INDUCTION BY CATERPILLARS OF STORED AND EMITTED VOLATILES AMONG POPULATIONS OF WILD COTTON (*GOSSYPIUM HIRSUTUM*)

Short title: Plant volatiles of wild cotton chemotypes

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ABSTRACT

Upland cotton (*Gossypium hirsutum*) plants constitutively store volatile terpenes in their leaves, which are steadily emitted at low levels. Herbivory leads to a greater release of these stored volatiles. Additionally, damaged plants increase terpene accumulation and emit other terpenes and additional volatiles. This has been well characterised for cultivated cotton, but little is known about volatile emissions in wild cotton. We investigated how herbivory by the beet armyworm (*Spodoptera exigua*) affects both leaf-stored and emitted volatiles in wild cotton plants from populations found along the Yucatan coast and assessed different scales of intraspecific variation in induced volatiles. Furthermore, we examined how leaf-terpene chemotypes differ in volatile emissions from intact and damaged plants. Herbivory triggered changes in stored and emitted volatiles in a manner similar to what is known for cultivated cotton. However, we report for the first time the emission of volatile aldoximes by cotton plants, which were only detected in the headspace upon herbivory, and displayed interpopulation variation. Intraspecific variation was also observed in the induced emissions of nitriles and some terpenes. In addition, chemotypes differed in their induction of the (*E*)-β-ocimene in leaves. Distinctions between terpene chemotypes were reflected in the emissions from both intact and damaged plants, suggesting differences in how dominant terpenes of each chemotype might affect airborne interactions. However, these variable terpenes showed weak inducibility, raising questions about their functions. This comprehensive insight into herbivore-induced volatiles in wild cotton may help in the development of future pest-management strategies for cotton crops.

Keywords: *Gossypium hirsutum*; wild cotton; herbivore-induced plant volatiles (HIPVs); intraspecific variation; chemotype; terpenes; aldoximes

INTRODUCTION

Plants emit volatiles that can play various defensive roles against insect herbivores. Volatile plant metabolites can function as toxins, repel insect feeding and oviposition, and attract natural enemies of their attackers (Unsicker et al., 2009; Turlings and Erb, 2018). Volatiles also mediate signaling within plants (Rodriguez-Saona and Frost, 2010) and may be passively used as protection, or actively perceived by neighboring plants (Karban et al., 2014b; Erb et al., 2015; Grof-Tisza et al., 2022). Unharmed plants can produce and emit certain volatiles constitutively, a phenomenon particularly prevalent in plant species that accumulate volatile terpenes in specialized structures. These stored terpenes are continuously emitted at low levels by intact plants and are released in larger quantities when the storage organs are physically damaged, for example by chewing herbivores (Loreto and Schnitzler, 2010; Lange, 2015; Bustos-Segura and Foley, 2018). Additionally, when plants detect an insect attack, they may actively synthesize so-called herbivore-induced plant volatiles (HIPVs), which can include compounds that are produced constitutively but synthesized in greater amounts upon damage, or compounds whose synthesis is triggered exclusively in response to herbivory (Dicke and Baldwin, 2010; Turlings and Erb, 2018).

Several wild plant species have been shown to exhibit intraspecific variation in their chemical phenotypes. This chemodiversity often has a genetic basis and can modulate the interactions between plants and their environment (Moore et al., 2014; Kessler and Kalske, 2018; Müller and Junker, 2022). Various species that constitutively produce volatile terpenes present discrete chemical polymorphisms (chemotypes hereafter) (e.g. Keefover-Ring et al., 2009; Taft et al., 2015; Clancy et al., 2016; Bustos-Segura et al., 2017; Grof-Tisza et al., 2021). Importantly, this variation has been associated with differences in resistance to abiotic stress (Amiot et al., 2005; Kleine and Müller, 2014), allelopathy (Linhart et al., 2015), defense against pathogens (Bustos-Segura et al., 2015) and herbivores (Linhart and Thompson, 1999; Kleine and Müller, 2011; Bustos-Segura et al., 2015; Karban et al., 2016; Senft et al., 2019), as well as airborne signaling between plants when stored terpenes are released by damage (Karban et al., 2014a; Grof-Tisza et al., 2022). This variation is likely linked to genetic polymorphisms of the synthetizing enzymes: for instance, variability in a terpene synthase (TPS) gene cluster underlies the constitutive chemotypes of *Melaleuca alternifolia* (Voelker et al., 2023).

Intraspecific variation in herbivory-induced volatiles has also been described (Hare, 2011). Differences in the induction of volatile emissions have been reported across several wild species, such as: *Nicotiana attenuata* (Halitschke et al., 2000; Schuman et al., 2009), *Datura wrightii*, (Hare, 2007), *Solanum carolinense* (Delphia et al., 2009; Kariyat et al., 2012), *Arabidopsis thaliana* (Huang et al., 2010), *Asclepias syriaca* (Wason et al., 2013), *Quercus robur* (Ghirardo et al., 2012) and *Vicia sepium* (Rasmann et al., 2014). As with constitutive volatiles, variation in induced volatiles can be linked to differences in synthetic pathways. In *N. attenuata* for instance, differences in the emission rates of the herbivore-induced terpenes linalool, (*E*)-β-ocimene and (*E*)-α-bergamotene are associated with allelic variations of *TPS* genes (He et al., 2019; Xu et al., 2020). However, fluctuations in (*E*)-α-bergamotene are also correlated with differences in the accumulation of the phytohormone jasmonic acid (JA) (Schuman et al., 2009); showing that variation in volatile induction can also be associated to differences in the endogenous signaling cascades that regulate the plants' response to herbivory.

Upland cotton (*Gossypium hirsutum* L. Malvaceae) is cultivated worldwide as a major source of natural fiber and suffers from high levels of herbivory from multiple insect pests (Hagenbucher et al., 2013). Increasing our understanding of the natural defense mechanisms of cotton could aid in the advancement of sustainable pest control strategies and the development of more resistant cultivars (Mitchell et al., 2016; Pickett and Khan, 2016; Turlings and Erb, 2018; Villamar-Torres et al., 2018). Cotton plants constitutively store volatile mono- and sesquiterpenes in specialized glands present in their leaf tissues (Elzen et al., 1985; Hagenbucher et al., 2013). Herbivory on older leaves induces an increase in the concentrations of these terpenes in young undamaged leaves (Opitz et al., 2008; Mamin et al., 2023). These leaf-stored terpenes are steadily emitted at low levels from intact leaves, however large quantities are immediately released following gland rupture, as caused by chewing insects (Loughrin et al., 1994; McCall et al., 1994; Röse et al., 1996; Paré and Tumlinson, 1997). Therefore, the volatile emissions instantly resulting from insect damage primarily comprise locally released leaf mono- and sesquiterpenes, together with green leaf volatiles (GLVs; aldehydes and alcohols), that are linked to tissue disruption (Loughrin et al., 1994; McCall et al., 1994). Herbivory also induces a delayed emission of mono-, sesqui- and homoterpenes, which are systematically emitted (i.e. also by undamaged parts) following *de novo* synthesis, and concurrently also triggers the emissions of other newly synthesized volatiles, such as the aromatic indole and GLV esters (Loughrin et al., 1994; McCall et al., 1994; Röse et al., 1996; Paré and Tumlinson, 1997; McAuslane and Alborn, 1998; Röse and Tumlinson, 2005; Arce et al., 2021). Thus, volatile emissions from cultivated cotton plants sustaining caterpillar herbivory mainly comprise terpenes released from constitutively stored pools at damaged sites, alongside compounds whose emissions are truly induced, with the latter coming from biosynthesis activated in response to herbivory. When active physical damaging ceases, the emission of constitutive leaf-stored terpenes drops rapidly, while induced compounds continue to be emitted (Loughrin et al., 1994). The distinction between constitutive and truly inducible terpenes is not so clear cut with some studies reporting systemic emissions of terpenes described as being constitutively stored in leaves (Röse and Tumlinson, 2005; Arce et al., 2021). Collectively, volatile emissions of insect-damaged cotton plants appear to serve as direct and indirect defenses (reviewed in Hagenbucher et al., 2013), and are involved in plant-plant interactions (Zakir et al., 2013; Llandres et al., 2018; Briones-May et al., 2023).

Given the depletion of genetic diversity observed in modern cultivars of *G. hirsutum* (Yuan et al., 2021), exploring useful defensive traits in wild cotton should be considered. While volatile production in cultivated cotton has been well characterized, less is known about the volatiles produced by wild cotton (but see Loughrin et al., 1995; Hagenbucher et al., 2016; Quijano-Medina et al., 2021; Briones-May et al., 2023). *G. hirsutum* was domesticated at least 4,000 years ago in the Yucatán Peninsula (southeast Mexico) (Yuan et al., 2021), where wild populations still grow naturally along its northern coastline (Wegier et al., 2011; Coppens d'Eeckenbrugge and Lacape, 2014). Recently, we described two heritable constitutive leaf-terpene chemotypes in wild cotton plants from the Yucatan coast: one chemotype containing none or low amounts of γ-terpinene (and other co-expressed monoterpenes), and the other exhibiting distinctively higher abundances of these compounds in their leaves (Clancy et al., 2023). It is worthwhile to note that production of γ-terpinene has been only described in wild/naturalized cotton (Loughrin et al., 1995; Hagenbucher et al., 2016). If γ-terpinene variation in leaves influences the composition of the volatile emissions of intact and/or herbivore-damaged wild cotton plants, it could impact the plants' interactions with organisms that use these volatiles as a cue, such as herbivores looking for a host plant, their natural enemies, or neighboring plants.

