# *Iris lutescens* Lam. on serpentine soil: volatile emission profiles in different organs of its two colour morphs

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**Abstract (150-250 words)**

*Iris lutescens* Lam. is a rhizomatous species of the Iridaceae family, generally found in the dry areas of the Mediterranean basin regions flora. It is characterised by large flowers, exhibiting a colour polymorphism in two varieties (yellow and purple). Even though it can grow on calcareous soils, it is reported as a serpentine-preferential taxon. In this work, the volatile emission in the headspaces of flowers, leaves and rhizomes of specimens of both the colour morphs growing on an ultramafic garigue have been analysed. The flower and rhizome headspaces had greater overall similarities compared to the leaves; flowers were the organs for which the volatile emission differed the most between the two colour morphs. Moreover, a comparison with a published headspace composition of *I. lutescens* yellow and purple flowers growing on calcareous soil evidenced quali-quantitative differences, as well as a greater differentiation of the volatile organic compounds emitted by the two colour morphs growing in a serpentine environment. To the best of our knowledge, this is the first report on the volatile emission of different organs *I. lutescens* specimens growing on serpentine soil.

**Keywords (4-6):** ultramafic soil; headspace solid phase micro-extraction; gas chromatography – mass spectrometry; Iridaceae; floral colour polymorphism

## Introduction

*Iris lutescens* Lam. is a rhizomatous species of the Iridaceae family. It is a frequently occurring flowering plant of the dry regions facing the Mediterranean basin, like Northern Italy, Southern France and Western Spain. Its stems are erect, with sword-shaped leaves and one large and colourful flower for each specimen, with an early flowering onset in the late February-early April period (Filella et al. 2013). A peculiarity of *I. lutescens* is the colour polymorphism of its flowers: they can occur as two possible colour morphotypes, namely yellow or purple petals. Intra-specific variation in the floral traits is quite uncommon, and true, stable genetic-based color polymorphisms are rare (Weiss 1995), and are generally found in the Orchidaceae family (Imbert et al. 2014). In a rewardless and self-incompatible (even though hermaphroditic) species like *I. lutescens*, colour polymorphism represents a mechanism to delay the pollinators avoidance of the flowers, as it completely relies on them for its reproduction (Imbert et al. 2014). Its main pollinators are bumblebees (*Bombus terrestris*) and bees (*Apis mellifera*), whose colour perception allows them to differentiate between the two morphs: the purple ones are perceived as blue, whilst the yellow ones as blue-green (Wang et al. 2013). Reports on their colour preference, though, are contrasting: some report their preference for yellow flowers (Goulson et

al. 2007), whilst others report they favor purple hues (Spaethe et al. 2001). In general, Apoid pollinators tend to visit the most frequent phenotype (yellow, in this case) over the rarer one in a population (Vallius et al. 2008): for *I. lutescens*, though, the phenotypic selection between the two morphotypes is not pollinators-driven (Souto-Vilarós et al. 2018).

Even though frequently found on calcareous bedrocks, *I. lutescens* is a facultative basiphilous serpentinophyte: a larger number of specimens is generally reported in ultramafic soils (Selvi 2007). These soils are characterised by high concentrations of heavy metals (magnesium, iron, and frequently chromium, cobalt and nickel), coupled with a very low amounts of mineral nutrients (silicon, phosphorus, potassium, and calcium) and a range of pH varying from basic to ultra-basic. CIT STACHYS (Proctor 1999; Stevanovic et al. 2003). These outcrops, though, represent a chemically toxic environment for most plants to grow. Furthermore, they do not retain water well and are characterised by high temperatures, due to the dark colour conferred them by the metals (Proctor 1999; Stevanovic et al. 2003). Plants adapted to ultramafic crops generally develop peculiar morphological characteristics, like xeromorphic foliage and reduced sizes, to ensure their survival in these environments (Brady et al. 2005). *I. lutescens* specimens growing on ultramafic soils, though, do not exhibit different morphological traits compared to their counterparts growing on calcareous soil. Its behaviour as serpentine-preferential taxa is mainly believed to be due to its lack of competitiveness with other species: the serpentine soil, though, with its scarceness of flora, represents an easier habitat for *I. lutescens* (Gestri 2007).

