response to herbivory. Numerous studies have investigated VOC emissions in *Populus* spp. associated with insect attacks, including attacks by coleopteran and other insect species e.g., [21–27]. Specifically, Lucia et al. [19] observed quantitative and qualitative differences in VOC emissions, particularly terpenes, between Conti 12 cv. trees attacked by *M. mutatus* and those that were not attacked.

This study aimed to investigate the composition and variability of VOCs emitted in response to *M. mutatus* attacks in two of the most cultivated poplar clones in the Cuyo region. We hypothesise that Harvard and Conti clones differ in their VOC emissions (profile and quantity) given their different susceptibility to *M. mutatus*. This study follows FAO and International Poplar Commission recommendations to base poplar management on local research [28]. We characterized VOCs from Harvard and Conti 12 cultivars of different ages and infestation conditions, all grown in the same plantation, and identified several volatiles previously unreported in poplars. These findings provide insights for developing improved pest control strategies across ecological and physiological contexts.

2. Results

In the Conti poplars, 37 trees were infested, and 63 were non-infested, while among the Harvard poplars, 21 trees were infested, and 79 were non-infested. The binomial GLM analysis of poplar infestation (p -value = 0.01222; residual deviance/df = 1.18) indicated that Conti trees had 2.209 times higher odds of infestation than Harvard trees. A total of 31 VOCs were putatively annotated and categorized into various groups described in Figure 1. Under our analytical conditions, eight VOCs were detected only in Harvard samples and nine only in Conti samples, while 14 were shared between the two cultivars. Twelve of these compounds, to our knowledge, have not been previously reported in *Populus* VOC profiles (Figure 1). Sixteen VOCs were detected in infested Harvard trees and 13 in infested Conti trees. Adult non-infested Conti trees had 19 VOCs, while Harvard had 17. Young Conti trees exhibited 13 VOCs, and young Harvard trees had 14. Supplementary Table S1 presents the means and standard errors for each VOC, along with references to previous studies [19,21,22,25,26,29–36] where some of these VOCs have been previously reported in poplar species.

Putatively annotated VOCs	Chemical group	young non-infested Conti	young non-infested Harvard	adult non-infested Conti	adult non-infested Harvard	adult infested Conti	adult infested Harvard	retention time (min)
hexanal	GLV							1.51
2-hexenal	GLV							3.09
2,4-hexadienal	GLV							9.17
1-hexanol	GLV							7.65
2-hexen-1-ol	GLV							8.57
3-hexen-1-ol	GLV							8.49
4-hexen-3-one, 5-methyl *	GLV							16.71
4-penten-2-ol	PLV							1.02
3,4-dimethylpentanol *	PLV							7.73
5h-tetrazol-5-amine *	tetrazol derived							34.54
isolekene *	terpene							16.06
terpinolene	terpene							14.08
borneol	terpene							20.31
copaene	terpene							10.52
calamenene	terpene							24.98
linalool oxide	terpene							10.60
cubebene	terpene							12.9
eucalyptol	terpene							2.6
2-decanol *	alcohol							6.61
2-octen-1-ol *	alcohol							11.25
3-ethyl-4-methylpentanol *	alcohol							13.37
6-undecanol *	alcohol							16.65
furan, tetrahydro-3-methyl-4-methylene *	aromatic compound							3.11
benzamide, 2-benzylsulfonyl- 4,6-dinitro *	aromatic compound							17.65
benzaldehyde, 2 hydroxy	aromatic compound							18.60
azulene *	aromatic compound							19.1
naphthalene	aromatic compound							21.33
benzyl alcohol	phenolic compound							29.26
phenylethyl alcohol	phenolic compound							30.73
1,2-cyclohexanediol	cyclohexane derived							31.82
1-isopropenyl-3-propenylcyclopentane *	cyclic hydrocarbon							17.21

Figure 1. Putatively annotated VOCs detected in *Populus* cultivars, their assignment to chemical groups, and retention times (min). Coloured cells indicate that a given VOC was detected under our analytical conditions in the corresponding genotype × age × infestation class; white cells indicate no detection. Asterisks (*) denote putatively annotated compounds that, to our knowledge, have not been previously reported in *Populus* VOC profiles. GLV = green leaf volatile, and PLV = pentyl leaf volatile.

GLMs showed that, across cultivars, total VOC abundances were approximately 14.5-fold higher in Harvard than in Conti (Table 1). Constitutive VOCs (i.e., compounds detected in all samples) included hexanal, 2-hexenal, 1-hexanol, 3-hexen-1-ol, 4-penten-2-ol, 3,4-dimethylpentanol and benzaldehyde, 2 hydroxy. Altogether, these compounds were approximately 52-fold higher in infested Harvard trees than in infested Conti trees and 10-fold higher than in Harvard non-infested trees (Table 1).

Table 1. Significant results from GLMs on the grouping of VOCs.

	Sample	Mean (ng mg ⁻¹)		95% CI	p-Value	% of Total VOCs
total VOCs	Conti	25.246	a	[9.91, 64.32]	<0.001	
	Harvard	365.409	b	[143.42, 931]		
constitutive VOCs	Conti infested	13.98	a	[3.94, 49.51]	<0.001	98.06 %
	Conti non-infested	29.2	a	[11.94, 71.42]		94.99 %
	Harvard non-infested	72.93	a	[29.82, 178.39]		93.57 %
	Harvard infested	729.38	b	[205.87, 2584.14]		77.57 %
total terpenes	Conti infested	0.119	a	[0.03, 0.7]	<0.001	0.84 %
	Conti adult non-infested	2.766	b	[0.6, 13.0]		9 %
	Harvard non-infested	4.674	b	[1.6, 14.0]		6 %
	Harvard infested	203.472	c	[43.3, 957.1]		21.64 %
GLVs	Conti infested	11.82	a	[2.42, 57.7]	0.021	82.91 %
	Conti non-infested	19.39	a	[6.32, 59.5]		63.08 %
	Harvard non-infested	43.75	a	[14.25, 134.31]		56.13 %
	Harvard infested	679.84	b	[139.16, 3321.36]		72.3 %
PLVs	Conti	10.681	a	[2.7, 42.9]	0.009	42.31 %
	Harvard	35.883	b	[10.0, 128.4]		9.82 %
GLVs + PLVs	Conti infested	13.88	a	[3.73, 51.67]	0.009	97.35 %
	Conti non-infested	28.98	a	[11.44, 73.39]		94.27 %
	Harvard non-infested	72.35	a	[28.67, 183.22]		92.83 %
	Harvard infested	709.61	b	[190.68, 2640.79]		75.46 %

Mean values are semi-quantitative VOC abundances normalised to the internal standard and should be interpreted as relative comparisons among treatments rather than absolute concentration estimates. CI = confidence interval. Means sharing letters are not statistically different from each other (Tukey's HSD, $p > 0.05$).

Regarding terpenes, Harvard showed seven detectable compounds, of which five were detected only in this genotype under our analytical conditions, whereas Conti showed three terpenes, with one detected only in Conti. In young Conti trees, terpene levels were not detected under our conditions. Among adult Conti trees, non-infested individuals showed ~23-fold higher terpene emissions than infested individuals. In Harvard, infested trees exhibited greater terpene abundance and diversity. Under infestation, Harvard showed ~44-fold higher total terpene levels than its healthy counterpart and ~1710-fold higher levels compared to infested Conti (Table 1).

GLVs and GLVs + PLVs were ~57-fold and ~51-fold higher, respectively, in infested Harvard trees compared to infested Conti trees. Similarly, GLVs and GLVs + PLVs were ~16-fold and ~10-fold higher in infested Harvard trees compared to Harvard non-infested trees, respectively. When analysing PLVs alone, their levels were ~3.4-fold higher in Harvard than in Conti trees. LOX derivatives were the dominant compounds emitted across all sampling groups (Table 1).

The hierarchical clustering analysis of GLVs produced a dendrogram (Figure 2) with two primary clusters at a Euclidean distance of 5.4. The upper cluster contained only adult-infested Harvard samples, whereas all other samples were grouped in the lower cluster. For terpenes, this analysis revealed two main clusters at a Euclidean distance of 5.6. The upper cluster again comprised only adult-infested Harvard samples. In the lower cluster, two subgroups were distinguished: the upper subgroup included adult non-infested Harvard samples, and the lower subgroup consisted of Conti samples (where terpenes were not detected in young Conti samples under our analytical conditions) and young non-infested Harvard samples.