The present study investigated the volatile emissions of wild cotton plants, and the induction by caterpillar herbivory of foliar terpenes as well as volatiles emitted to the headspace. We determined the consistency of leaf-terpene chemotypes in the emissions of intact and damaged plants. Furthermore, we evaluated differences in the induction of stored and emitted volatiles between the two chemotypes and at different scales of intraspecific variation. To this end, we analyzed the stored volatiles in leaves and headspace volatile emissions of both undamaged plants and plants that were continuously damaged for two days by the beet armyworm (*Spodoptera exigua* (Hübner; Lepidoptera; Noctuidae)). Plants were grown in a common garden environment from seeds collected from sixteen wild cotton populations forming four distinct geographic zones distributed along the Yucatan coastline. Prevalence of the two chemotypes along the coast was previously found to follow a geographic gradient, with increasing relative abundance of the γ-terpinene chemotype from west to east (Clancy et al., 2023). We examined the variation in the increase of volatiles upon herbivory (i.e. group-by-herbivory interaction) and the variation in production rates of volatiles only produced by damaged plants (i.e. direct effect of the group of interest) between chemotypes and across the three nested levels: genotype, population and the geographic region grouping the populations. The results presented here shed new light on the production of volatiles by wild cotton plants in response to caterpillar herbivory, and uncover sources of variation, which may be genetically based, thereby opening new avenues to study and exploit cotton HIPVs as a defense mechanism against insect pests.

Results

1 Volatile terpenes in leaves

We analyzed volatile content from the leaves of undamaged (n=353) and damaged (n=322) wild cotton plants with using hexane extraction (Fig. 1). A total of 15 monoterpenes and 18 sesquiterpenes were quantified in the leaf extracts (Table S2).

1.1 Terpene chemotypes in leaves

Undamaged and damaged plants were chemotyped based on the contribution of six strongly correlated compounds relative to the total monoterpene concentration (γ-terpinene, limonene, α-thujene, terpinolene, p-cymene, and α-terpinene, in order of abundance; *sensu* Clancy et al. 2023; Fig. S1 and S2 and Table S2). Plants containing higher proportions (> 4%) of these compounds were assigned to chemotype A; plants with less than 4% were assigned to chemotype B (Fig. S3).

1.2 Effect of herbivory on the accumulation of volatile terpenes in leaves

Following herbivory on the first and second leaves of four-leaf plants, the total leaf concentration of mono- and sesquiterpenes increased by 9% on average in the undamaged fourth leaves (Fig. 2A, $\chi^2_{(1)} = 12.407$, $p < 0.001$). The same compounds were detected in the leaf terpene profiles of undamaged and damaged plants (Table S2), but a partial redundancy analysis (pRDA) revealed that herbivory affected their relative abundances (Fig. 2B, $F_{(1,670)} = 6.414$, $p = 0.001$). This was mainly due to the increase in the proportion of the monoterpene (*E*)-β-ocimene upon herbivory, followed by several sesquiterpenes, notably δ-cadinene, α-copaene (Fig. 2B). The induction of (*E*)-β-ocimene depended on chemotype (Fig. 2A; chemotype x herbivory: $\chi^2_{(1)} = 7.694$, $p = 0.006$), with a 64% increase in chemotype A plants (contrast of EMMs: $p < 0.001$) and a 108% increase in chemotype

134 B plants (contrast of EMMs: $p < 0.001$). Leaf content of the sesquiterpenes δ-cadinene and (*E*)-β-caryophyllene increased
135 following herbivory, by 27% (Fig. 2A, $\chi^2_{(1)} = 27.201$, $p < 0.001$) and 11% (Fig. 2A: $\chi^2_{(1)} = 14.254$, $p < 0.001$) respectively. In
136 contrast, levels of α-pinene, the most abundant monoterpene in leaves (Table S2), did not change upon herbivory (Fig. 2A,
137 $\chi^2_{(1)} = 0.437$, $p = 0.509$). This was also the case for γ-terpinene, the main monoterpene characteristic for chemotype A (Fig. 2A,
138 $\chi^2_{(1)} = 0.766$, $p = 0.381$). The total accumulation of (*E*)-β-ocimene increased with the amount of leaf tissue consumed by *S.*
139 *exigua,* however this effect of damage intensity was not significant for the other terpenes tested (Fig. S4: (*E*)-β-ocimene: $\chi^2_{(1)}$
140 $= 5.619$, $p = 0.018$).

141 ### 1.2 Variation in the induction of volatile terpenes in leaves

142 We tested variation in induction (i.e. variation in the increase in leaf concentrations in response to herbivory; group-by-her-
143 bivory interaction) for the total leaf terpene content and for the aforementioned compounds between the two chemotypes
144 and among genotypes, populations and the four geographic regions (Table 1). As mentioned above, induction of (*E*)-β-oci-
145 mene in wild cotton leaves varied between the two chemotypes (Fig. 2A and Table 1; chemotype x herbivory: $\chi^2_{(1)} = 7.694$, p
146 $= 0.005$), with a stronger induction observed in chemotype B plants. Chemotype A plants exhibited constitutively higher
147 amounts of (*E*)-β-ocimene in their leaves than chemotype B plants (Fig. S5, $\chi^2_{(1)} = 8.247$, $p = 0.004$); this difference was no
148 longer significant following herbivory (Fig. S5, $\chi^2_{(1)} = 0.793$, $p = 0.373$). We did not find any significant variation in induction of
149 any tested compounds among genotypes, populations, and regions (Table 1).

150 ## 2 Headspace volatile emissions

151 The volatile emissions of undamaged and damaged wild cotton plants were collected and characterized in a subset of the
152 plants that were afterwards used for leaf extraction (Fig. 1; 45 undamaged and 48 damaged plants). We quantified a total of
153 54 compounds in the headspace (Fig. 3A and Table S3). Terpenes comprised the most diverse group, with 13 monoterpenes,
154 13 sesquiterpenes, and the homoterpenes DMNT and TMTT identified (Fig. 3A). Additionally, headspace emissions contained
155 many fatty acids derivatives, which comprised GLV aldehydes, alcohols, and esters, and (*Z*)-jasmone (Fig. 3A). Also, we iden-
156 tified three aliphatic aldoximes and several aromatic compounds including two nitriles. Most of the mono- and sesquiterpenes
157 detected in the headspace were also found in the leaf extracts, as well as a GLV aldehyde (Fig. 3A).

158 ### 2.1 Terpene chemotypes in volatile emissions

159 Of the six monoterpenes that were used to define chemotypes A and B using leaf extracts, the following compounds were
160 also detected in the headspace emissions (in order of abundance): γ-terpinene, limonene, p-cymene, and α-thujene. For both
161 undamaged and damaged plants, volatile emissions of the two chemotypes were clearly distinguishable by the prevalence of
162 γ-terpinene, p-cymene, and α-thujene (Fig. 3B and 4A), which were highly correlated (Fig. S6 and S7). The ratio of γ-terpinene
163 to α-pinene emissions was highly correlated to their ratios in the leaves (Fig. 5).

164 ### 2.2 Effect of herbivory on volatile emissions

165 The volatile blend emitted by undamaged plants was mainly composed of mono- and sesquiterpenes that were also found in
166 leaf extracts, with (*E*)-β-caryophyllene and α-pinene dominating the median profile of both chemotype A and B plants (Fig.
167 3B). Herbivory caused the total volatile emissions to increase 8.7-fold (Fig. 4B, $\chi^2_{(1)} = 146.449$, $p < 0.001$) and triggered quali-
168 tative and quantitative changes in their composition (Fig. 3, 4A and S8). Damaged plants released several compounds that
169 were absent from the headspace of intact plants, specifically aliphatic aldoximes, benzyl nitrile and another unidentified ni-
170 trile, the aromatics indole and methyl anthranilate, butyric and hexenoic acid esters of GLVs, (*Z*)-jasmone, the acyclic sesquit-
171 erpenes (*E*)-β-farnesene and (*E,E*)-α-farnesene, and monoterpene (*E*)-myroxide (Fig. 3). Other compounds such as the acyclic
172 monoterpenes (*E*)-β-ocimene, linalool and (*Z*)-linalool oxide, the homoterpenes DMNT and TMTT, and the GLV ester (*Z*)-3-
173 hexenyl acetate were emitted in low amounts by some of the undamaged plants, but their prevalence greatly increased fol-
174 lowing herbivory (Fig. 3B, 4A and S8). Indole, DMNT, (*Z*)-3-hexenyl acetate, and (*E*)-β-ocimene were major constituents of the
175 volatile blend from damaged plants of both chemotypes (Fig. 3B). The emission rates of the mono- and sesquiterpenes that
176 were also found in the leaf extracts generally exhibited small increases upon herbivory (Fig. 4B). However, due to greater
177 increases of other compounds, their relative contribution to the emissions of damaged plants decreased (Fig. 3B and 4A). This
178 was not the case of (*E*)-β-ocimene, which exhibited a distinctly high increase in response to herbivory compared to the other
179 terpenes found in both headspace and leaves. Irrespective of chemotype ($\chi^2_{(1)} = 1.901$, $p = 0.168$), the amounts emitted of (*E*)-
180 β-ocimene rose 26-fold in response to herbivory (Fig. 4B, $\chi^2_{(1)} = 139.057$, $p < 0.001$). In contrast, (*E*)-β-caryophyllene and α-
181 pinene only increased 2.6-fold (Fig. 4B, $\chi^2_{(1)} = 33.800$, $p < 0.001$) and 3.2-fold (Fig. 4B, $\chi^2_{(1)} = 56.859$, $p < 0.001$) respectively.
182 Emissions of δ-cadinene showed an intermediate increase of 11-fold (Fig. 4B, $\chi^2_{(1)} = 62.593$, $p < 0.001$). A particularly low
183 response was observed for γ-terpinene, with only a marginal increase in the headspace of 1.7-fold following herbivory (Fig.
184 4B, $\chi^2_{(1)} = 3.868$, $p = 0.049$). Emissions of γ-terpinene were independent of damage level (Fig 4C, $\chi^2_{(1)} = 1.299$, $p = 0.254$), similar
185 to p-cymene, α-thujene, and limonene (Fig. S9). The emissions of all other terpenes detected in both headspace and leaf
186 extracts were positively correlated with damage intensity (Fig. S9).