In the present study, *I. lutescens* of both the colour morphs were collected on an ultramafic garigue in Tuscany (Italy): in this region, serpentine crops are located near the coastline and are mostly composed by lherzolitic serpentinites, but gabbro and basalt are also present (Chiarucci 2003). The spontaneous volatile emissions in the flower, leaf and rhizome headspaces of *I. lutescens*, in both the yellow and the purple morphotypes, have been analysed by means of headspace solid phase micro-extraction (HS-SPME) coupled with gas chromatography – mass spectrometry (GC–MS). The aim of this study was the evaluation of the differences in the volatile organic compounds (VOCs) emission of the three organs in the two morphotypes. To the best of our knowledge, there is no other published study on the volatile emission of *I. lutescens* specimens collected in a serpentine environment.

**Materials and methods**

*Plant material*

Three flowering specimens for each of the two morphotypes of *Iris lutescens* Lam. have been collected in early April 2017 between Nibbiaia and Gabbro (province of Livorno, Italy; GPS coordinates: 43°30'01"N, 10°25'33"E) in the same phenological stage, on ultramafic soil, facing SE, at 200 m above sea level, in a garigue with *Alyssum bertolonii* Desv. subsp. *bertolonii*, *Armeria denticulata* (Bertol.) DC., *Juniperus oxycedrus* L. subsp. *oxycedrus*, *Thymus* sp. and

*Trifolium vesiculosum* Savi. Here the ultramafic soil originated mainly from serpentinites (Marchiori and Tornadore Marchiori 1977). The samples have been transported into separated pots to preserve them until the analyses.

*Headspace solid phase micro-extraction (HS-SPME) analyses*

One flower, two leaves and a complete rhizome have been put in separated glass containers tight-sealed with a pierceable septum to avoid air contact and kept refrigerated until the analysis was performed. Prior to analysis, each sample was left to equilibrate for 30 min at room temperature before the fibre insertion. To ensure complete homogeneity of the analyses, all samples have been stored and analysed in the same conditions. The adsorption of the volatile analytes has been performed with the Supelco polydimethylsiloxane fibre assembly (100 μm coating thickness) preconditioned according to the manufacturer instructions. After the equilibration time, the septum of each vial is perforated by the holder (syringe) and the fibre is exposed to the head space of the sample for 30 min at room temperature. Once the sampling is complete, the fibre is retracted into the holder and directly injected in the GC–MS apparatus for separation and analysis. All the SPME sampling and desorption conditions were identical for all the samples. Furthermore, blanks were performed before each first SPME extraction and randomly repeated during each series. Quantitative comparisons of relative peaks areas were performed between the same chemicals in the different samples.

*Gas Chromatography Coupled With Mass Spectrometry and Compounds Identification*

Gas chromatography–electron impact mass spectrometry (GC–EI-MS) analyses were performed with a Varian CP-3800 gas chromatograph equipped with a DB-5 capillary column (30 m × 0.25 mm; film thickness 0.25 μm) and a Varian Saturn 2000 ion trap mass detector. Analytical conditions were as follows: injector and transfer line temperatures 220 and 240 °C, respectively; oven temperature programmed from 60 to 240 °C at 3 °C $min^{-1}$; carrier gas helium at 1 ml/min; splitless injection. Identification of the constituents was based on a comparison of the retention times with those of the authentic samples, comparing their linear retention indices relative to the series of *n*-hydrocarbons. Computer matching was also used against commercial (NIST 14 and ADAMS) and laboratory-developed library mass spectra built up from pure substances and components of known oils and MS literature data (Stenhagen et al. 1974; Masada 1976; Jennings and Shibamoto 1982; Davies 1990; Adams 1995).