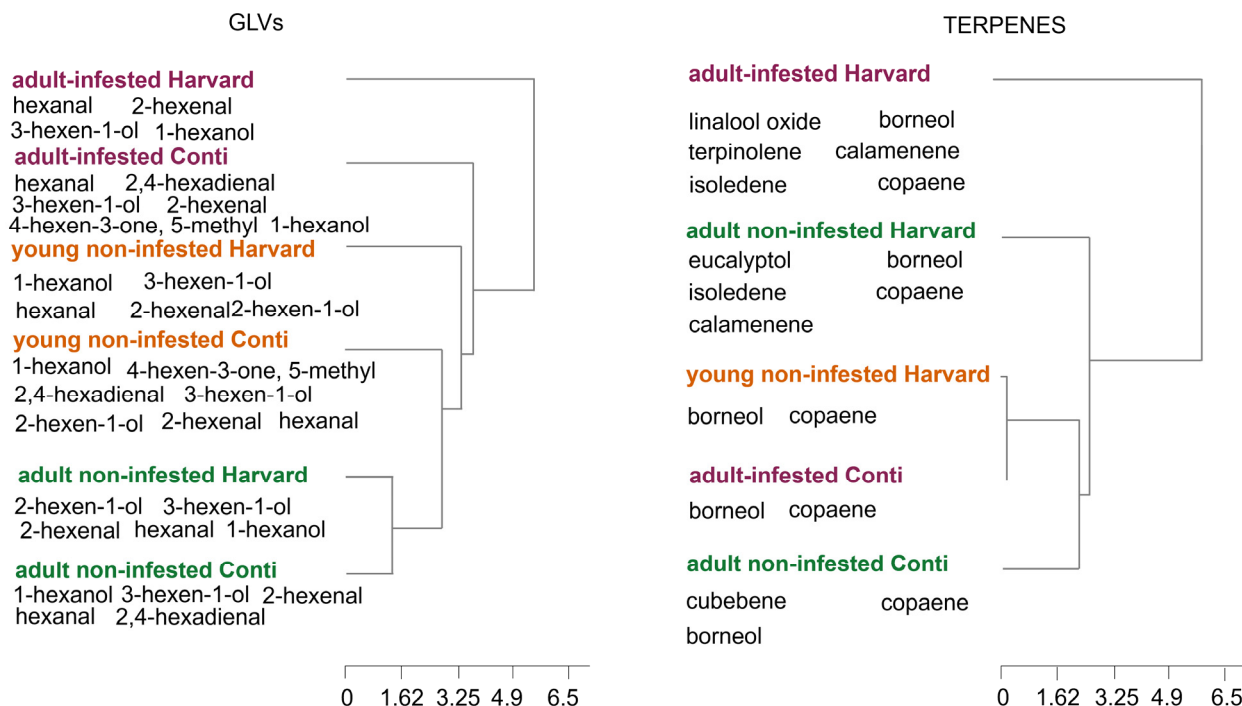


Figure 2. Hierarchical clustering of volatile organic compound (VOC) profiles. The left panel shows the cluster analysis based on green leaf volatiles (GLVs) and the right panel on terpenes. For each treatment, the VOCs that contributed to the cluster are listed under the corresponding label. Dendrograms were obtained from hierarchical cluster analysis of VOC emission profiles (mean normalised peak areas per treatment) using Euclidean distance (horizontal axis).

In the principal component analysis (PCA; Figure 3), the first two components explained 73.5% of the total variance (PC1: 43%, PC2: 30.5%). Eigenvalues and variable loadings for the main components are provided in Supplementary Tables S2 and S3. In the PC1–PC2 space, adult-infested Harvard trees were clearly separated from the other groups towards the positive side of both axes. Meanwhile, young non-infested trees, adult non-infested Harvard and adult-infested Conti trees clustered together on the negative side of PC1 axis. Adult non-infested Conti trees occupied a position in the second quadrant. This ordination indicates that VOC profiles differ jointly according to genotype, age and infestation status.

The results of the individual compound analyses are presented in Table 2. Among GLVs, adult-infested Harvard samples had, on average, ~33-fold higher hexanal levels than the mean of the other treatment groups. Harvard trees exhibited 2-hexenal levels that were approximately 2.8 times higher than those in Conti, while young trees exhibited approximately 5-fold higher levels than adult trees. GLV 1-hexanol was ~10-fold higher in infested compared to non-infested trees. Another GLV, 2-hexen-1-ol, was ~2-fold higher in young than in adult non-infested trees. Under infestation, 3-hexen-1-ol was ~23-fold higher in Harvard compared to Conti, and ~21-fold higher than in Harvard non-infested samples. 2,4-hexadienal was detected only in adult Conti trees under our analytical conditions and showed ~7-fold higher relative levels in infested than in non-infested individuals. Finally, 4-hexen-3-one, 5-methyl was ~7-fold higher in adult-infested Conti trees than in young non-infested Conti trees.

PLV 4-penten-2-ol was ~3-fold higher in Harvard than in Conti. The other PLV, 3,4-dimethylpentanol, was ~83-fold higher in infested Harvard trees than in their Conti counterparts and ~130-fold higher than in non-infested Harvard trees.

When analysing terpenes, copaene was ~5-fold higher in Harvard than in Conti. In Harvard, isodene was ~32-fold higher in adult-infested compared to adult non-infested samples. In the same cultivar, calamenene was ~23-fold higher in adult-infested than in adult non-infested trees, and borneol levels were ~10-fold higher in infested than in non-infested samples.

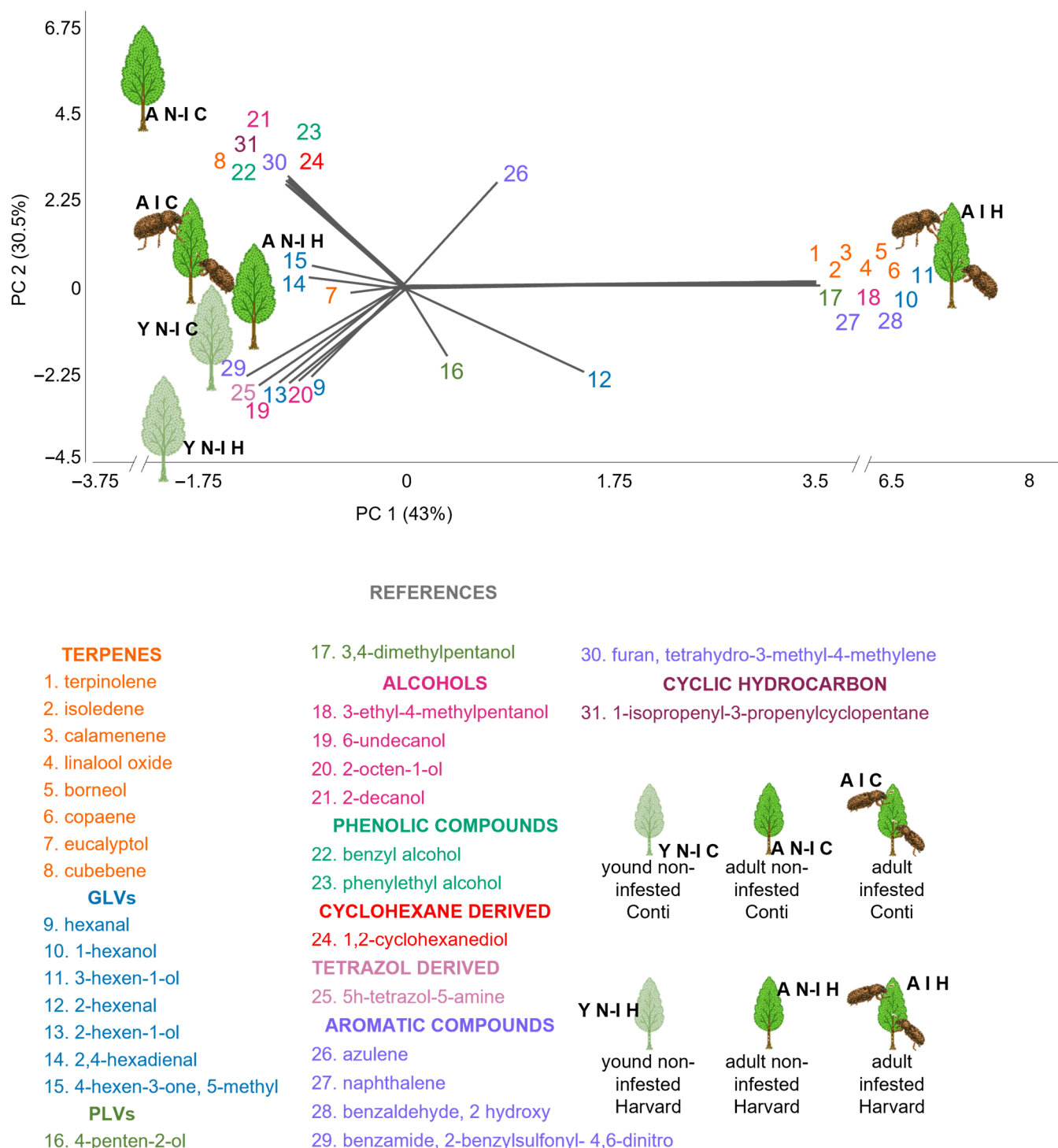


Figure 3. PCA biplot of VOC profiles in *Populus* cultivars under *M. mutatus* infestation. Symbols represent the scores of young and adult trees under infested and non-infested conditions. Numbers at the end of each loading vector identify individual VOCs, as listed in the figure legend.

Table 2. Significant results from GLM on different VOCs.