187 ### 2.3 Variation in herbivory-induced volatile emissions

188 We investigated whether there were differences in the volatile emissions induced by *S. exigua* between chemotypes, as well
189 as among regions and populations. Our analyses focused on highly inducible volatiles in order to evaluate variation in response
190 to herbivory. The highly inducible volatiles were defined as the compounds with a negative score on the first axis of the pRDA
191 in Figure 4A. Total emissions of these highly inducible compounds did not differ between chemotypes (Fig. S10, $\chi^2_{(2)} = 0.003$,
192 $p = 0.954$), nor among regions (Fig. S10, $\chi^2_{(3)} = 2.893$, $p = 0.408$) or populations ($\chi^2_{(1)} = 1.344$, $p = 0.246$). However, the pRDA
193 revealed differences between chemotypes (Fig. S11, $F_{(1,42)} = 1.189$, $p = 0.009$) and among regions (Fig. S12, $F_{(3,38)} = 1.904$, $p =$
194 0.005) in the composition of their HIPV emissions. Of the compounds highlighted by the pRDAs, the terpenes (*E,E*)-α-farne-
195 sene, (*E*)-myroxide, the three aldoximes and the two nitriles showed statistically significant differences in the emission rates
196 (Table 2). These compounds were all only detected in the headspace of damaged plants. We also observed variations in the
197 emissions of TMTT and δ-cadinene (Fig. S11 and S12); these volatiles were also found in undamaged plants but in lower
198 amounts. The absence of significant interactions between region/chemotype and herbivory suggests that the observed differ-
199 ences might not be specifically linked to a distinct response to herbivory (Fig. S11 and S12). Emission rates of (*E,E*)-α-farnesene

200 and (*E*)-myroxide varied among regions, as well as among populations, but not between chemotypes (Table 2, Fig. 6 and Fig.
201 S10). The three aldoximes, which were strongly correlated (Fig. S7), varied both among regions and between chemotypes.
202 Plants from Celestún (far west) and Sisal (west) produced higher quantities of aldoximes compared to plants from regions
203 further east (Table 2, Fig. 6 and Fig. S10). Chemotype B plants released higher amounts of these compounds than chemotype
204 A plants (Table 2, Fig. 6 and Fig. S10). Thus, variation could stem both from the chemotype and the geographic region, which
205 are partially nested. However, even when taking into account the effect of chemotype, significant variation was observed at
206 the population level for the two methylbutyraldoximes (Table 2). Benzyl nitrile showed the same trend in variation as the
207 aldoximes, while the opposite was observed for the unknown nitrile (Table 2, Fig. 6). For these latter two compounds, how-
208 ever, no evidence of variation among population was observed (Table 2).

209 Discussion

210 In this study, we investigated the effect of caterpillar herbivory on quantitative and qualitative changes in leaf-stored and
211 emitted volatiles of wild cotton plants from 16 population along the northern coast of the Yucatán Peninsula. Moreover, we
212 show that two previously described chemotypes found within these populations could also be distinguished based on their
213 headspace emissions, which was true for both undamaged and caterpillar-damaged plants. Responses of wild cotton plants
214 to herbivory were found to differ between chemotypes in the induction of (*E*)-β-ocimene in leaves; for the emission of several
215 HIPV chemical classes there were differences between chemotypes and among regions and/or populations.

216 1 Induction of volatile mono- and sesquiterpenes in leaves

217 Two days of herbivory on the first and second leaves led to a rapid accumulation of several volatile terpenes in the undamaged
218 fourth leaf of the same plants. The leaf terpenes differed in their inducibility, which resulted in compositional changes in leaf
219 volatile profiles triggered by herbivory. A similar variation in inducibility among compounds has previously been described for
220 domesticated varieties, with (*E*)-β-ocimene being the most responsive to damage, and with sesquiterpenes exhibiting a
221 stronger response than monoterpenes (Opitz et al., 2008; Mamin et al., 2023). The higher inducibility of (*E*)-β-ocimene may
222 allow for the increased synthesis of heliocides H1 and H4, the most inducible gland-stored, non-volatile defensive terpenoid
223 aldehydes produced by cotton, for which (*E)*-β-ocimene is a precursor, together with hemigossypolone (Stipanovic et al.,
224 1978; McAuslane et al., 1997; Opitz et al., 2008).

225 2 Induction of volatile emissions

226 The constitutive volatile emissions of wild cotton consisted mostly of terpenes that were also found accumulated in the leaves:
227 several cyclic terpenes, along with the linear terpenes β-myrcene and (*E*)-β-ocimene. This parallels previous descriptions of
228 cultivated varieties, where these compounds are known to be stored in glands and constitutively released in small amounts
229 (Elzen et al., 1985; Loughrin et al., 1994; Paré and Tumlinson, 1997). For most of these terpenes, we found a small increase in
230 their emission rates following herbivory. As there was no active damage occurring on the plant during sampling, this increase
231 could reflect passive release from storage pools in induced undamaged leaves, although we cannot exclude some leakage

from very fresh wounds, nor can a release from sources other than storage pools be fully ruled out (Gershenzon et al., 2000; Bustos-Segura and Foley, 2018). The latter is already known for (*E*)-β-ocimene in cultivated cotton, which is not only accumulated in the leaves but is also *de novo* synthesized and systemically emitted upon induction (Paré and Tumlinson, 1997). Consistent with this previously observed phenomenon, we found a particularly strong induction of (*E*)-β-ocimene emissions in comparison to the other terpenes detected in both leaves and headspace. Together with (*E*)-β-ocimene, the major compounds induced by *S. exigua* herbivory in wild cotton plants included indole, (*Z*)-3-hexenyl acetate, and several terpenes that were distinct from those found in stored pools, namely the linear terpenoids linalool, (*E*)-β-farnesene, (*E,E*)-α-farnesene, DMNT, and TMTT. This aligns with previous findings in cultivated cotton, showing that these compounds are newly synthesized following damage (Loughrin et al., 1994; McCall et al., 1994; Röse et al., 1996; Paré and Tumlinson, 1997; McAuslane and Alborn, 1998; Arce et al., 2021).

We identified several compounds that to the best of our knowledge have not yet been reported for cotton, including aliphatic aldoximes, nitriles, and the aromatic compound 2-phenylethanol. A nitrile compound previously described in wild cotton from Yucatán (Briones-May et al., 2023) likely corresponds to the nitrile we could not conclusively identify. Aldoximes are nitrogenous compounds synthesized from amino acids by cytochrome P450 monooxygenases of the CYP79 family, found across all angiosperms, and are precursors to nitriles (Irmisch et al., 2013; Sørensen et al., 2018). Aldoximes and nitriles may be precursors to volatile alcohols, such as 2-phenylethanol (Irmisch et al., 2014; Sørensen et al., 2018). Various plant species, including several Fabaceae, Populus, and Erythroxylum species, *Solanum melongena*, *Zea mays, Cucumis sativus*, and *Gerbera jamesonii* emit volatile aliphatic aldoximes in response to herbivory or jasmonic acid treatment (Sørensen et al., 2018). In *Populus trichocarpa,* herbivore-induced CYP79 enzymes produce (*E/Z*)-2-methylbutyraldoximes from L-isoleucine in response to caterpillar herbivory (Irmisch et al., 2013), and CYP71 enzymes convert aldoximes into nitriles, including benzyl nitrile, from the semi-volatile compound phenylacetaldoxime (Irmisch et al., 2014). Volatile aldoximes and nitriles could be involved in cotton indirect defenses; in *Populus nigra*, methylbutyraldoximes and benzyl nitrile are central to the recruitment of parasitoid wasps, despite being only minor components of the full induced volatile blend (Clavijo McCormick et al., 2014b). Benzyl nitrile is also involved in direct defense mechanisms of *Populus trichocarpa and P. nigra* (Irmisch et al., 2014; McCormick et al., 2016). Aldoximes and nitriles might be emitted in small amounts by cultivated *G. hirsutum*, and therefore more difficult to detect with classic sampling and analyses (Clavijo McCormick et al., 2014a). Our results seem to imply wild cotton plants produce more aldoximes and nitriles than cultivated varieties. This might be of interest for future studies as it could offer an opportunity to enhance the resistance of cultivated cotton varieties to herbivorous pests.

