

# Diterpenoid fingerprints in pine foliage across an environmental and chemotypic matrix: Isoabienol content is a key trait differentiating chemotypes

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## ABSTRACT

Diterpenoids constitute an important part of oleoresin in conifer needles, but the environmental and genetic controls on diterpenoid composition are poorly known. We studied the presence of diterpenoids in four pine populations spanning an extensive range of nitrogen (N) availability. In most samples, isoabienol was the main diterpenoid. Additionally, low contents of (Z)-biformene, abietadiene isomers, manoyl oxide isomers, labda-7,13,14-triene and labda-7,14-dien-13-ol were quantified in pine needles. According to the occurrence and content of diterpenoids it was possible to distinguish 'non diterpenoid pines', 'high isoabienol pines', 'manoyl oxide – isoabienol pines' and 'other diterpenoid pines'. 'Non diterpenoid pines', 'high isoabienol pines' and 'other diterpenoid pines' were characteristic to the dry forest, yet the majority of pines (>80%) of the bog Laeva represented 'high isoabienol pines'. 'Manoyl oxide – isoabienol pines' were present only in the wet sites. Additionally, orthogonal partial least-squares analysis showed, that in the bogs foliar nitrogen content per dry mass ( $N_M$ ) correlated to diterpenoids. Significant correlations existed between abietadienes, isoabienol and foliar  $N_M$  in 'manoyl oxide – isoabienol pines', and chemotypic variation was also associated by population genetic distance estimated by nuclear microsatellite markers. Previously, the presence of low and high  $\Delta$ -3-carene pines has been demonstrated, but the results of the current study indicate that also diterpenoids form an independent axis of chemotypic differentiation. Further studies are needed to understand whether the enhanced abundance of diterpenoids in wetter sites reflects a phenotypic or genotypic response.

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## 1. Introduction

Conifer trees, including the extremely wide-spread Scots pine

(*Pinus sylvestris* L.), have characteristically high longevity, which is associated with multiple traits, in particular, with presence of oleoresin in their woody tissues and leaves (Lewinsohn et al., 1991a,b). Oleoresin is contained in the resin ducts and it protects trees against a wide range of herbivores, fungal and bacterial pathogens, providing a very successful broad-spectrum defense system (Croteau et al., 1987; Lewinsohn et al., 1991a,b; Phillips and Croteau, 1999). The biosynthetic pathways of oleoresin constituents have been widely investigated (Bohlmann and Keeling, 2008; Keeling et al., 2010; Memari et al., 2013; Rosenkranz and

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Schnitzler, 2013). Oleoresin is composed of turpentine fraction consisting of mono- and sesquiterpenoids and rosin fraction consisting of diterpenoids and their derivatives, in particular diterpenoid acids (Phillips and Croteau, 1999). Oleoresin can effectively seal the injuries resulting from direct mechanical stresses such as wind damage, but also from browsing by large herbivores, from insect feeding and pathogen damage (Phillips and Croteau, 1999; Loreto et al., 2000).

Diterpenoids are toxic to microorganisms and arthropods, and thus play an important role in plant defense (Bailey et al., 1974; Ulubelen et al., 1994; Jasinski et al., 2001; Falara et al., 2010; Koutsaviti et al., 2011; Chaturvedi et al., 2012). For example, labdane-type diterpene (11E,13E)- labda-11,13-diene-8 $\alpha$ ,15-diol named as WAF-1 contributes to the activation of pathogen- or wound-induced reactions in tobacco leaves (Seo et al., 2003). Additionally, labdane-type diterpenoids (Fig. 1) participate in the biosynthesis of diterpenoid acids, also called resin acids (Phillips and Croteau, 1999; Lee et al., 2001; Keeling and Bohlmann, 2006), composition of which is significantly modified by biotic stress (Kainulainen et al., 1993; Miller et al., 2005). Due to their toxicity, resin acids inhibit mycelial growth of pathogenic fungi carried by bark beetles (Kopper et al., 2005). In Sitka spruce (*Picea sitchensis*), accumulation of dehydroabietic acid is associated with tree resistance against white pine weevil (*Pissodes strobe*) (Robert et al., 2010). Hence, obtaining detailed insight about the factors controlling the content and composition of diterpenoids in oleoresin will help to understand the overall role of diterpenoids in induced defense reactions in gymnosperms.