*Statistical analyses*

The multivariate statistical analyses were carried out with the JMP software package (SAS Institute, Cary, NC, USA). For the statistical evaluation of the volatile composition, the covariance data matrix was a 139 x 6 matrix (139 individual compounds x 6 samples = 834 data). The principal component analysis (PCA) was performed selecting the

two highest principal components (PCs) obtained by the linear regressions operated on mean-centered, unscaled data; as an unsupervised method, this analysis aimed at reducing the dimensionality of the multivariate data of the matrix, whilst preserving most of the variance (Choi et al. 2004). The chosen PC1 and PC2 cover 53.20 and 24.66% of the variance, respectively, for a total explained variance of 77.86%. The hierarchical cluster analysis (HCA) was performed by the Ward's method. Both the HCA and the PCA methods can be applied to observe groups of samples even when there are no reference samples that can be used as a training set to establish the model.

The percentage of dissimilarity contribution of the all the compounds in the organs headspaces has been evaluated by means of the Similarity Percentage test (SIMPER) with the Bray-Curtis distance/similarity measure. The statistical significance of the difference in the relative abundances of the compounds accounting for at least 1.00% in the dissimilarity rate of the emissions has been evaluated using the F- or T-test, for compounds with equal or unequal variances, respectively. The SIMPER, F- and T-tests have been performed with the Past 3.20 Software (Hammer et al. 2001).

**Results**

*Headspace compositions*

The complete headspace compositions are reported in Table 1: 139 volatile organic compounds (VOCs) in total have been identified. Among all the samples, 6 compounds were common to the three analysed organs (flowers, leaves and rhizomes) of both morphotypes: 3 monoterpene hydrocarbons (α-pinene, β-pinene, and myrcene), 2 sesquiterpene hydrocarbons (β-caryophyllene and α-humulene), and 1 non-terpene derivative (2-ethylhexyl salicylate). In the yellow morph, the only other common compound to all its organs was α-terpinene. In the purple morph, instead, 10 more compounds were detected in all its organs: 2 monoterpene hydrocarbons (myrcene and limonene), 1 oxygenated monoterpene (1,8-cineole), 3 sesquiterpene hydrocarbons (cyclosativene, germacrene D, and δ-cadinene), and 1 apocarotenoid ((*E*)-geranyl acetone).

The flower samples exhibited the least variation: out of 10 compounds contributing to at least 1.00% of the total dissimilarity, 7 were detected in statistically relevant different relative concentrations between the two morphs (Table 2). Moreover, only 9 compounds were exclusively identified in the flower headspaces out of all the analysed organs: 5 were exclusive of the yellow flowers (*cis*-β-terpineol, dihydro carveol, guaiol, 5-*epi*-7-*epi*-α-eudesmol, and humulane-1,6-dien-3-ol), 3 of the purple ones (*p*-anisaldehyde, (*E*)-β-farnesene, and hydroxy-neoisolongifolane), while elemol was common to both colours. The differences in the headspace emissions of the two colours were mainly in the relative abundance of the same compounds. Limonene accounted for up to 65.09% in the yellow sample, followed by α-pinene

(9.60%); in the purple flower emission, instead, α-pinene reached up to 51.21%, whilst limonene followed (17.91%). For the yellow morph, β-pinene was the third most quantitatively relevant VOC, accounting for 7.35%; in the purple sample, instead, 1,8-cineole was found at as high as 10.27%, despite not being detected in the yellow morph. In both these headspaces, monoterpene hydrocarbons represented the most abundant chemical class of compounds: in the yellow morph they accounted for up to 93.83%, and for 76.65% in the yellow one. The oxygenated monoterpenes were more abundant in the purple flowers, as well as the sesquiterpene hydrocarbons. The oxygenated sesquiterpenes, instead, were more represented in the yellow flower headspace.