3 Chemotypes and their volatile terpene emissions

The two previously reported leaf-terpene chemotypes (Clancy et al., 2023) were also distinct in their headspace emissions, as the variation in the leaf content of γ-terpinene and its correlated compounds was mirrored in the emissions from both undamaged and damaged plants. This suggests that, in both cases, the primary source of emission for these compounds are the leaf storage pools, and that the chemotypes of wild cotton plants could differ in their airborne interactions with their environment. Volatile terpenes likely released from stored pools have been found to repel adult moths and piercing-sucking pests of

cultivated cotton (Jenkins et al., 1966; Zhang et al., 2020), and appear to function as foraging cues for some species of parasitoid wasps (Elzen et al., 1984, 1986; McCall et al., 1993; Zhang et al., 2020). Additional research is needed to evaluate how the two chemotypes may impact wild cotton's interactions with its insect herbivores and their natural enemies. Our results suggest that their role in this context may be of lesser importance, as γ-terpinene exhibited a notably low inducibility in comparison to other monoterpenes. Measurements at additional time points would be required to confirm this, but it appears that the TPSs associated with γ-terpinene synthesis are not responsive to caterpillar herbivory, suggesting that this compound is not involved in defense against *S. exigua*. As induction of volatiles in cotton can be specific to the species of an attacking herbivore (Rodriguez-Saona and Crafts-Brandner, 2003; Ngumbi et al., 2009; Harris et al., 2012; Huang et al., 2022), we recommend that future work investigates the response of wild cotton chemotypes to other herbivore species.

Increased production of monoterpenes has also been reported in several plant species in response to abiotic stresses such as drought and excessive temperatures, against which they may offer protective effects (Loreto and Schnitzler, 2010; Holopainen, 2011; Selmar and Kleinwächter, 2013; Tian et al., 2020; Bertamini et al., 2021). Interestingly, some plant species specifically increase γ-terpinene concentrations in their tissues under drought conditions (Alavi-Samani et al., 2015; Razavizadeh and Komatsu, 2018), and it has been demonstrated that γ-terpinene has a particularly high antioxidant capacity (Ruberto and Baratta, 2000; De Sousa et al., 2023). Previous work on Yucatanese wild cotton documented that populations in higher-temperature environments tend to exhibit a greater density of glands (albeit non-significantly), while herbivory pressure and gland density are not correlated among populations (Abdala-Roberts et al., 2019). This finding suggests that abiotic conditions could potentially be significant factors driving variation in gland density and their chemical content. Considering the particularly harsh environments in which wild cotton grows, it would be interesting to investigate the relationship between γ-terpinene content and tolerance to extreme environmental conditions.

4 Variation in the induction of leaf-stored volatiles and in HIPV emissions

In terms of leaf volatile content, the two chemotypes varied in their inducibility (magnitude of the increase in leaf concentrations) of the monoterpene (*E*)-β-ocimene, whereas there was no difference between chemotypes in the induction of (*E*)-β-ocimene in the headspace emissions. This is likely due to the possibility, as mentioned earlier, that most of its induced emissions may derive from *de novo* synthesis rather than stored pools (Paré and Tumlinson, 1997). Nevertheless, this variation in the inducibility of (*E*)-β-ocimene in leaves could have implications for wild cotton plants' airborne interactions, particularly in scenarios involving subsequent leaf damage, as it would lead to the release of the induced stored pools (Röse et al., 1996; McAuslane and Alborn, 1998). As for headspace HIPV emissions, we observed considerable intraspecific variation at the population and region levels in the emissions of the terpenes (*E,E*)-α-farnesene and (*E*)-myroxide, as well as in the emissions of aldoximes. Nitriles were also found to differ, to a lesser extent, among regions. Aldoximes and nitriles were also observed to vary between the two leaf-terpene chemotypes. As the prevalence of the two chemotypes was partially nested within region, the source of variation in emissions of these compounds cannot be conclusively ascertained. Having said this, the similarity between damaged plants from Chicxulub (high proportion of chemotype B) and Coloradas (dominance of chemotype A) in the production of both classes of compounds suggests that this variation is more likely linked to interpopulation differences than

300 to the chemotypes themselves. In contrast, chemotype-specific responses to caterpillar herbivory have been described in
301 another species (*Tanacetum vulgare*) for both leaf-stored and emitted volatiles (Clancy et al., 2020). Despite being confined
302 to coastal habitats, Yucatanese wild cotton is subjected to substantial spatial variability in herbivore pressure and abiotic
303 conditions (Abdala-Roberts et al., 2019; Munguía-Rosas et al., 2019; Quijano-Medina et al., 2019, 2021), which could be asso-
304 ciated with the origin of the observed variation in HIPVs. Further work is required to understand the drivers of these differ-
305 ences. Given the multiple proposed functions of HIPVs in plant defense against insect herbivores (Turlings and Erb, 2018), the
306 differences in HIPVs that we observed could have consequences for wild cotton's resistance to biotic and abiotic stresses,
307 which is worthy of further exploration. Genotypes producing higher amounts of various HIPVs that improve their direct or
308 indirect defenses or those of neighboring plants could be a valuable genetic resource in the development of more resistant
309 cotton cultivars.

310 MATERIALS AND METHODS

311 1 PLANTS AND INSECTS

312 Wild *Gossypium hirsutum* seeds were collected in 2019 and 2020 on the northern coast of the Yucatán Peninsula (Mexico) and
313 grown as described in Clancy et al. (2023). Seeds were sampled from several mother plants from 16 populations in four regions
314 along the coast (Table S1 and Fig. 1). As cotton cross-pollinates, seeds from the same mother are either full or half-siblings, of
315 unknown paternal source. Offspring from the same mother plant is referred to here as genotype. Plants were grown in a
316 greenhouse for around four weeks. Eventually, we obtained plants from one to six mother plants for each population, repre-
317 senting around 35 to 60 individuals per population, except for a few populations with particularly low germination rates (Table
318 S1). To induce volatile production in the cotton plants we used larvae of the moth *Spodoptera exigua* (Hübner; Lepidoptera;
319 Noctuidae), a cosmopolitan generalist pest that feeds on cotton. Eggs were supplied by Entocare (Wageningen, The Nether-
320 lands) and reared in the laboratory on wheat germ-based artificial diet (Frontier Scientific Services, Newark, USA).

321 2 EXPERIMENTAL PROCESS AND SAMPLE COLLECTION

322 Plants were used when the fourth leaf was fully expanded but still developing. A total of 322 plants were subjected to her-
323 bivory and 353 were left undamaged, in six experimental batches. The numbers of replicates per region and population are
324 described in Table S1. Second to early third-instar *S. exigua* larvae fed on the first and second leaves for two days, with a single
325 larva enclosed on each leaf in clip cages (4.52 cm^2, BioQuip product, USA). Undamaged and damaged plants were kept in two
326 adjacent rooms with similar configurations and conditions (L14:D10, T=28°C), to prevent any signaling effect of HIPVs. The
327 treatments were alternated between rooms after each batch. After two days of herbivory, we collected the volatile emissions
328 of a subset of the plants. A total of 45 undamaged and 48 damaged individuals were used in four batches for headspace
329 collection, chosen to represent the various populations (Table S1). Afterwards, the fourth leaf of all plants was harvested,
330 photographed, frozen in liquid nitrogen, and stored at -80 °C until processed. Photographs of all leaves were taken to quantify

the total leaf area consumed by *S. exigua*, as well as to determine the area (size) of the fourth leaves and the total leaf area (including cotyledons and secondary leaves) of the plants used for the headspace collections. For this purpose, we used the Fiji distribution of ImageJ software (Schindelin et al., 2012).

3 Headspace volatile collection and GC-MS analyses

S. exigua larvae were removed before headspace sampling, to avoid the release of volatiles due to physical tissue disruption by active feeding. The caterpillars' frass was removed from the leaves. Pots were covered with aluminum foil to limit potential emissions from the soil. Headspace volatiles were collected in a push-pull air system of custom-made glass bottles (VTQ SA, Switzerland). Charcoal-purified and humidified air was pushed at 1 L min^{-1} and pulled at 0.6 L min^{-1} through trapping filters (25 mg of 80/100 mesh Hayesep-Q adsorbent, Sigma, Switzerland) for two hours. Filters were eluted with 100 µL of dichloromethane, with the addition of 10 µL of internal standard solution (nonyl-acetate, 20 ng μL^{-1}). Samples were stored at -80 °C before being run on a gas chromatograph (GC Agilent 7890B) coupled to a mass spectrometer (MSD Agilent 5977B): 1.5 µL were autoinjected in splitless mode onto an Agilent HP-5MS column (30 m × 250 µm × 0.25 µm). The temperature was kept at 40 °C for 3.5 min, then ramped to 100 °C at 8 °C min^{-1} and to 230 °C at 5 °C min^{-1}. Helium was used as the carrier gas, with a stable flow of 0.9 mL min^{-1}.

4 Hexane leaf extractions and GC-MS analyses

Hexane leaf extractions and subsequent analyzes were performed as described in Clancy et al. (2023). Briefly, 100 mg of grounded frozen leaf material was extracted with 1 mL of hexane and kept at 4 °C for 24 hours. We recovered 800 µL and added 8 µL of internal standard solution (nonyl acetate, 2000 ng μL^{-1}). The samples were directly injected into a gas chromatograph (GC Agilent 8890A) coupled to a mass spectrometer (MSD Agilent 5977B): 1.5 µL were injected in splitless mode onto an Agilent HP-5MS column (30 m × 250 µm × 0.25 µm). Temperature started at 40°C for 0 min, ramped to 130 °C at 15 °C min^{-1}, then to 190 °C at 60 °C min^{-1}, and to 290 °C at 30 °C min^{-1}, then held for 0.5 min. Helium was used as carrier gas, with a stable flow of 0.9 mL $min^{-1.}$

5 GC-MS data processing

PyMS (O'Callaghan et al., 2012) was used to integrate and align peaks from the total ion chromatograms of all samples (https://github.com/bustossc/PyMS-routine/). Analytes were quantified using relative response factors obtained from a series of external calibration curves of commercial analytical standards in comparison to nonyl acetate (Table S2 and S3). For compounds lacking available response factors, we employed the relative response factor associated with the closest standard in retention time and similar chemical structure, while normalizing by molecular masses (Kreuzwieser et al. 2014). When possible, analytes were identified based on comparison with commercial standards. Aldoximes were identified with synthesized standards kindly provided by Prof. Tobias Köllner. Compounds with no standard available were identified based on mass

361 spectra comparison with NIST 2.3 mass spectral library, an in-house library, and Kovats retention indices (Van den Dool and
362 Kratz, 1963) (Table S2 and S3). Components retained in the analyzes were present in at least 10% of the samples. For the
363 hexane extracts, values were normalized by the fresh weights of the leaves (units: ng mg^{-1} FW). For headspace samples, values
364 were normalized by hours of collection and the total leaf area of the plants (units: ng h^{-1} cm^{-2}).