VOC	Samples	Mean (ng mg ⁻¹)		95% CI	p-Value
hexanal	Conti infested	9.47	a	[1.6, 54.4]	<i>p</i> -value _(genotype/infestation)
	Conti non-infested	15.92	a	[4.6, 54.8]	0.023
	Harvard non-infested	31.312	a	[9.1, 107.9]	
	Harvard infested	624.2	b	[108.5, 3589.8]	
2-hexenal	Conti	3.01	a	[1.3, 7.2]	<i>p</i> -value _(genotype)
	Harvard	8.3	b	[4.5, 15.5]	0.004
	adult	2.27	a	[0.89, 5.81]	<i>p</i> -value _(age)
	young	11.01	b	[6.28, 19.3]	<0.001
1-hexanol	non-infested	1.24	a	[0.5, 3.0]	<i>p</i> -value _(infestation)
	infested	12.08	b	[3.5, 41.5]	0.003
4-penten-2-ol	Harvard	32.7	a	[8.5, 125.5]	<i>p</i> -value _(genotype)
	Conti	9.8	b	[2.3, 42.5]	0.011
3,4-dimethylpentanol	Harvard non-infested	0.07	a	[0.03, 0.16]	<i>p</i> -value _(genotype/infestation)
	Conti non-infested	0.08	a	[0.04, 0.16]	<0.001
	Conti infested	0.11	a	[0.05, 0.2]	
	Harvard infested	9.15	b	[8.9, 9.3]	
benzaldehyde, 2 hydroxy	Conti infested	0.16	a	[0.03, 0.8]	<i>p</i> -value _(genotype/infestation)
	Conti non-infested	0.26	a	[0.09, 0.8]	0.004
	Harvard non-infested	0.63	a	[0.2, 1.9]	
	Harvard infested	19.78	b	[4.1, 94.4]	
2,4-hexadienal	Conti non-infested	0.006	a	[0.004, 0.009]	<i>p</i> -value _(infestation)
	Conti infested	0.041	b	[0.037, 0.046]	<0.001
2-hexen-1-ol	adult non-infested	0.03	a	[0.03, 0.03]	<i>p</i> -value _(age/infestation)
	young non-infested	0.06	b	[0.06, 0.07]	<0.001
3-hexen-1-ol	Conti non-infested	0.63	a	[0.26, 1.54]	<i>p</i> -value _(genotype/infestation)
	Conti infested	0.83	a	[0.24, 2.92]	0.012
	Harvard non-infested	0.91	a	[0.36, 2.22]	
	Harvard infested	19.38	b	[5.5, 68.1]	
4-hexen-3-one,5-methyl	Conti young non-infested	0.004	a	[0.004, 0.004]	<i>p</i> -value _(age/infestation)
	Conti adult-infested	0.027	b	[0.026, 0.029]	<0.001
6-undecanol	Conti	0.002	a	[0.002, 0.002]	<i>p</i> -value _(genotype)
	Harvard	0.021	b	[0.020, 0.022]	<0.001
3-ethyl-4-methylpentanol	Harvard adult non-infested	0.08	a	[0.04, 0.17]	<i>p</i> -value _(genotype/infestation)
	Harvard adult-infested	1.76	b	[1.66, 1.88]	<0.001
copaene	Conti	8.58	a	[0.57, 128.39]	<i>p</i> -value _(genotype)
	Harvard	43.12	b	[3.06, 606.98]	0.04
isolekene	Harvard adult non-infested	0.01	a	[0.01, 0.03]	<i>p</i> -value _(age/infestation)
	Harvard adult-infested	0.32	b	[0.30, 0.34]	<0.001
borneol	non-infested	0.13	a	[0.045, 0.391]	<i>p</i> -value _(infestation)
	Infested	1.42	b	[0.379, 5.297]	0.006
calamenene	Harvard adult non-infested	0.09	a	[0.02, 0.41]	<i>p</i> -value _(age/infestation)
	Harvard adult-infested	2.1	b	[0.46, 9.6]	0.004
5H-tetrazol-5-amine	Conti	0.005	a	[0.003, 0.007]	<i>p</i> -value _(genotype)
	Harvard	0.044	b	[0.035, 0.057]	<0.001
2-octen-1-ol	young non-infested Conti	0.021	a	[0.018, 0.024]	<i>p</i> -value _(genotype)
	young non-infested Harvard	0.083	b	[0.08, 0.087]	<0.001
azulene	adult-infested	0.07	a	[0.05, 0.09]	<i>p</i> -value _(age/inf)
	adult non-infested	0.11	b	[0.08, 0.14]	0.013
naphthalene	Harvard adult non-infested	0.16	a	[0.04, 0.74]	<i>p</i> -value _(age/inf)

Harvard adult-infested	5.65	b	[1.22, 26.14]	0.001
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Mean values are semi-quantitative VOC abundances normalised to the internal standard and should be interpreted as relative comparisons among treatments rather than absolute concentration estimates. CI = confidence interval. Means sharing letters are not statistically different from each other (Tukey's HSD, $p > 0.05$).

Regarding alcohols, 6-undecanol was ~10-fold higher in Harvard than in Conti. 3-ethyl-4-methylpentanol was ~22-fold higher in adult-infested compared to adult non-infested trees. Detected in both genotypes, 2-octen-1-ol was ~4-fold higher in the young of Harvard than in Conti. Compound 5H-tetrazol-5-amine was ~9-fold higher in Harvard than in Conti. Among aromatic compounds, benzaldehyde, 2 hydroxy, showed a ~124-fold increase in infested Harvard compared with infested Conti trees and was ~31-fold higher than in non-infested Harvard trees. Azulene was ~1.6-fold higher in adult non-infested samples compared to adult-infested samples. Naphthalene was not detected in Conti samples under our analytical conditions, whereas in Harvard it was ~35-fold higher in adult-infested than in adult non-infested samples.

3. Discussion

The present study compared VOC profiles of two poplar clones grown in a commercial plantation under natural *M. mutatus* infestation. Field infestation data showed that Conti trees had more than twice the odds of infestation compared to Harvard trees, indicating a higher probability of infestation for Conti under the conditions studied. We then asked whether differences in semi-quantitative VOC blends—including putatively annotated constitutive compounds, GLVs, PLVs, and terpenes—might help to explain the lower field infestation levels and apparent tolerance observed in Harvard, as well as the lower infestation in young trees. Since no behavioural or no-choice bioassays were performed, any proposed roles of individual VOCs as attractants, repellents or resistance factors in the *Populus*–*M. mutatus* system remain hypothetical and are inferred from the literature rather than demonstrated directly.

In Conti trees, both total and constitutive VOC abundances remained relatively stable across infestation status. Constitutive VOCs represented ~95–98% of total VOCs in Conti (infested and non-infested) and in non-infested Harvard, whereas this fraction was lower in infested Harvard (~78%; Table 1). This indicates that infestation in Harvard was accompanied by an increased contribution of non-constitutive VOCs, rather than a loss of the constitutive background. Additionally, Harvard trees not only showed higher total and constitutive semi-quantitative VOC abundances than Conti overall, but under infestation they also reached higher levels than non-infested trees of either cultivar. Similar increases in total VOC emissions after herbivore attack have been reported in other plant–insect systems e.g., [37–39], including *Populus yunnanensis*, where total VOC output correlates negatively with odour choice and oviposition [40]. These patterns point to genotype-dependent differences in inducible VOC responses to *M. mutatus*, although their consequences for attraction and infestation still need to be tested experimentally.

In total, 31 VOCs were putatively annotated and assigned to GLVs, PLVs, terpenes, alcohols, aromatic compounds and phenolic compounds, cyclohexane derivatives, cyclic hydrocarbons and tetrazole derivatives (Figure 1). Patterns of detection and semi-quantitative abundance across samples suggest that VOC blends are modulated by genotype, tree age and herbivory under our field conditions.

Terpenes may contribute importantly to Harvard's VOC response. Total terpene abundances were lowest in infested Conti adults, intermediate in Harvard non-infested trees (regardless of age) and in Conti non-infested adults, and highest in infested Harvard adults (Table 1). In addition, infested Harvard adults emitted a more diverse terpene

blend and a larger terpene proportion of total VOCs than Conti, and terpenes were not detected in young Conti trees under our analytical conditions. These patterns are consistent with genotype- and age-related differences in terpene emission capacity, although alternative explanations such as insect-mediated suppression, genotype-specific induction thresholds, or analytical detection limits cannot be ruled out.

Importantly, the percentage contribution of each VOC class (Table 1) indicates that infestation in Harvard involves not only higher absolute VOC output but also a marked compositional shift. In infested Harvard adults, terpenes accounted for ~22% of total VOCs, whereas they represented only ~0.8–9% in Conti and ~6% in non-infested Harvard, consistent with a strong induction of terpenes under attack. Although LOX-derived volatiles (GLVs + PLVs) increased strongly in absolute abundance in infested Harvard, their percentage contribution to total VOCs was comparatively lower than in the other groups because infestation in Harvard was accompanied by an increase in non-LOX compounds (mostly terpenes). Interestingly, PLVs represented a larger fraction of total VOCs in Conti, reflecting a lower contribution of non-LOX compounds in this genotype.

Cluster analysis reinforced these trends. Adult-infested Harvard trees formed a distinct group characterised by higher abundances of six terpenes, including linalool oxide and terpinolene, both reported as insecticidal or repellent in other systems [26,41,42]. Adult non-infested Harvard trees formed a second terpene-rich cluster and were the only group in which eucalyptol was detected, a compound that can disrupt insect behaviour and attract natural enemies [43–45]. Its lack of detection in infested samples could reflect changes in host metabolism, potentially including insect-mediated suppression [46,47], although detection limits or context-dependent induction cannot be excluded. Cubebene occurred only in non-infested adult Conti trees, in contrast with the presence of β -cubebene in attacked Conti reported by Lucia et al. [19], possibly reflecting differences in insect genotype, environmental conditions, tree age or infestation intensity. Isolatedene and calamenene, detected only in adult Harvard trees and elevated under infestation, agree with previous reports of release after mechanical damage and antifeedant activity [48–50] and may also reflect ontogenetic changes in terpene metabolism. Copaene abundances were higher in Harvard than in Conti, and borneol—reported to repel coleopterans and other insects [51,52] and previously associated with *M. mutatus* attraction together with copaene [19]—was elevated in infested samples. Overall, the net effect of these terpenes on the behaviour of *M. mutatus* is likely to be complex and will require targeted behavioural and physiological studies.