The leaf samples dissimilarity was mainly (88.82%) due to 13 compounds, of which 8 showed statistically significant quantitative difference among the two colour morphotypes. The leaf exclusive compounds detected in the two samples were 12, of which 4 in the yellow one (*n*-dodecane, β-gurjunene, *cis*-muurola-4(14),5-diene, and germacrene A), α-neoclovene was only found in the purple one, and 7 were common to both ((*E*)-3-hexen-1-ol, 1-hexanol, (*Z*)-3-hexenol acetate, *n*-hexyl acetate, β-bourbonene, β-copaene, and *trans*-β-guaiene). Like the flower headspaces, the leaf samples emission were mainly characterised by the same three compounds but in different relative abundances. Germacrene D was the most abundant (30.13%) compound in the yellow morph leaves (*vs* 5.35% in the yellow sample). In the purple specimen ones, (*Z*)-3-hexenol acetate accounted for up to 59.97% (*vs* 27.69% in the yellow morph leaves). β-Caryophyllene was detected in significant relative amounts in both the samples, accounting for 11.96 and 9.20% in the yellow and purple specimens, respectively. Sesquiterpene hydrocarbons and non-terpene derivatives were the most abundant class of VOCs in the leaf headspaces, but with inverted relevance in the two morphs: the former represented more than 55% of the yellow morph headspace (*vs* 20.08% in the purple one), whilst the latter accounted for almost 70% of the total purple morph emission (*vs* 31.68% in the yellow one).

The rhizomes of the two colour morphs exhibited the biggest differences, with 28 VOCs contributing to at least 1.00% of the dissimilarity, of which 24 detected in relative abundances with statistically significant difference among the two colour morphs. As much as 61 VOCs were exclusively detected in the rhizome headspaces, of which 21 in the yellow sample, 25 in the purple one, and 15 were common to both the morphotypes. For the yellow specimen rhizome, α-terpinene was the main detected compound (9.52%), followed by methyl carvacrol (7.38%) and 1,8-cineole (6.64%). In the purple one, instead, 1,8-cineole was the VOC detected with the highest (13.88%) relative percentage, followed by α-pinene (8.16%) and 7-*epi*-silphiperfol-5-ene (6.74%). Monoterpene and sesquiterpene hydrocarbons were the two most abundant chemical classes of VOCs in both the morphs: the latter, though, was more relevant in the purple morph, whilst the non-terpene derivatives were more represented in the yellow headspace. The oxygenated monoterpenes were detected in comparable content in both the colours.

*Multivariate statistical analyses*

The hierarchical cluster analysis (HCA) performed on the complete headspace compositions of the organs of the two morphotypes evidenced a distribution in three clusters (Fig. 1). The yellow flower headspace was the only sample in the red cluster of the dendrogram (Fig. 1), whilst the purple flower one was part of the green cluster with both the rhizome headspaces. The two leaf headspaces were grouped in the blue cluster. The distribution in the dendrogram evidenced the higher level of variation in terms of headspace composition among the two morphs flower headspaces. Moreover, the leaf headspaces showed more diverse compositions compared to the other two organs. The flower emissions are, indeed, more similar to the related rhizome ones.

This greater difference in the leaf emission was also evident in the principal component analysis (PCA) score plot (Fig. 2): these were the only samples plotted in the upper left quadrant (PC1<0, PC2>0). Germacrene D and (*Z*)-3-hexenol acetate were the VOCs responsible for the yellow and purple morph plotting, respectively. As in the HCA dendrogram, the yellow flower sample was the only plotted in the upper right quadrant (PC1>0, PC2>0), due to its limonene relative content. The bottom right quadrant (PC1>0, PC2<0) comprised the other three samples. The rhizomes were plotted close to each other, as the two compounds responsible for this placement, namely α-terpinene and 1,8-cineole, were detected in significant relative amounts in both the colour specimens. The purple flower sample was slightly outdistanced on the right of the same quadrant, due to its α-pinene content.