365 STATISTICAL ANALYZES

366 Statistical analyzes were carried out with R 4.2.3 (R Core Team, 2022). A significance level of $\alpha = 0.05$ was used for all analyzes.
367 Plots were built with "ggplot2" (v. 3.3.6, Wickham, 2016).

368 1 MULTIVARIATE ANALYZES OF VOLATILES COMPOSITION: PRDAS AND CLUSTERING

369 Multivariate analyzes were always performed on the proportions of compounds relative to the sum of all analytes of interest.
370 To deal with the left-censored and compositional nature of the data, zeroes were imputed by multiplicative simple replace-
371 ment with multRepl() from "zCompositions" (v. 1.4.0.1, Palarea-Albaladejo and Martin-Fernandez, 2015), using the smallest
372 non-zero value of each compound as detection limits and a delta of 0.65. We subsequently employed a centered log-ratio
373 (clr) transformation with clr() from "compositions" (v. 2.0.5, Boogaart et al., 2023). Data were finally scaled and centered with
374 scale() from the R base package. To evaluate correlations among compounds, hierarchical clustering was performed on the
375 correlation-based (Pearson) dissimilarity matrix with Ward's minimum variance method (Ward.D2) with pvclust() from
376 "pvclust" (v. 2.2.0, Suzuki et al., 2019). Approximately Unbiased p-values were computed by multiscale bootstrap resampling
377 with 10,000 replications. Correlations heatmaps were plotted with "ComplexHeatmap" (v. 2.16.0, Gu. Z., 2022). Partial redun-
378 dancy analyzes (pRDAs) were conducted with rda() from "vegan" (v. 2.6.4 Oksanen et al., 2022). Models' structures are de-
379 scribed in the following paragraphs. We then performed a type II permutation test with MVA.anova() from "RVAideMemoire"
380 (v. 0.9.81.2, Hervé, 2022). Pairwise comparisons were performed with pairwise.factorfit() from the same package.

381 2 ANALYZES OF SINGLE COMPOUNDS: GLMMS

382 Univariate analyzes of concentrations of compounds in leaves or emission rates were performed with generalized linear mixed
383 models (GLMMs) using glmmTMB (v. 1.1.5, Brooks et al., 2017) with Gamma or Tweedie exponential families of distribution,
384 depending on models' fit. Models' fits were checked with the package "DHARMa" (v. 0.4.6, Hartig, 2022). Effects of the ex-
385 planatory variables were tested with Wald chi-squared tests (type-II) using Anova() from "car" (v. 3.1.1, Fox and Weisberg,
386 2019). We plotted estimated marginal means and their 95% confidence intervals (CI), extracted from the models with ggem-
387 means() from "ggeffects" (v. 1.2.0, Lüdecke, 2018). When plotted, data points represented observed values. In all models, we
388 controlled for the effects of plants "size" (leaf extracts: fourth leaf area; headspace emissions: total leaf area) and of experi-
389 mental batches (leaf extracts: n = 6; headspace emissions: n = 4) by including them as fixed effects (Table 3 and 4). γ-Terpinene
390 was analyzed within the producing chemotype only, as the other chemotype does not produce it, or only in very low amounts.
391 Population and genotype were included as random intercepts in all models, except for those relying solely on the headspace
392 emissions of damaged plants, where 86% of the data consisted of individual data points per genotype (Table 3 and 4). When

necessary, pairwise comparisons were performed with emmeans() from “emmeans”, with multiple test adjustment (FDR). (v. 1.8.7, Lenth, 2023).

3 Volatile terpenes in leaves: herbivory and variation in induction

To assess how herbivory affected the leaf composition in volatile terpenes for the two chemotypes, a pRDA was performed on the relative abundances of all leaf mono- and sesquiterpenes. Herbivory, chemotype and their interaction were used as explanatory variables while leaf area was partialled out. Then, we analyzed the effect of herbivory and damage intensity (total leaf area consumed by caterpillars) on the total concentrations of the leaf volatile terpenes and a subset of compounds using GLMMs (Table 3: model structures A and E). We tested whether there was variation in the induction (i.e. increase in the leaf concentrations; group-by-herbivory interaction) of volatile terpenes between the two chemotypes and among nested levels of intraspecific variation: 88 genotypes, 16 populations and four geographic regions. Variation in the response of genotypes and populations to herbivory was modelled with random slopes and their significance was tested by comparing nested models with a random slope component to a model without (Restricted Maximum Likelihood method) with Likelihood ratio tests. Chemotype was included in the fixed effects of these models (Table 3: model structures B and C). The random slope component included a term for the variance in slopes and one for the covariance between slopes and intercepts unless the model did not converge. In that case, the covariance term was removed. Variation in response to herbivory among region and chemotypes was modelled as interaction between these groups and herbivory, set as fixed effects). Because of their geographic distribution, chemotypes were partially nested in regions. Therefore, to avoid collinearity, they were always analyzed separately (Table 3: model structures A and D).

4 Headspace volatile emissions: herbivory and variation in induced compounds

To examine whether the intraspecific variation observed for the leaf-stored terpenes by Clancy et al. (2023) was translated to the emissions, we performed Spearman correlation tests, separately for undamaged and damaged plants, on the ratio of concentrations of γ-terpinene and α-pinene (the dominant leaf-stored monoterpene) in leaves and in headspace emissions. To visualize the composition of the emitted blends of undamaged and damaged plants of both chemotypes, we plotted the median proportions with “treemapify” (v. 2.5.5, Wilkins 2021). To further understand how herbivory and chemotypes affected the composition of headspace emissions a pRDA was conducted on the relative abundances of all emitted volatiles together. Herbivory, chemotype and their interaction were used as explanatory variables while the total leaf area was partialled out. Then, we analyzed the effect of herbivory and damage intensity (total leaf area consumed by caterpillars) on the total emission rates and on the emissions of same terpenes analyzed for the leaves (Table 4: model structures A and C).

Variation in the volatile emissions induced by caterpillar herbivory was evaluated between chemotypes, as well as two levels of intraspecific variation: among the four regions and 16 populations. Genotypes were not assessed because of the lack of replication at this level. To evaluate variation in the volatile response to herbivory rather than pre-existing differences in compounds already emitted by intact plants, we selected only highly inducible volatiles, defined from the pRDA assessing the effect of herbivory on the headspace emissions. We first evaluated whether there was variation in the total emissions of these highly inducible compounds (Table 4, model structures C, D and E). Variation among population was modelled through random

intercepts (Table 4: model structures E) and their significance was tested by comparing nested models with random intercept component to models without (Restricted Maximum Likelihood method) with Likelihood ratio tests. Chemotypes and regions were analyzed as fixed effects, and separately, as mentioned above. To unveil potential variation in the composition of the induced emissions, pRDAs were performed on the proportions of highly inducible volatiles, selected from the transformed and scaled matrix of the relative abundances of all compounds emitted by damaged plants, separately for chemotype and region. Chemotype/region, the leaf surface damaged and their interaction were used as explanatory variables while the total leaf area was partialled out. We then further tested whether chemotypes and regions varied significantly in their emission rates of the different candidate compounds highlighted by the pRDAs with GLMMs, as explained for the total induced emissions (Table 4, model structure C and D). Compounds with significant variations were also assessed for variation among populations (Table 4, model structure E). For inducible compounds differing between chemotypes or regions but also emitted by undamaged plants, the interaction effect between chemotype/region and herbivory was tested (Table 4, model structure A and B). A significant interaction implied that chemotypes/regions differed in their response to herbivory, not solely by pre-existing disparities.

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Author contributions

T.C.J.T. and L.A-R., C.B-S., M.V.C. and M.M. designed the research. L.A-R., T.Q-M. and B.P.-N. collected the cotton seeds. C.B-S., M.V.C., M.M. and G.F. performed the experiment and processed the samples. M.M. and C.B-S. processed and analyzed the data. M.M. wrote the first draft of the manuscript with contributions by all authors.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data and code can be found at: https://doi.org/10.5281/zenodo.10927508

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TABLES

Table 1: Summary of the GLMMs analyzing the variation in induction (group-by-herbivory interaction) of volatile terpenes concentration in wild cotton leaves among genotypes and populations (random slopes; Likelihood ratio tests on nested models), as well as among geographic regions and between chemotypes (fixed effects; Wald chi-squared tests). Because they were partially nested, the effects of chemotype and region were analysed in separate models. Chemotype was included as fixed effect when testing variation among populations and genotypes. Chi-squared (χ^2) values are shown, and statistically significant ($p < 0.05$) effects are indicated in bold. Df = Degrees of freedom of χ^2 tests. The random slope component includes a term for the variance in slopes and one for the covariance between slopes and intercepts, unless the model could not converge, and the covariance term was excluded (italicized values).