GLVs + PLVs derived from the LOX pathway dominated the VOC blend, whereas non-LOX VOCs contributed only minor fractions (Table 1). Overall, Conti was more strongly dominated by LOX derivatives and emitted fewer and less diverse non-LOX VOCs than Harvard. Across infestation statuses, Harvard consistently emitted more PLVs than Conti, and under infestation it showed higher GLV and GLV + PLV abundances than both non-infested Harvard and Conti at either age. This might indicate a stronger LOX-related response to attacks.

Several GLVs showed patterns consistent with defensive or signalling functions. Adult Harvard infested trees showed higher hexanal than any other group, and 2-hexenal was higher in Harvard than in Conti. Hexanal has reported to have antifungal activity [53,54] that could help limit fungal colonisation in gallery tissues. The higher levels of 1-hexanol and 3-hexen-1-ol in infested samples might influence coleopteran behaviour as seen in related isomers [21,22,55]. 2,4-hexadienal, detected only in Conti, has been associated with mechanical damage and antifungal activity [56,57]. Together, these GLVs may contribute to the lower infestation levels and apparent tolerance observed in Harvard.

The PLVs 4-penten-2-ol and 3,4-dimethylpentanol may influence fungal communities, as related pentanol isomers show antifungal activity [58]. In our data, 4-penten-2-ol

was higher in Harvard than in Conti, and 3,4-dimethylpentanol increased with infestation only in Harvard, indicating genotype-dependent PLV induction, although any defensive role is still speculative.

Among the remaining VOCs, benzamide, 2-benzylsulfonyl-4,6-dinitro, detected only in young Harvard trees, and related benzamide derivatives can affect insect growth [59–61], suggesting a defensive role. Naphthalene, a fumigant, was not detected in Conti but increased in infested adult Harvard trees, as seen in *P. nigra* under attack [26]. Benzaldehyde, 2-hydroxy increased in infested Harvard trees; although benzoids are insect repellents [62,63], their role in poplar remains debated [64]. Azulene was higher in non-infested samples and may help limit opportunistic microbial infections [65,66]. Additional VOCs with insecticidal, deterrent, or antifungal properties—for example, aromatic and phenolic compounds, some alcohols, and cyclohexane- and tetrazole-derived compounds [21,22,25–27,36,64,67–77]—were mainly detected in young or non-infested trees, or showed higher abundances in Harvard than Conti, indicating possible roles in early defence or fungal interactions.

From a multivariate perspective, the PCA indicates that infestation reshapes the VOC bouquet more strongly in Harvard than in Conti. Infested adult Harvard trees were associated with higher abundances of several VOC classes (mainly terpenes, GLVs/PLVs and aromatics), whereas infested adult Conti trees clustered close to young/non-infested individuals, suggesting only modest infestation-related shifts. Adult non-infested Conti trees occupied an intermediate position, without the marked terpene enrichment seen in infested Harvard adults. Overall, these patterns are consistent with Harvard undergoing a stronger reconfiguration of its VOC blend upon infestation, while Conti shows a comparatively weaker response.

Growing evidence underscores the importance of VOC blends in plant–insect interactions [9]. The lower field infestation in Harvard compared with Conti may partly reflect differences in their VOC mixtures against *M. mutatus*. In other species, combinations of GLVs and terpenes can trigger defence metabolism, modulate herbivore warning systems and influence host choice or repellence [78,79]. In our study, infested adult Harvard trees emitted VOC blends relatively richer in terpenes and LOX derivatives than Conti, which could strengthen defensive signalling or alter beetle attraction. Moreover, VOC-mediated interactions between neighbouring plants, described in other systems [80,81], might also occur between closely planted Conti and Harvard trees, modifying their emission profiles and apparent susceptibility. Both possibilities merit further investigation and will require behavioural and no-choice assays.

In summary, this study revealed genotype- and age-dependent differences in semi-quantitative VOC profiles in the bark surrounding *M. mutatus* galleries in Harvard and Conti. Most of the VOCs putatively annotated here have previously been associated with defence-related processes in poplars or other plant species, suggesting that they may contribute to the response to *M. mutatus*. Harvard trees, particularly adults, tended to show a stronger VOC-based response to infestation than Conti, in line with their lower field infestation levels. These patterns are correlative and based on two clones, and VOCs are likely to act together with other traits (e.g., cell wall architecture, tissue density, immune perception and signalling). VOC profiles should therefore be regarded as one component of a broader defence phenotype rather than the sole determinant of susceptibility or resistance. Moreover, we cannot rule out that some VOCs were released from other tissues.

The VOCs that, to our knowledge, have not been previously reported in poplar profiles provide additional candidates for defence and signalling roles in plant–herbivore interactions, especially given their links to biotic stress in other systems. Particular attention should be paid to VOCs detected only under specific conditions or enriched in adult trees. In our data, compounds such as linalool oxide, terpinolene, isodene, calamenene,

hexanal, 3,4-dimethylpentanol, 3-hexen-1-ol, benzaldehyde, 2-hydroxy, 3-ethyl-4-methylpentanol and naphthalene were especially abundant in adult Harvard trees under infestation and therefore represent promising candidates for induced defence or signalling roles. Meanwhile, eucalyptol, 2-hexenal, 2-hexen-1-ol, 2-octen-1-ol and azulene were more prominent in non-attacked or young trees and may reflect anticipatory or ontogenetically programmed defences. Clarifying whether these VOCs or their blends causally affect *M. mutatus* attraction or performance will require experiments targeting key biosynthetic or signalling pathways, together with behavioural and no-choice assays across a broader panel of poplar clones. In the longer term, if some of these candidates prove to be effective deterrents or modulators of insect behaviour, enhancing their production through breeding, genetic engineering or silvicultural practices could support improved trapping schemes and cultivar selection for integrated pest management.

4. Materials and Methods

4.1. Plant Material and Experimental Design

The experiment was conducted in a commercial poplar plantation located in Tunuyán (33°34'00" S, 69°01'00" W), Mendoza, Argentina, on 16 March 2021, which coincides with the second peak of *M. mutatus* adult flight activity for mating. Samples were taken between 10:00 and 12:00 h. The plantation consisted of *Populus deltoides* cv. Harvard I63/15 and *P. × canadensis* cv. Conti 12, hereafter referred to as Harvard and Conti, respectively. The sampled plots are depicted in Figure 4. Trees within each plot were numbered, and a subset was randomly selected using computer-generated random numbers. To avoid edge effects and potential mixing of genotypes, we left a buffer zone of at least two unsampled trees between sampled trees and plot borders, as well as between adjacent rows of Conti and Harvard.



Figure 4. Sampling site and plot layout. Google Maps image of the commercial poplar plantation in Tunuyán, Mendoza, Argentina. Dashed lines delineate the four sampling plots corresponding to adult and young trees of *Populus deltoides* cv. Harvard and *P. × canadensis* cv. Conti 12.

M. mutatus infestation was assessed in adult trees (trunk diameter ≥ 15 cm, according to Marquina et al. [20] in both poplar genotypes, as insects were not found in trees with smaller diameters (young trees). A total of 100 randomly selected trees from each cultivar (Conti and Harvard) were visually inspected for infestation. Trees were categorized as infested if one or more tunnel entrances of the insect were present on the main trunk and as non-infested if no such entrances were found (Figure 5). Host preference was analysed using a binomial GLM ($\alpha = 0.05$) with a logit link function.



Figure 5. (a) Infestation of *Populus deltoides* cv. Harvard by *Megaplatypus mutatus*, with conspicuous exudates visible along the trunks. (b,c) Adult *M. mutatus* emerging from their internal galleries, illustrating active beetle exit behaviour. (d,e) Close-up views of gallery entrance holes and the associated exudation characteristic of the Harvard cultivar's response to attack.

4.2. Chemical Analysis

Wood bark samples were collected from the trunks of poplar trees at a height of 1.2 m using a metal hollow punch (1 cm in diameter) for chemical analysis [19]. This VOC sampling strategy characterises the local microenvironment directly affected by *M. mutatus* rather than whole-tree emissions. For each combination of cultivar, age category (young and adult) and infestation condition (infested and non-infested), two bark samples were taken.