*Pinus* species are widely known for their extensive genetic variance (Dering et al., 2017). For example, pines of  $\Delta$ -3-carene,  $\alpha$ -pinene (Hiltunen et al., 1975; Sjödin et al., 1996, 2000; Bäck et al., 2012; Kännaste et al., 2013) and isoabienol chemotypes (Gref, 1981) are known. Moreover, the resin composition of pines is strongly influenced by environmental factors (Hiltunen et al., 1975; Taft et al., 2015), especially due to the variability in timing and

severity of simultaneous abiotic stressors in different ecosystems (Niinemets, 2010). Although the genetic variability within and among pine populations has been studied to some extent (Pazouki et al., 2016; Dering et al., 2017), our understanding of the association between chemotypes and environment of pine populations is still limited (Kännaste et al., 2013; Pazouki et al., 2016). *Pinus* species including *P. sylvestris* can occupy highly varying habitats including fertile well-drained mineral soils, excessively drained sandy soils or infertile waterlogged peat soils. Given this high plasticity in coping with habitat conditions, it is surprising that the environmentally-driven variations in key stress-dependent specialized metabolites have been poorly examined across pine populations (Hornoy et al., 2015). Understanding such associations is particularly relevant as long-term stress-induced changes at the molecular level can lead to formation of novel pine chemotypes (phenotypes with different chemical composition) (Jablonka, 2013). To our knowledge, chemotypic differences associated with stress-dependent changes in diterpenoids have been only studied in Norway spruce (*Picea abies*) clones exposed to ozone stress (Kainulainen et al., 1995).

Although there are basic controls on specialized metabolism, pathway fluxes to different terpenoid classes are often regulated differently (Dudareva et al., 2004; Tholl, 2006; Chen et al., 2011). This is particularly true for differences among cytosol-synthesized sesquiterpenoids and plastid-synthesized mono- and diterpenoids, but even within plastids, mono- and diterpene biosynthesis can be differently controlled by the availability of C<sub>10</sub> substrate geranyl diphosphate (GDP) and C<sub>20</sub> substrate geranylgeranyl diphosphate (GGDP) (Orlova et al., 2009; Rajabi Memari et al., 2013). In our previous study, which was based on pines from three wet sites and one dry site, we reported a large variation in mono- and sesquiterpenoid signatures over short spatial distances in *P. sylvestris* populations spanning wet organic soils and dry mineral soils (Kännaste et al., 2013). Specifically,  $\Delta$ -3-carene was the main monoterpene effectively differentiating the populations (Kännaste et al., 2013). To further differentiate among the *P. sylvestris* chemotypes, we studied here the content and composition of diterpenoids in the same four populations dispersed over a large gradient of soil conditions (Kännaste et al., 2013). We hypothesized that in addition to  $\Delta$ -3-carene, diterpenoids form an additional axis of chemical differentiation for *P. sylvestris* populations. Based on the nutrient-dependent variation in mono- and sesquiterpenoid content across the sites (Kännaste et al., 2013), we suggested that diterpenoid contents in pine needles scale negatively with site N availability. In addition, given that the genetic distance among the studied populations has been estimated on the basis of microsatellite markers (Pazouki et al., 2016), we further hypothesized that chemotype-level differentiation is associated with genetic distance among the studied pine populations.

## 2. Results and discussion

### 2.1. Variations of diterpenoid contents and compositions

Diterpenoids were present in more than 90% of 218 analyzed samples (Table 1). High isoabienol content was characteristic to the majority of pine samples. Moreover, isoabienol contents were similar in the bog samples, but foliage isoabienol content was greater in dry forest samples than in bogs Laeva and Parika (Fig. 2). Isoabienol has been previously found in the needles of *Juniperus communis* (Adams et al., 2010) and in the wood of *Cunninghamia koshii* (Cheng et al., 2012); but also in *P. sylvestris* samples from Sweden and Finland (Gref, 1981; Manninen et al., 2002). In the Finnish and Swedish samples, it was only found in a few cases (Gref, 1981; Manninen et al., 2002). Thus, widespread and high rate of

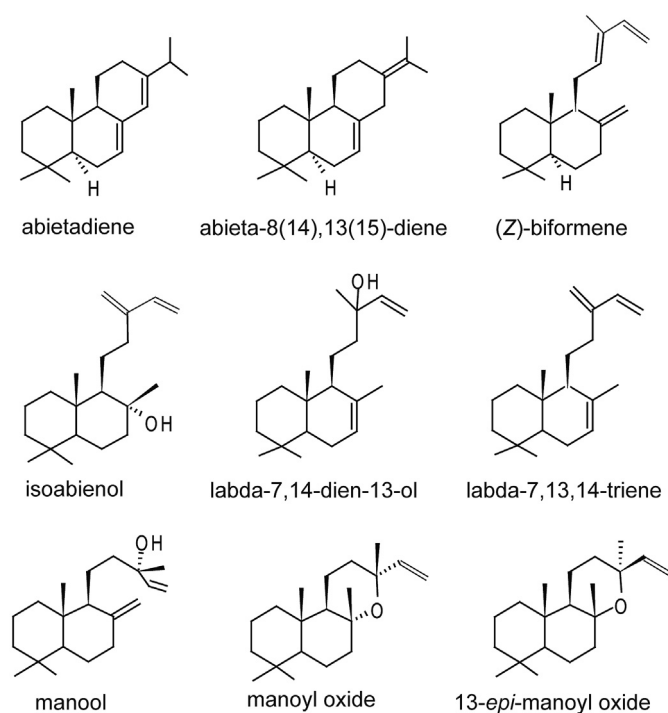


Fig. 1. Molecular structures of diterpenoids quantified in *Pinus sylvestris* L. needles.

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