Leaf volatiles	***Genotype x herbivory*** ***(χ^2 value, df = 2)***	***Population x herbivory*** ***(χ^2 value, df = 2)***	***Region x herbivory*** ***(χ^2 value, df = 1)***	***Chemotype x herbivory*** ***(χ^2 value, df = 1)***
Total terpenes	0.35	1.22	2.88	0.19
(E)-β-Ocimene	5.23	0.71	2.02	**7.69**
δ-Cadinene	*0.00*	0.88	0.94	0.29
β-Caryophyllene	0.02	0.48	4.00	0.02
α-Pinene	*0.00*	1.42	3.25	0.01
γ-Terpinene	0.04	0.59	1.35	-

Table 2: Summary of the GLMMs analyzing the variation in HIPV emission rates from damaged wild cotton plants among populations (random intercept; Likelihood ratio tests on nested models), as well as among geographic regions and between chemotypes (fixed effects; Wald chi-squared tests). Because they were partially nested, the effects of chemotype and region were analysed in separate models. Chemotype was included as fixed effect when testing variation among populations. Damage intensity was controlled for in all models. Chi-squared (χ 2) values are shown, and statistically significant ($p < 0.05$) effects are indicated in bold. Df = Degrees of freedom. Ce: Celestún, Si: Sisal, Ch: Chixculub, Co: Coloradas; A: chemotype A. B: chemotype B.

HIPV emitted	***Population*** ***(χ^2 value, df = 1)***	***Region*** ***(χ^2 value, df = 3)***	***Effect***	***Chemotype*** ***(χ^2 value, df = 1)***	***Effect***	***Figure***
Total HIPVs	1.34	2.89	-	0.00	-	Fig. S10
(*E*,*E*)-α-Farnesene	**4.23**	**25.45**	Ch < Co ≤ Ce ≤ Si	0.72	-	Fig. 6
(*E*)-Myroxide	**21.88**	**11.44**	Ch ≤ Co ≤ Ce ≤ Si	0.04	-	Fig. S10
(*E*)-Methylbutyraldoxime	**19.25**	**62.02**	Co ≤ Ch < Ce ≤ Si	**7.24**	B > A	Fig. 6
(Z)-Methylbutyraldoxime	**20.86**	**71.29**	Co ≤ Ch < Ce ≤ Si	3.50	-	Fig. S10
Unknown oxime	1.89	**25.79**	Co ≤ Ch < Ce ≤ Si	**5.07**	B > A	Fig. 6
Benzyl nitrile	0.11	**8.83**	Ch ≤ Co ≤ Si ≤ Ce	**4.71**	B > A	Fig. 6
Unknown nitrile	1.55	**8.03**	Ce ≤ Si ≤ Ch ≤ Co	**7.10**	A > B	Fig. 6

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Table 3: structures of the GLMMs used to analyze concentrations of volatile terpenes in wild cotton leaves. Chemo = chemotype, Area = fourth leaf area, Damage = damage intensity (total leaf area consumed by *S. exigua*). Full fixed effects are shown, interaction terms were removed if not significantly contributing to the model.

All plants			
	Effects tested	**Fixed effects**	**Random effects (intercepts and slopes)**
A	Herbivory / Chemotype / Chemotype-by-herbivory interaction	Herbivory + Chemo + Chemo:Herbivory + Area + Batch + Area:Batch	Population + Genotype
B	Genotype-by-herbivory interaction	Herbivory + Chemo + Chemo:Herbivory + Area + Batch + Area:Batch	Population + Herbivory:Genotype
C	Population-by-herbivory interaction	Herbivory + Chemo + Chemo:Herbivory + Area + Batch + Area:Batch	Herbivory: Population + Genotype
D	Region-by-herbivory interaction	Herbivory + Region + Region:Herbivory + Area + Batch + Area:Batch	Population + Genotype
Damaged plants			
	Effects tested	**Fixed effects**	**Random effects (intercepts and slopes)**
E	Damage intensity	Damage + Chemo + Chemo:Damage + Area + Batch + Area: Batch	Population + Genotype

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Table 4: structures of the GLMMs used to analyze emission rates of volatiles by wild cotton plants. Chemo = chemotype, Area = fourth leaf area, Damage = damage intensity (total leaf area consumed by *S. exigua*). Full models are shown, interaction terms were removed if not significantly contributing to the model.

All plants			
	Effects tested	**Fixed effects**	**Random effects (intercepts)**
A	Herbivory / Chemotype-by-Herbivory int.	Herbivory + Chemo + Chemo:Herbivory + Area + Batch + Area:Batch	Population + Genotype
B	Region-by-Herbivory int.	Herbivory + Region + Region:Herbivory + Area + Batch + Area:Batch	Population + Genotype
Damaged plants			
	Effects tested	**Fixed effects**	**Random effects (intercepts)**
C	Chemotype / Damage intensity	Chemo + Damage + Chemo:Damage + Area + Batch + Area:Batch	Population
D	Region	Region + Damage + Region:Damage + Area + Batch + Area:Batch	Population
E	Population	Chemo + Damage + Chemo:Damage + Area + Batch + Area:Batch	Population

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FIGURES

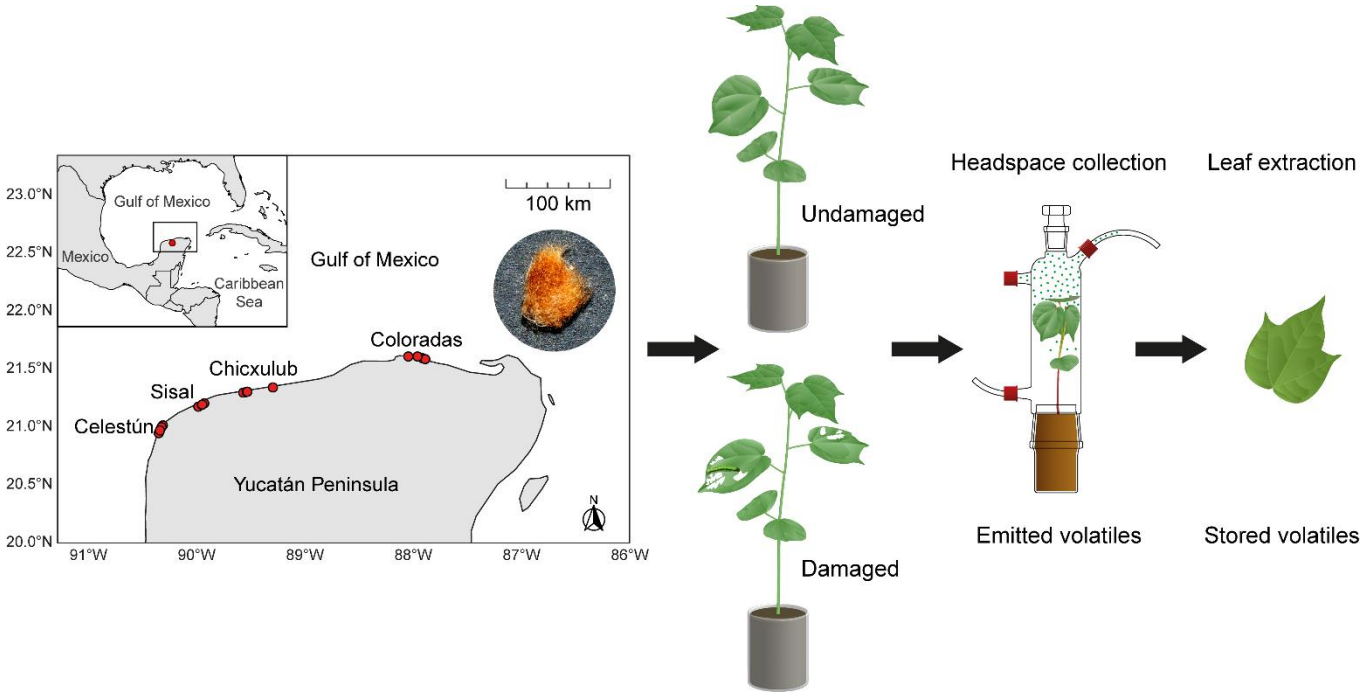


Figure 1. Illustration of the experimental process. Seeds were collected from 16 populations (red points) in four regions along the northern coast of the Yucatán Peninsula. Plants were grown in a common greenhouse until they developed the fourth leaf, at which time half of the plants were damaged by *Spodoptera exigua* larvae on their first and second leaves for two days and the other half was kept intact. Emitted volatiles were collected by headspace sampling and stored leaf volatiles by hexane extraction of the undamaged fourth leaves.