Volatile compounds were then extracted using solid-phase microextraction (SPME), a method well-suited for analysing VOCs in plant tissues described by Cara et al. [82]. Immediately after grinding, 1 g of bark powder was rapidly transferred to amber vials containing 7 mL of saturated NaCl solution (25% *w/v*) to minimise volatilization and photodegradation and to increase ionic strength, thereby enhancing the partitioning of VOCs into the headspace and onto the SPME fibre. Although this procedure was designed to reduce losses of very volatile compounds as much as possible, partial loss of the lightest VOCs during sample handling cannot be completely excluded. An aliquot of 10 μ L of 4-methyl-2-pentanone (Sigma-Aldrich, Chromasolv for HPLC, St. Louis, MO, USA) was added as an internal standard and used to normalise VOC peak areas, allowing semi-quantitative comparisons among samples rather than absolute quantification. Moreover, compounds detected in some samples but not in others may still be present, but fall below our detection and/or quantification limits. The vials were then immediately and hermetically sealed with polypropylene hole caps and PTFE/silicone septa (Supelco, Bellefonte, PA, USA). The samples were equilibrated for 10 min in a temperature-controlled vial agitator tray (25 $^{\circ}$ C, $\sim$ 900 rpm). Next, an SPME fibre (PDMS/DVB/CAR 50/30 μ m; Supelco, Bellefonte, PA, USA) was manually inserted into the sealed vial through the septum and exposed to the aqueous samples for 30 min at 25 $^{\circ}$ C. After sampling, the SPME device was immediately inserted into the GC-MS system for splitless injection and thermally desorbed for 4 min at 250 $^{\circ}$ C. The splitter, set to 10 mL min $^{-1}$, was then opened for an additional 4 min. Fibres were thermally conditioned according to the manufacturer's recommendations before their initial use. Additionally, before each sampling procedure, the fibres were reconditioned for 10 min in the GC injection port at 250 $^{\circ}$ C. This reconditioning ensured no peaks in blank runs and provided a good balance between chromatography

runs and extraction procedures. The column used was a Phenomenex Zebron ZB-WAX Plus (30 m × 0.32 mm ID × 0.25 µm). The temperature program started at 35 °C, increasing to 70 °C at a rate of 3 °C min⁻¹ after 5 min, held for 2 min, and then raised to 165 °C at 2 °C min⁻¹ with a final hold of 1 min. The helium carrier gas flow was maintained at a constant rate of 1 mL min⁻¹, with the injector and interface temperatures set at 240 °C and 200 °C, respectively. GC-MS analysis was performed using a PerkinElmer Clarus 500 model (Shelton, CA, USA). The total analytical cycle time was optimized to 67 min. Each sample was analysed in triplicate.

In line with current metabolomics reporting standards [83], the VOCs reported here are MSI level 2 (putatively annotated compounds), rather than level 1 identifications. Annotations were based on comparison of EI mass spectra (70 eV) with entries in the NIST 2005 [84] library and on their retention times under our chromatographic conditions. Library search results were inspected manually, and peaks were annotated only when the top NIST candidate showed forward and reverse match factors ≥ 800 and a fragmentation pattern consistent with the library spectrum, without obvious signs of co-elution. When several candidates had similarly high match factors and indistinguishable spectra, no specific structure was assigned, and the peak was either reported only at a generic/class level or not included in the VOC list. Only peaks that fulfilled all of the following criteria were assigned a putative identity: (i) clear baseline separation from neighbouring peaks; (ii) EI spectra without obvious signs of co-elution and with NIST match factors ≥ 800; and (iii) integrated peak areas above 1.0×10^8 (minimum area threshold used for peak integration). Since our method did not distinguish structural or stereoisomers, compounds are reported using generic names.

4.3. Data Analysis

The sum of all putatively annotated VOCs was calculated as total VOCs and expressed as semi-quantitative values. VOCs detected in all samples were considered putative constitutive VOCs. In addition, total terpenes, GLVs and GLVs + PLVs were calculated.

For each individual VOC and VOC sum, we fitted generalised linear models (GLMs) with alternative distributional assumptions: Gaussian (identity link function), lognormal (log link) and Gamma (log link). Model selection followed an information-theoretic approach: all competing models and their distributional assumptions were compared using Akaike's Information Criterion (AIC), its small-sample correction (AICc) and the Bayesian Information Criterion (BIC), which quantify the trade-off between goodness of fit and model complexity. For each compound, we retained as the final model the candidate that achieved the best overall support (lowest information criteria) while satisfying diagnostic criteria.

Model assumptions were evaluated using Dunn–Smyth residuals with the R package 'DHARMA' v 0.4.6. For every candidate GLM, we assessed uniformity of residuals using Kolmogorov–Smirnov test, dispersion tests, and a Levene's test to check homoscedasticity. Only models with no evidence of major violations (all diagnostic *p*-values ≥ 0.05) were retained. All candidate GLMs that passed these diagnostic checks, together with their fixed-effects structure, error family, link function, information criteria (AIC, AICc, BIC) and diagnostic statistics, are reported in Supplementary Table S4, where the model retained for inference for each VOC is highlighted. Confidence intervals were obtained from the fitted means and their standard errors. For Gaussian models with identity link, 95% confidence intervals were calculated directly on the original response scale (multiplying $1.96 \times \text{SE}$). For lognormal and Gamma models with log link, we first computed the intervals on the log (link) scale and then back-transformed them to the original scale, which results in asymmetric confidence intervals around the mean.

Inference on fixed effects was based on Type II Wald χ^2 tests within the selected GLM for each compound. Where fixed effects or their interactions were significant ($\alpha = 0.05$), post hoc multiple comparisons among factor levels were carried out using Tukey's Honest Significant Difference procedure to control the family-wise error rate. We report the model-based mean abundances and their 95% confidence intervals, calculated from the fitted GLMs." Several mean estimates show wide 95% confidence intervals, consistent with high inter-tree variability under natural field infestation. Therefore, although fold-changes are reported for completeness, our interpretation focuses on consistent directional patterns and compositional shifts.

In the main text and figures we focus on statistically supported and biologically relevant patterns (in particular, compounds showing significant effects of infestation), while VOCs for which no fixed effects were significant are summarised in the text and fully documented in Supplementary Table S2. These analyses were conducted using R (version 4.4.2) [85].

Chemical profiles of terpenes and GLVs were additionally examined by hierarchical cluster analysis (standardised data, Euclidean distance and average-linkage clustering). A principal component analysis (PCA) was performed on the matrix of VOC abundances to summarise multivariate patterns in emission profiles. The analysis was conducted in InfoStat (Grupo InfoStat, FCA-UNC, Córdoba, Argentina) using the correlation matrix after standardising each variable to zero mean and unit variance. The resulting scores on the first two principal components (PC1 and PC2) were graphically displayed, using genotype, infestation condition and age as grouping criteria to facilitate the visual interpretation of group separation. Both analyses were conducted in InfoStat Software v. 2020 [86].

5. Conclusions

This study provides new evidence of genotype- and age-dependent differences in semi-quantitative volatile organic compound (VOC) emissions in the bark tissues surrounding *M. mutatus* galleries of *Populus deltoides* cv. Harvard and *P. × canadensis* cv. Conti 12 growing in the same plantation under natural infestation. Harvard tended to show a stronger and more diversified VOC response to infestation than Conti, particularly through enhanced emissions of total VOCs, total terpenes, green leaf volatiles (GLVs) and pentyl leaf volatiles (PLVs), in patterns that are compatible with defensive and/or signalling roles reported for these compounds in other systems, although their specific functions in the poplar–*M. mutatus* interaction remain to be demonstrated. In contrast, Conti displayed more stable, largely constitutive emissions and lower overall VOC diversity under our analytical conditions, suggesting a more limited VOC plasticity in response to attack. The novel VOCs putatively annotated here that, to our knowledge, have not been previously reported in poplar VOC profiles broaden the currently recognised chemical repertoire potentially involved in defence. Future research integrating behavioural and no-choice assays with transcriptomic analyses will be essential for clarifying the regulatory mechanisms underlying these VOC responses and their ecological significance. This will allow us to assess their potential application in breeding programmes and integrated pest management strategies for sustainable poplar forestry.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/stresses6010006/s1>, Table S1: Means and standard errors of putatively annotated VOCs and references to previous studies where some of these VOCs were identified in poplar species; Table S2: Eigenvalues of PCA; Table S3: Loadings (eigenvectors) PC1 y PC2 and Table S4: Candidate generalized linear models (GLMs) fitted to individual putatively annotated VOCs and VOC sums, with information criteria and diagnostic statistics.

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References

1. Pierik, R.; Ballaré, C.L.; Dicke, M. Ecology of plant volatiles: Taking a plant community perspective. *Plant Cell Environ.* **2014**, *37*, 1845–1853. <https://doi.org/10.1111/pce.12330>.
2. Lazazzara, V.; Bueschl, C.; Parich, A.; Pertot, I.; Schuhmacher, R.; Perazzolli, M. Downy mildew symptoms on grapevines can be reduced by volatile organic compounds of resistant genotypes. *Sci. Rep.* **2018**, *8*, 1618. <https://doi.org/10.1038/s41598-018-19776-2>.
3. Rosenkranz, M.; Chen, Y.; Zhu, P.; Vlot, A.C. Volatile terpenes—mediators of plant-to-plant communication. *Plant J.* **2021**, *108*, 617–631. <https://doi.org/10.1111/tpj.15453>. Correction in *Plant J.* **2021**, *108*, 1849–1850. <https://doi.org/10.1111/tpj.15594>.
4. Lackus, N.D.; Morawetz, J.; Xu, H.; Gershenzon, J.; Dickschat, J.S.; Köllner, T.G. The sesquiterpene synthase PtTPS5 produces (1S,5S,7R,10R)-guaia-4(15)-en-11-ol and (1S,7R,10R)-guaia-4-en-11-ol in oomycete-infected poplar roots. *Molecules* **2021**, *26*, 555. <https://doi.org/10.3390/molecules26030555>.
5. Matsui, K.; Engelberth, J. Green leaf volatiles—The forefront of plant responses against biotic attack. *Plant Cell Physiol.* **2022**, *63*, 1378–1390. <https://doi.org/10.1093/pcp/pcac117>.
6. Allmann, S.; Baldwin, I.T. Insects betray themselves in nature to predators by rapid isomerization of green leaf volatiles. *Science* **2010**, *329*, 1075–1078. <https://doi.org/10.1126/science.1191634>.
7. Gorman, Z.; Tolley, J.P.; Koiwa, H.; Kolomiets, M.V. The synthesis of pentyl leaf volatiles and their role in resistance to anthracnose leaf blight. *Front. Plant Sci.* **2021**, *12*, 719587. <https://doi.org/10.3389/fpls.2021.719587>.
8. Tolley, J.P.; Gorman, Z.; Lei, J.; Yeo, I.C.; Nagashima, Y.; Joshi, V.; Koiwa, H. Overexpression of maize ZmLOX6 in *Arabidopsis thaliana* enhances damage-induced pentyl leaf volatile emissions that affect plant growth and interaction with aphids. *J. Exp. Bot.* **2023**, *74*, 1990–2004. <https://doi.org/10.1093/jxb/erac522>.
9. Fitzky, A.C.; Peron, A.; Kaser, L.; Karl, T.; Graus, M.; Tholen, D.; Rewald, B. Diversity and interrelations among the constitutive VOC emission blends of four broad-leaved tree species at seedling stage. *Front. Plant Sci.* **2021**, *12*, 708711. <https://doi.org/10.3389/fpls.2021.708711>.
10. Kegge, W.; Weldegergis, B.T.; Soler, R.; Eijk, M.V.V.; Dicke, M.; Voisenek, L.A.; Pierik, R. Canopy light cues affect emission of constitutive and methyl jasmonate-induced volatile organic compounds in *Arabidopsis thaliana*. *New Phytol.* **2013**, *200*, 861–874. <https://doi.org/10.1111/nph.12407>.

11. Brilli, F.; Hörtnagl, L.; Bamberger, I.; Schnitzhofer, R.; Ruuskanen, T.M.; Hansel, A.; Wohlfahrt, G. Qualitative and quantitative characterization of volatile organic compound emissions from cut grass. *Environ. Sci. Technol.* **2012**, *46*, 3859–3865. <https://doi.org/10.1021/es204025y>.
12. Quintero, C.; Barton, K.E.; Boege, K. The ontogeny of plant indirect defenses. *Perspect. Plant Ecol. Evol. Syst.* **2013**, *15*, 245–254. <https://doi.org/10.1016/j.ppees.2013.08.003>.
13. Malik, T.G.; Gajbhiye, T.; Pandey, S.K. Plant specific emission pattern of biogenic volatile organic compounds (BVOCs) from common plant species of Central India. *Environ. Monit. Assess.* **2018**, *190*, 631. <https://doi.org/10.1007/s10661-018-7015-6>.
14. Chen, J.; Tang, J.; Yu, X. Environmental and physiological controls on diurnal and seasonal patterns of biogenic volatile organic compound emissions from five dominant woody species under field conditions. *Environ. Pollut.* **2020**, *259*, 113955. <https://doi.org/10.1016/j.envpol.2020.113955>.
15. Casaubon, E.; Cueto, G.; Spagarino, C. Diferente comportamiento de *Megaplatypus mutatus* (= *Platypus sulcatus*) (Chapuis, 1865) en un ensayo comparativo de rendimiento de 30 clones de *Populus deltoides* Batr. en el bajo Delta Bonaerense del Río Paraná. *Rev. Investig. Agropecu.* **2006**, *35*, 103–115.
16. Ceriani-Nakamurakare, E.; Robles, C.; González-Audino, P.; Dolinko, A.; Mc Cargo, P.; Corley, J.; Carmarán, C. The ambrosia beetle *Megaplatypus mutatus*: A threat to global broad-leaved forest resources. *J. Integr. Pest Manag.* **2022**, *13*, 21. <https://doi.org/10.1093/jipm/pmac016>.
17. Alfaro, R.I.; Humble, L.M.; Gonzalez, P.; Villaverde, R.; Allegro, G. The threat of the ambrosia beetle *Megaplatypus mutatus* (Chapuis) (= *Platypus mutatus* Chapuis) to world poplar resources. *Forestry* **2007**, *80*, 471–479. <https://doi.org/10.1093/forestry/cpm029>.
18. Ceriani-Nakamurakare, E.; Slodowicz, M.; Gonzalez-Audino, P.; Dolinko, A.; Carmaran, C. Mycobiota associated with the ambrosia beetle *Megaplatypus mutatus*: Threat to poplar plantations. *Forestry* **2016**, *89*, 191–200. <https://doi.org/10.1093/forestry/cpw001>.
19. Lucia, A.; González-Audino, P.; Masuh, H. Volatile organic compounds from the clone *Populus × canadensis* “Conti” associated with *Megaplatypus mutatus* attack. *Psyche A J. Entomol.* **2014**, *2014*, 793298. <https://doi.org/10.1155/2014/793298>.
20. Marquina, J.L.; Marlats, R.; Núñez Cresto, M. Susceptibilidad clonal del álamo (*Populus* sp.) al ataque de *Platypus mutatus* en Buenos Aires, Argentina. *Bosque* **2006**, *27*, 92–97. <https://doi.org/10.4067/S0717-92002006000200003>.
21. Borden, J.H.; Chong, L.J.; Savoie, A.; Wilson, I.M. Responses to green leaf volatiles in two biogeoclimatic zones by striped ambrosia beetle, *Trypodendron lineatum*. *J. Chem. Ecol.* **1997**, *23*, 2479–2491. <https://doi.org/10.1023/B:JOEC.0000006661.99953.26>.
22. Borden, J.H.; Wilson, I.M.; Gries, R.; Chong, L.J.; Pierce, H.D., Jr.; Gries, G. Volatiles from the bark of trembling aspen, *Populus tremuloides* Michx. (Salicaceae) disrupt secondary attraction by the mountain pine beetle, *Dendroctonus ponderosae* Hopkins (Coleoptera: Scolytidae). *Chemoecology* **1998**, *8*, 69–75. <https://doi.org/10.1007/PL00001806>.
23. Hu, Z.-H.; Yang, D.; Shen, Y.-B. Difference in volatiles of poplar induced by various damages. *J. For. Res.* **2004**, *15*, 280–282. <https://doi.org/10.1007/BF02844952>.
24. Chi, D.; Li, X.; Yu, J.; Xie, X.; Wang, G. The EAG response and behavior of *Saperda populnea* L. to volatiles from poplar branches. *Acta Ecol. Sin.* **2011**, *31*, 334–340. <https://doi.org/10.1016/j.chnaes.2011.09.003>.
25. Gao, G.; Dai, L.; Gao, J.; Wang, J.; Chen, H. Volatile organic compound analysis of host and non-host poplars for *Trypophloeus klimeschi* (Coleoptera: Curculionidae: Ipinae). *Russ. J. Plant Physiol.* **2018**, *65*, 916–925. <https://doi.org/10.1134/S1021443718060067>.
26. Fabisch, T.; Gershenzon, J.; Unsicker, S.B. Specificity of herbivore defense responses in a woody plant, black poplar (*Populus nigra*). *J. Chem. Ecol.* **2019**, *45*, 162–177. <https://doi.org/10.1007/s10886-019-01050-y>.
27. Günther, J.; Lackus, N.D.; Schmidt, A.; Huber, M.; Stödtler, H.J.; Reichelt, M.; Köllner, T.G. Separate pathways contribute to the herbivore-induced formation of 2-phenylethanol in poplar. *Plant Physiol.* **2019**, *180*, 767–782. <https://doi.org/10.1104/pp.19.00059>.
28. Bustamante, J.A.; Perez, S.A. Comportamiento de clones de álamos en Barreal, San Juan, Argentina. *Rev. Fac. Cienc. Agrar.* **2008**, *40*, 73–77.
29. Đurković, J.; Bubeníková, T.; Gužmerová, A.; Fleischer, P.; Kurjak, D.; Čaňová, I.; Milenković, I. Effects of *Phytophthora* inoculations on photosynthetic behaviour and induced defence responses of plant volatiles in field-grown hybrid poplar tolerant to bark canker disease. *J. Fungi* **2021**, *7*, 969. <https://doi.org/10.3390/jof7110969>.
30. Tang, F.; Fu, Y.Y.; Ye, J.R. The effect of methyl salicylate on the induction of direct and indirect plant defense mechanisms in poplar (*Populus × euramericana* ‘Nanlin 895’). *J. Plant Interact.* **2015**, *10*, 93–100. <https://doi.org/10.1080/17429145.2015.1020024>.
31. Pellegrini, E.; Cioni, P.L.; Francini, A.; Lorenzini, G.; Nali, C.; Flamini, G. Volatiles emission patterns in poplar clones varying in response to ozone. *J. Chem. Ecol.* **2012**, *38*, 924–932. <https://doi.org/10.1007/s10886-012-0162-2>.