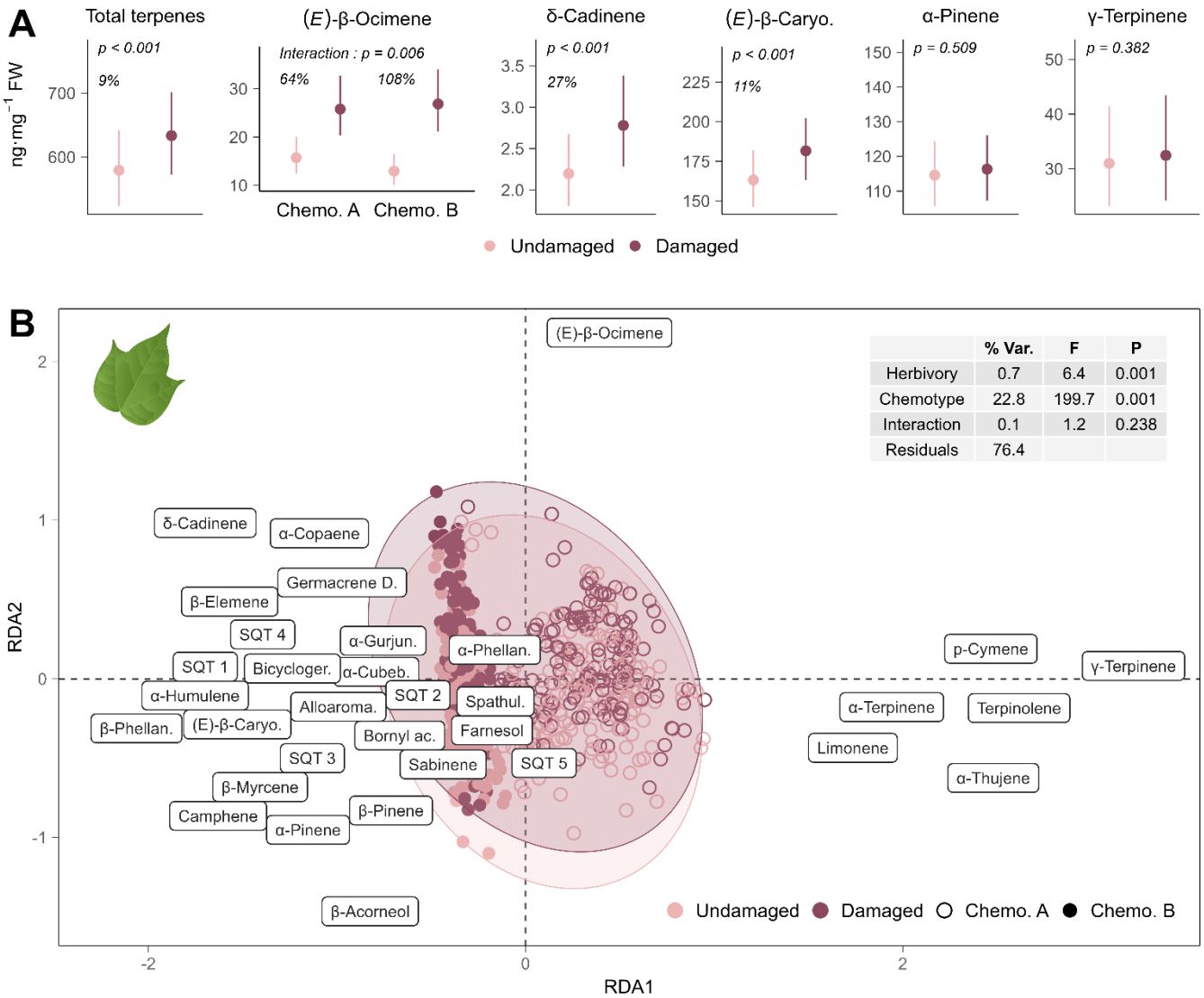


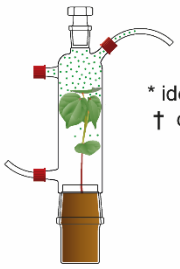
Figure 2. Effect of herbivory on stored leaf mono- and sesquiterpenes for both wild cotton chemotypes. The volatile content was extracted from the fourth leaves of 353 undamaged wild cotton plants and 322 plants damaged by *Spodoptera exigua* for two days on their first and second leaves. **A:** Effect of herbivory on the leaf concentrations of a subset of terpenes. Estimated marginal means and 95% CI from GLMMs. γ-Terpinene was analyzed within chemotype A while all other compounds were analyzed for both chemotypes together, with chemotype set as fixed factor. **B**: Biplot with symmetric scaling of a pRDA on the relative abundances (clr-transformed) of leaf mono- and sesquiterpenes.

A

Leaf + Headspace	RI	
1. (*E*)-2-Hexenal*	857	FA
2. α-Thujene	928	MT
3. α-Pinene*	934	
4. Camphene	949	
5. β-Pinene*	977	
6. β-Myrcene*	992	
7. p-Cymene*	1026	
8. Limonene*	1030	
9. (*E*)-β-Ocimene*	1049	
10. y-Terpinene*	1060	
11. Unknown SQT 1	1331	SQT
12. Unknown SQT 2	1341	
13. α-Copaene*	1381	
14. β-Elemene†	1396	
15. (*E*)-β-Caryophyllene*	1426	
16. α-Humulene*	1460	
17. Alloaromadendrene	1467	
18. Bicyclogermacrene	1502	
19. δ-Cadinene	1528	
20. Spathulenol	1584	

Headspace only	RI	
21. Unknown aldoxime*†	-	Ox.
22. (*E*)-2-Methylbutyraldoxime*†	862	
23. (*Z*)-2-Methylbutyraldoxime*†	868	
24. (*Z*)-3-Hexenol*	859	FA
25. (*E*)-2-Hexenol*	871	
26. 2-Methylbutyl acetate	881	
27. (*Z*)-2-Pentenyl acetate	917	
28. Methyl (*Z*)-3-hexenoate†	936	
29. Methyl (*E*)-2-hexenoate†	969	
30. (*Z*)-3-Hexenyl acetate*	1008	
31. n-Hexyl acetate	1015	
32. (*Z*)-2-Hexenyl acetate	1018	
33. (*Z*)-3-Hexenyl isobutyrate	1143	
34. (*E*)-3-Hexenyl butyrate †	1187	
35. (*E*)-2-Hexenyl butyrate †	1195	
36. (*Z*)-3-Hexenyl 2-methylbutyrate †	1232	
37. (*E*)-2-Hexenyl 2-methylbutyrate †	1238	
38. (*Z*)-Jasmone*†	1402	
39. (*Z*)-Linalool oxide	1074	MT
40. (*E*)-Linalool oxide	1090	
41. Linalool*	1100	
42. (*E*)-Myroxide†	1142	

Headspace only (cont.)	RI	
43. Methyl benzoate*	1097	Ar.
44. 2-Phenylethanol *	1115	
45. Benzyl nitrile†	1140	
46. Unknown nitrile†	1184	
47. Methyl salicylate*	1197	
48. Indole*†	1296	
49. Methyl anthranilate*†	1344	
50. (*E*)-β-Farnesene*†	1459	SQT
51. (*E,E*)-α-Farnesene†	1510	
52. Caryophyllene oxide	1590	
53. DMNT	1116	HT
54. TMTT	1580	



* identification confirmed
† damaged plants only

B

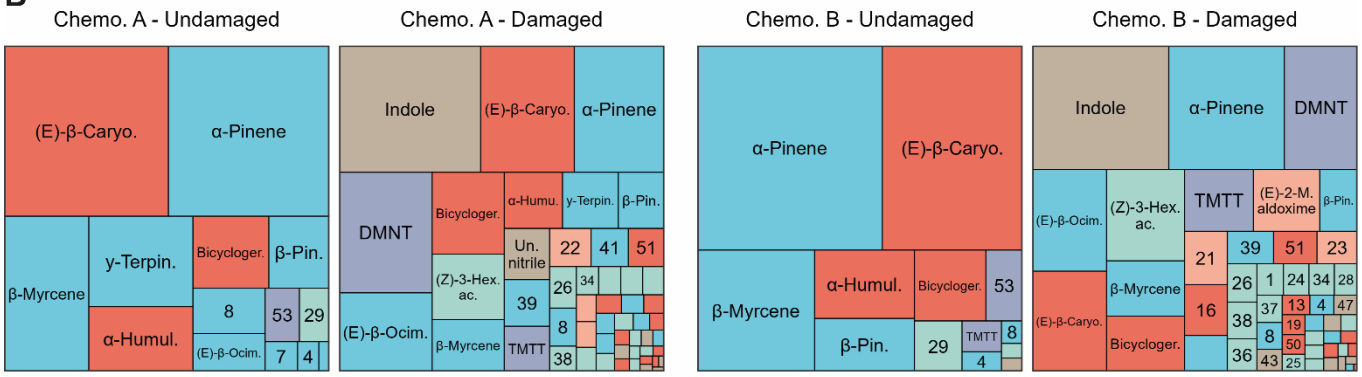


Figure 3: Composition of the headspace volatiles emitted by undamaged wild cotton plants and plants damaged for two days by *Spodoptera exigua*. A: Compounds detected both in the plants' leaves extracts and headspace, or in their headspace only. RI = Retention indices. The retention index for the unknown aldoxime could not be calculated because it eluted before the smallest alkane. † indicates compounds specific to damaged plants (detected in less than 10% of undamaged plants, but in between 43% and 100% of damaged plants). * indicates compounds whose identity was confirmed with standards. Distinction between the two 2-methylbutyraldoximes isomers is tentative. FA = fatty acid derivatives; MT = monoterpenes; SQT= sesquiterpenes; Ox. = aldoximes; Ar. = aromatics; HT = homoterpenes. **B:** Composition of medians emitted volatile profiles of undamaged and damaged plants of both chemotypes. Area of the rectangles is proportional to the contribution of the compound to the profile. Numbers refer to A.