32. Wu, H.; Li, X.; Zhang, Q.; Zhang, K.; Xu, X.; Xu, J. Promoting the conversion of poplar to bio-oil based on the synergistic effect of alkaline hydrogen peroxide. *Renew. Energy* **2022**, *192*, 107–117. <https://doi.org/10.1016/j.renene.2022.04.101>.
33. Ibrahim, M.A.; Mäenpää, M.; Hassinen, V.; Kontunen-Soppela, S.; Malec, L.; Rousi, M.; Oksanen, E.J. Elevation of night-time temperature increases terpenoid emissions from *Betula pendula* and *Populus tremula*. *J. Exp. Bot.* **2010**, *61*, 1583–1595. <https://doi.org/10.1093/jxb/erq034>.
34. Kuś, P.M.; Okrińczyc, P.; Jakovljević, M.; Jokić, S.; Jerković, I. Development of supercritical CO₂ extraction of bioactive phytochemicals from black poplar (*Populus nigra* L.) buds followed by GC–MS and UHPLC-DAD-QqTOF-MS. *J. Pharm. Biomed. Anal.* **2018**, *158*, 15–27. <https://doi.org/10.1016/j.jpba.2018.05.041>.
35. Schepetkin, I.A.; Özek, G.; Özek, T.; Kirpotina, L.N.; Kokorina, P.I.; Khlebnikov, A.I.; Quinn, M.T. Neutrophil immunomodulatory activity of nerolidol, a major component of essential oils from *Populus balsamifera* buds and propolis. *Plants* **2022**, *11*, 3399. <https://doi.org/10.3390/plants11233399>.
36. Isidorov, V.A.; Vinogorova, V.T. GC–MS analysis of compounds extracted from buds of *Populus balsamifera* and *Populus nigra*. *Z. Naturforsch. C* **2003**, *58*, 355–360. <https://doi.org/10.1515/znc-2003-5-612>.
37. Vázquez-González, C.; Quiroga, V.; Martín-Cacheda, L.; Rasmann, S.; Röder, G.; Abdala-Roberts, L.; Moreira, X. Effect of herbivore load on VOC-mediated plant communication in potato. *Planta* **2023**, *257*, 42. <https://doi.org/10.1007/s00425-023-04075-6>. Correction in *Planta* **2023**, *260*, 139. <https://doi.org/10.1007/s00425-024-04546-4>.
38. Degenhardt, D.C.; Lincoln, D.E. Volatile emissions from an odorous plant in response to herbivory and methyl jasmonate exposure. *J. Chem. Ecol.* **2006**, *32*, 725–743. <https://doi.org/10.1007/s10886-006-9030-2>.
39. Rieksta, J.; Li, T.; Michelsen, A.; Rinnan, R. Synergistic effects of insect herbivory and changing climate on plant volatile emissions in the subarctic tundra. *Glob. Chang. Biol.* **2021**, *27*, 5030–5042. <https://doi.org/10.1111/gcb.15773>.
40. Lin, T.; Zhu, G.; He, W.; Xie, J.; Li, S.; Han, S.; Zhu, T. Soil cadmium stress reduced host plant odor selection and oviposition preference of leaf herbivores through the changes in leaf volatile emissions. *Sci. Total Environ.* **2022**, *814*, 152728. <https://doi.org/10.1016/j.scitotenv.2021.152728>.
41. Irmisch, S.; Jiang, Y.; Chen, F.; Gershenzon, J.; Köllner, T.G. Terpene synthases and their contribution to herbivore-induced volatile emission in western balsam poplar (*Populus trichocarpa*). *BMC Plant Biol.* **2014**, *14*, 270. <https://doi.org/10.1186/s12870-014-0270-y>.
42. Menezes, I.O.; Scherf, J.R.; Martins, A.O.B.P.B.; Ramos, A.G.B.; Quintans, J.D.S.S.; Coutinho, H.D.M.; de Menezes, I.R.A. Biological properties of terpinolene evidenced by in silico, in vitro and in vivo studies: A systematic review. *Phytomedicine* **2021**, *93*, 153768. <https://doi.org/10.1016/j.phymed.2021.153768>.
43. Andersson, M.N.; Larsson, M.C.; Blaženec, M.; Jakuš, R.; Zhang, Q.H.; Schlyter, F. Peripheral modulation of pheromone response by inhibitory host compound in a beetle. *J. Exp. Biol.* **2010**, *213*, 3332–3339. <https://doi.org/10.1242/jeb.044396>.
44. Kuhns, E.H.; Martini, X.; Tribuiani, Y.; Coy, M.; Gibbard, C.; Peña, J.; Stelinski, L.L. Eucalyptol is an attractant of the redbay ambrosia beetle, *Xyleborus glabratus*. *J. Chem. Ecol.* **2014**, *40*, 355–362. <https://doi.org/10.1007/s10886-014-0427-z>.
45. Wang, J.Z.; Qi, Y.T.; Zhang, J.W.; Fei, C.; Yuan, Y.K.; Du, S.S. Contact toxicity and repellent activity of essential oils from *Alpinia zerumbet* cv. ‘Variegata’ against stored product insects. *Int. J. Food Prop.* **2023**, *26*, 3433–3444. <https://doi.org/10.1080/10942912.2023.2286896>.
46. Nabity, P.D.; Haus, M.J.; Berenbaum, M.R.; DeLucia, E.H. Leaf-galling phylloxera on grapes reprograms host metabolism and morphology. *Proc. Natl. Acad. Sci. USA* **2013**, *110*, 16663–16668. <https://doi.org/10.1073/pnas.1220219110>.
47. Nabity, P.D. Insect-induced plant phenotypes: Revealing mechanisms through comparative genomics of galling insects and their hosts. *Am. J. Bot.* **2016**, *103*, 979–981. <https://doi.org/10.3732/ajb.1600111>.
48. Kanagendran, A.; Pazouki, L.; Bichele, R.; Külheim, C.; Niinemets, Ü. Temporal regulation of terpene synthase gene expression in *Eucalyptus globulus* leaves upon ozone and wounding stresses: Relationships with stomatal ozone uptake and emission responses. *Environ. Exp. Bot.* **2018**, *155*, 552–565. <https://doi.org/10.1016/j.envexpbot.2018.08.002>.
49. Melcher, E.; Jüngel, P.; Möllendorf, B.; Schmitt, U. Identification of a hydroxy substituted calamenene—A sesquiterpene associated with wound reactions in non-infected xylem of *Tilia* spp. *Phytochemistry* **2003**, *62*, 707–713. [https://doi.org/10.1016/S0031-9422\(02\)00362-X](https://doi.org/10.1016/S0031-9422(02)00362-X).
50. Morimoto, M.; Cantrell, C.L.; Libous-Bailey, L.; Duke, S.O. Phytotoxicity of constituents of glandular trichomes and the leaf surface of camphorweed, *Heterotheca subaxillaris*. *Phytochemistry* **2009**, *70*, 69–74. <https://doi.org/10.1016/j.phytochem.2008.09.026>.
51. Rozman, V.; Kalinovic, I.; Korunic, Z. Toxicity of naturally occurring compounds of Lamiaceae and Lauraceae to three stored-product insects. *J. Stored Prod. Res.* **2007**, *43*, 349–355. <https://doi.org/10.1016/j.jspr.2006.09.001>.