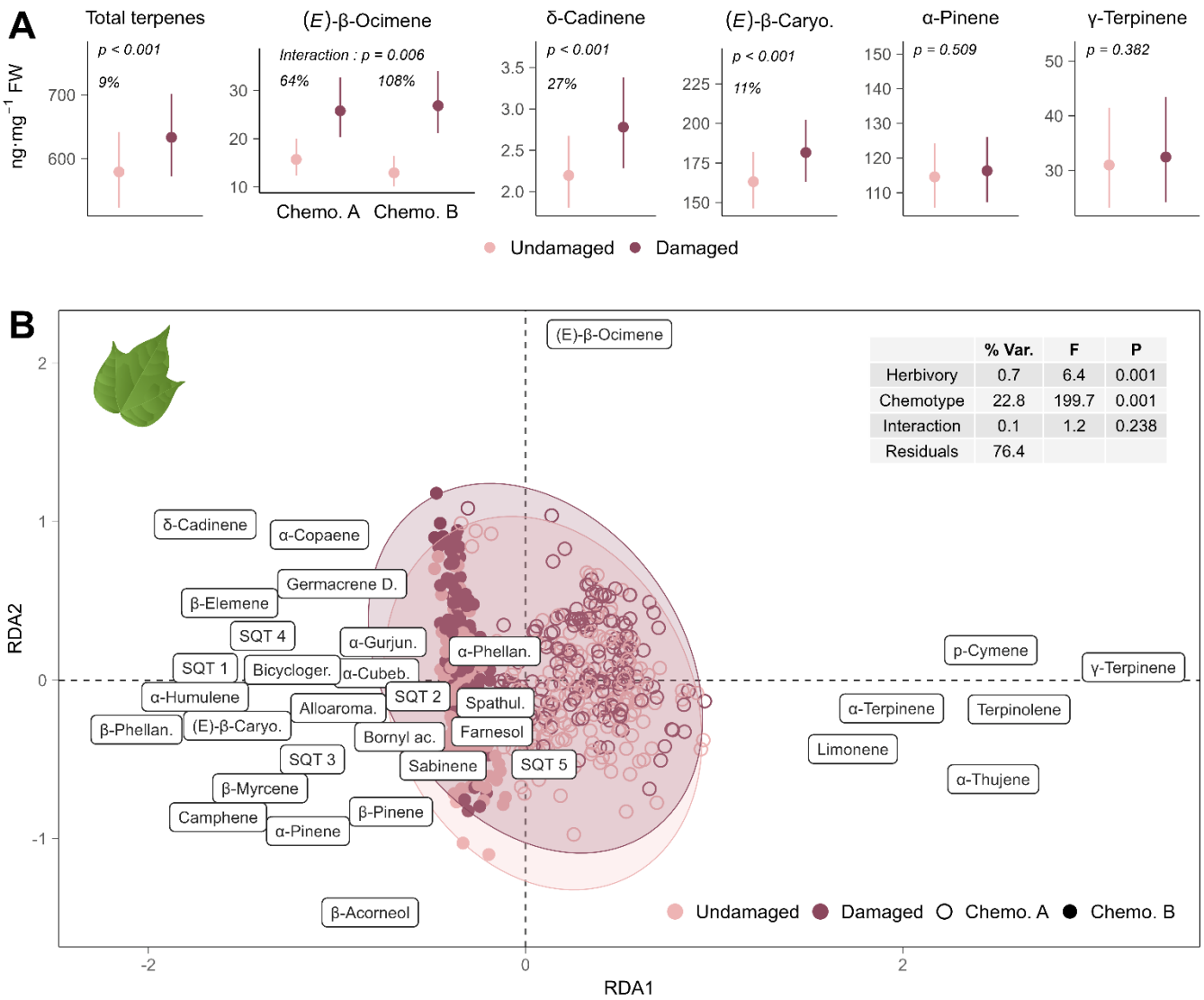


Figure 4. Effect of herbivory on the volatiles emitted by the two wild cotton chemotypes. Headspace volatiles were sampled from 45 undamaged wild cotton plants and 48 plants damaged by *Spodoptera exigua* for two days on their first and second leaves. **A:** Biplot with symmetric scaling of a pRDA on the relative abundances (clr-transformed) of all compounds quantified in the headspace samples. Only compounds accounting for more than 10% of inertia are plotted (full biplot in Fig. S8). **B**: Effect of herbivory on emission rates of all emitted volatiles and of a subset of emitted terpenes found also in the leaf extracts. Estimated marginal means and 95% CI from GLMMs are plotted. γ-Terpinene was analyzed within chemotype A while all other compounds were analyzed for both chemotypes together, with chemotype set as fixed factor. **C:** relationship between damage intensity (leaf area damaged) and the emission rates of a subset of terpenes. Left: multiplicative increases with the leaf area damaged (back-transformed coefficient estimates from GLMMs and their 95% CIs). The dotted line indicates a coefficient of 1, where quantities emitted remain constant with damaged area. Right: adjusted predictions and 95% CI from GLMMs with observed values as data points. γ-Terpinene was analyzed within chemotype A while all other compounds were analyzed for both chemotypes together, with chemotype set as fixed factor.

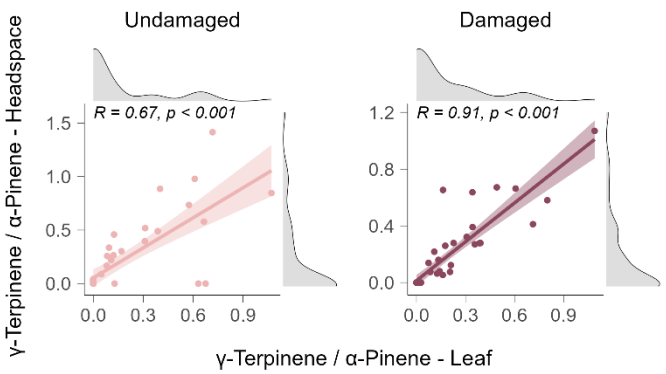


Figure 5. Influence of γ-terpinene variation in leaves on headspace emissions: correlation (Spearman) between the ratio of γ-terpinene and α-pinene concentrations in leaves (x-axis) and in headspace emissions (γ-axis).

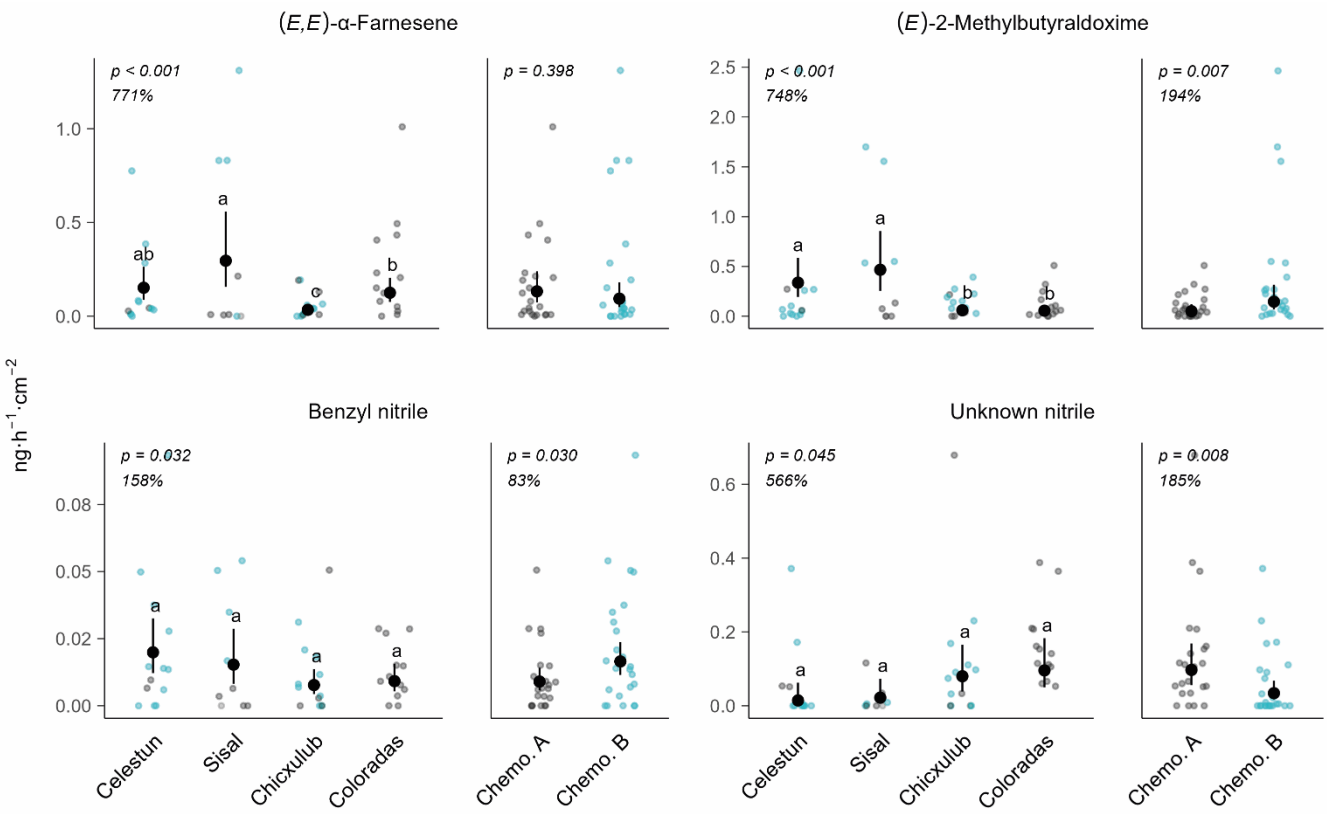


Figure 6. Variation in emissions of herbivory-induced volatiles among the four regions grouping wild cotton populations along the Yucatan coast and between the two terpene-chemotypes. Headspace volatile emissions were sampled from 48 wild cotton plant damaged by *Spodoptera exigua* for two days. Regions are displayed from west to east. Prevalence of chemotypes is nested with regions, as indicated by the color of data points (grey points indicate chemotype A; blue points indicate chemotype B), therefore they were analyzed separately. Estimated marginal means and 95% CI from GLMMs with observed values as data points. Damage intensity was controlled for as covariate. Letters indicate significant pairwise comparisons after multiple test adjustment (FDR). For regions, % values indicate the difference between the region with the lowest and highest estimated mean emission rates.

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