52. Lu, X.X.; Feng, Y.X.; Du, Y.S.; Zheng, Y.; Borjigidai, A.; Zhang, X.; Du, S.S. Insecticidal and repellent activity of *Thymus quinque-costatus* Celak. essential oil and major compositions against three stored-product insects. *Chem. Biodivers.* **2021**, *18*, e2100374. <https://doi.org/10.1002/cbdv.202100374>.
53. Major, R.T.; Marchini, P.; Spboston, T. Isolation from *Ginkgo biloba* L. of an inhibitor of fungus growth. *J. Biol. Chem.* **1960**, *235*, 3298–3299. [https://doi.org/10.1016/S0021-9258\(20\)81355-6](https://doi.org/10.1016/S0021-9258(20)81355-6).
54. Zhang, S.; Zheng, M.; Zhai, H.; Lyu, Y.; Hu, Y.; Cai, J. Effects of hexanal fumigation on fungal spoilage and grain quality of stored wheat. *Grain Oil Sci. Technol.* **2021**, *4*, 10–17. <https://doi.org/10.1016/j.gaost.2020.12.002>.
55. Dickens, J.C. Green leaf volatiles enhance aggregation pheromone of boll weevil, *Anthonomus grandis*. *Entomol. Exp. Appl.* **1989**, *52*, 191–203. <https://doi.org/10.1111/j.1570-7458.1989.tb01268.x>.
56. Gueldner, R.C.; Wilson, D.M.; Heidt, A.R. Volatile compounds inhibiting *Aspergillus flavus*. *J. Agric. Food Chem.* **1985**, *33*, 411–413. <https://doi.org/10.1021/jf00063a022>.
57. Andersen, R.A.; Hamilton-Kemp, T.R.; Hildebrand, D.F.; McCracken, C.T., Jr.; Collins, R.W.; Fleming, P.D. Structure–antifungal activity relationships among volatile C6 and C9 aliphatic aldehydes, ketones, and alcohols. *J. Agric. Food Chem.* **1994**, *42*, 1563–1568. <https://doi.org/10.1021/jf00043a033>.
58. Rahman, A.; Al-Reza, S.M.; Kang, S.C. Antifungal activity of essential oil and extracts of *Piper chaba* Hunter against phytopathogenic fungi. *J. Am. Oil Chem. Soc.* **2011**, *88*, 573–579. <https://doi.org/10.1007/s11746-010-1698-3>.
59. Jin, X.; Sun, T.; Guo, B.; Cui, J.; Ling, Y.; Zhang, L.; Yang, X. Design, synthesis, and biological activity of novel benzo[d][1,3]dioxole-6-benzamide derivatives: Multichitinase inhibitors as potential insect growth regulator candidates. *J. Agric. Food Chem.* **2023**, *71*, 8345–8355. <https://doi.org/10.1021/acs.jafc.3c00775>.
60. Bakry, M.; Mohammed, L.; Dabour, N.; Gad, M. Design and synthesis of novel N,N'-substituted benzamide derivatives as potential insecticidal agents against the white mango scale insect, *Aulacaspis tubercularis* (Hemiptera: Diaspididae). *Curr. Chem. Lett.* **2024**, *13*, 173–186. <https://doi.org/10.5267/j.ccl.2023.7.003>.
61. Napolitano, C.; Benfatti, F.; Hamdan, F.B.; Bristow, J.A.; Dapiaggi, F.; Firth, L.C.; Eterovic, M. Synthesis and insecticidal activity of N-(5-phenylpyrazin-2-yl)-benzamide derivatives: Elucidation of mode of action on chitin biosynthesis through symptomology and genetic studies. *Pestic. Biochem. Physiol.* **2024**, *199*, 105771. <https://doi.org/10.1016/j.pestbp.2024.105771>.
62. Eberl, F.; Hammerbacher, A.; Gershenzon, J.; Unsicker, S.B. Leaf rust infection reduces herbivore-induced volatile emission in black poplar and attracts a generalist herbivore. *New Phytol.* **2018**, *220*, 760–772. <https://doi.org/10.1111/nph.14565>.
63. Kessler, D.; Diezel, C.; Clark, D.G.; Colquhoun, T.A.; Baldwin, I.T. Petunia flowers solve the defence/apparency dilemma of pollinator attraction by deploying complex floral blends. *Ecol. Lett.* **2013**, *16*, 299–306. <https://doi.org/10.1111/ele.12038>.
64. Lackus, N.D.; Schmidt, A.; Gershenzon, J.; Köllner, T.G. A peroxisomal β -oxidative pathway contributes to the formation of C₆–C₁ aromatic volatiles in poplar. *Plant Physiol.* **2021**, *186*, 891–909. <https://doi.org/10.1093/plphys/kiab111>.
65. Peng, W.; Li, D.; Zhang, M.; Ge, S.; Mo, B.; Li, S.; Ohkoshi, M. Characteristics of antibacterial molecular activities in poplar wood extractives. *Saudi J. Biol. Sci.* **2017**, *24*, 399–404. <https://doi.org/10.1016/j.sjbs.2015.10.026>.
66. Bakun, P.; Czarczynska-Goslinska, B.; Goslinski, T.; Lijewski, S. In vitro and in vivo biological activities of azulene derivatives with potential applications in medicine. *Med. Chem. Res.* **2021**, *30*, 834–846. <https://doi.org/10.1007/s00044-021-02701-0>.
67. Rodriguez-Saona, C.; Maynard, D.F.; Phillips, S.; Trumble, J.T. Avocadofurans and their tetrahydrofuran analogues: Comparison of growth inhibitory and insecticidal activity. *J. Agric. Food Chem.* **2000**, *48*, 3642–3645. <https://doi.org/10.1021/jf9910638>.
68. Lande, S.; Westin, M.; Schneider, M. Development of modified wood products based on furan chemistry. *Mol. Cryst. Liq. Cryst.* **2008**, *484*, 367–378. <https://doi.org/10.1080/15421400801901456>.
69. Lu, Q.; Zhang, Z.F.; Dong, C.Q.; Zhu, X.F. Catalytic upgrading of biomass fast pyrolysis vapors with nano metal oxides: An analytical Py-GC/MS study. *Energies* **2010**, *3*, 1805–1820. <https://doi.org/10.3390/en3111805>.
70. Teixeira, M.G.; Alvarenga, E.S.; Pimentel, M.F.; Picanço, M.C. Synthesis and insecticidal activity of lactones derived from furan-2(5H)-one. *J. Braz. Chem. Soc.* **2015**, *26*, 2279–2289. <https://doi.org/10.5935/0103-5053.20150217>.
71. Rafedzi, E.A.K.; Bharudin, I.; Kamaruddin, S.; Diba, F.; Murad, A.M.A. Volatile organic compounds (VOCs) emission and antioxidant activities of rice treated with a consortium of plant growth-promoting rhizobacteria under drought conditions. *Univ. J. Agric. Res.* **2023**, *11*, 916–928. <https://doi.org/10.13189/ujar.2023.110516>.
72. Poland, T.M.; Pureswaran, D.S.; Ciaramitaro, T.M.; Borden, J.H. 1-Octen-3-ol is repellent to *Ips pini* (Coleoptera: Curculionidae: Scolytinae) in the midwestern United States. *Can. Entomol.* **2009**, *141*, 158–160. <https://doi.org/10.4039/n09-002>.
73. Macedo, G.E.; Vieira, P.D.B.; Rodrigues, N.R.; Gomes, K.K.; Rodrigues, J.F.; Franco, J.L.; Posser, T. Effect of fungal indoor air pollutant 1-octen-3-ol on levels of reactive oxygen species and nitric oxide as well as dehydrogenases activities in *Drosophila melanogaster* males. *J. Toxicol. Environ. Health A* **2022**, *85*, 573–585. <https://doi.org/10.1080/15287394.2022.2054887>.

74. Castracani, C.; Tamarri, V.; Grasso, D.A.; Le Moli, F.; Palla, G.; Millar, J.G.; Mori, A. Chemical communication in mating behaviour of the slave-making ant *Polyergus rufescens* (Hymenoptera, Formicidae): 3-ethyl-4-methylpentanol as a critical component of the queen sex pheromone. *Insectes Soc.* **2008**, *55*, 137–143. <https://doi.org/10.1007/s00040-008-0981-x>.
75. Iwamoto, N.; Nakamuta, K.; Millar, J.G. Sex attractant pheromone of the Japanese slave-making ant, *Polyergus samurai*. *J. Chem. Ecol.* **2020**, *46*, 520–523. <https://doi.org/10.1007/s10886-020-01179-1>.
76. Kostovcik, M.; Bateman, C.C.; Kolarik, M.; Stelinski, L.L.; Jordal, B.H.; Hulcr, J. The ambrosia symbiosis is specific in some species and promiscuous in others: Evidence from community pyrosequencing. *ISME J.* **2015**, *9*, 126–138. <https://doi.org/10.1038/ismej.2014.115>.
77. Duan, Y.; Chen, R.; Zhang, R.; Jiang, W.; Chen, X.; Yin, C.; Mao, Z. Isolation and identification of *Bacillus vallismortis* HSB-2 and its biocontrol potential against apple replant disease. *Biol. Control* **2022**, *170*, 104921. <https://doi.org/10.1016/j.biocontrol.2022.104921>.
78. Ueda, H.; Kikuta, Y.; Matsuda, K. Plant communication: Mediated by individual or blended VOCs? *Plant Signal. Behav.* **2012**, *7*, 222–226. <https://doi.org/10.4161/psb.18765>.
79. Van Tol, R.W.H.M.; Visser, J.H. Olfactory antennal responses of the vine weevil *Otiorhynchus sulcatus* to plant volatiles. *Entomol. Exp. Appl.* **2002**, *102*, 49–64. <https://doi.org/10.1046/j.1570-7458.2002.00924.x>.
80. Kigathi, R.N.; Weisser, W.W.; Veit, D.; Gershenzon, J.; Unsicker, S.B. Plants suppress their emission of volatiles when growing with conspecifics. *J. Chem. Ecol.* **2013**, *39*, 537–545. <https://doi.org/10.1007/s10886-013-0275-2>.
81. Kigathi, R.N.; Weisser, W.W.; Reichelt, M.; Gershenzon, J.; Unsicker, S.B. Plant volatile emission depends on the species composition of the neighboring plant community. *BMC Plant Biol.* **2019**, *19*, 48. <https://doi.org/10.1186/s12870-018-1541-9>.
82. Cara, N.; Piccoli, P.N.; Bolcato, L.; Marfil, C.F.; Masuelli, R.W. Variation in the amino acids, volatile organic compounds and terpenes profiles in induced polyploids and in *Solanum tuberosum* varieties. *Phytochemistry* **2020**, *180*, 112516. <https://doi.org/10.1016/j.phytochem.2020.112516>.
83. Salek, R.M.; Steinbeck, C.; Viant, M.R.; Goodacre, R.; Dunn, W.B. The role of reporting standards for metabolite annotation and identification in metabolomic studies. *Gigascience* **2013**, *2*, 2047–217X-2-13. <https://doi.org/10.1186/2047-217X-2-13>.
84. NIST/EPA/NIH Mass Spectral Library (NIST 05), 2005; National Institute of Standards and Technology, Gaithersburg, MD, USA.
85. R Core Team R: A Language and Environment for Statistical Computing; R Foundation for Statistical Computing: Vienna, Austria, 2024. Available online: <https://www.R-project.org/> (accessed on 13 January 2026).
86. Di Rienzo, J.A.; Casanoves, F.; Balzarini, M.G.; Gonzalez, L.; Tablada, M.; Robledo, C.W. InfoStat Versión 2020. Centro de Transferencia InfoStat, FCA, Universidad Nacional de Córdoba, Argentina. Available online: <http://www.infostat.com.ar> (accessed on 13 January 2026).

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