**Discussion**

The soil role is of utmost importance in plant development, but the type and the extent of changes induced by the ultramafic ones on the secondary metabolism are still unclear. It is reasonable to expect different modification to this metabolism, occurring as an adaptation response in some species, established to the point of defining these specimens as "serpentinites ecotypes": differences in the essential oil compositions, indeed, are reported for some of these species. *Thymus striatus* Vahl and its ultramafic counterpart *Thymus striatus* Vahl var. *ophioliticus* Lacaita EOs exhibited relevant differences in their compositions: nerolidol was only detected in the latter, whilst for other majorly represented compound the reported difference is quantitatively, more than qualitatively, relevant (i.e. myrcene relative abundance in the former is almost halved *vs* the latter) (Bini Maleci et al. 1997). Differences in the EO compositions has been reported for another Lamiaceae family species ecotypes: the volatile oil extracted from *Stachys recta* L. subsp. *recta*, which grows on calcareous soil, was mainly composed by terpenes, whereas in its serpentinophyte counterpart (*S. recta* L. subsp. *subcrenata* (Vis.) Briq.) non-terpene derivatives were the most abundant chemical class of compounds (CIT STACHYS). For *Iris lutescens* Lam., as of today there is no recognised classification in two different ecotypes based on the growth environment: it is reported as a serpentine-preferential taxa, but the botanical identity of its calcareous soil

counterpart is the same. Nevertheless, comparing the spontaneous emission profiles of the flowers of this study with published headspaces compositions of *I. lutescens* growing on calcareous soils, several differences emerge. A study on 31 *I. lutescens* flower headspaces (15 yellow, 16 purple) reported monoterpenes as the most abundant chemical class of VOCs, in accordance with the results of the present study (Wang et al. 2013). Their relative abundances, though, were quite different: limonene was more abundant in the purple morphs, whereas here the yellow ones are richer in this compound; moreover, α-pinene was detected in low abundance (purple) or at all (yellow), whilst in the present report it represented one of the most relevant compounds in both morphs (Wang et al. 2013). Myrcene, instead, was detected in relevant abundance in the calcareous species, and the purple morph was richer in it: both these findings are different from the results of this study (Wang et al. 2013). Differences emerged in the sesquiterpene hydrocarbons content, as well: unlike the flowers analysed in this report, the calcareous species headspaces exhibited a very relevant content of this class; moreover, (*E*)-β-ocimene, not detected at all in the ultramafic flowers, showed a significant presence in both the colour morphs growing on calcareous soil (Wang et al. 2013). To the best of our knowledge, there are no published headspace composition for the volatile emission of the leaves and rhizomes of *I. lutescens* grown on non-ultramafic soil, thus it is not possible to report a comparison. The rhizomes analysed in this study, though, exhibited a peculiar headspace emission profile, as they were the only organs emitting silphiperfolene-type compounds, which are tricyclic sesquiterpenoids typical of the Asteraceae family (Dobner et al. 2003): an increment in these VOCs content has been reported as a response to the oviposition of herbivorous insects in *Brassica nigra* (Fatouros et al. 2012). A comparison of the soil microbiota in serpentine and sandstone soils revealed a phytophagus nematodes content 6 times higher in the former (Hungate et al. 2000), which makes this soil even more challenging for plant growth. The ability of *I. lutescens* to produce these compounds might confer it the ability to thrive in a difficult habitat like the ultramafic soil, even though it lacks the competitiveness in other soils (Gestri 2007). Anyway, the metabolic pathways modified by the unusual concentration of heavy metals in the ultramafic crops are still to be defined, as well as the main mechanisms involved in their action. The metals hyperaccumulation is reported as a defensive benefit (Boyd 2010), but they are also reported as oxidative stress-inducers (Mithöfer et al. 2004). Moreover, these elements massive presence might be one of the causes of the "information-disruption effect", which induces an alteration of plant VOCs detection ability (Koricheva et al. 1998). Besides the significant concentration of these metals in the plants organs because of the absorption with the water, physical mechanisms might be involved in the plant VOCs perception alteration. The ultramafic soil dust is, obviously, rich in these elements, and they are dissolved in the rain and dew drops, as well: dusts and drops might enhance the penetration of the metals in the plants through the stomata (Greger 2004). A 2001 comparative study on 320 Ni-hyperaccumulating species and related non-hyperaccumulating serpentine floras, though, reported that the volatile emission and the essential oil (EO) production do not correlate with the nickel concentration

(Borhidi 2001). This finding, together with the already published results and those obtained in this study, might lead to two hypotheses: i) VOCs and EOs are influenced in their quality, rather than their quantity; ii) among the metals usually accumulating in the ultramafic crops, nickel does not interfere with the secondary metabolism pathways. Further studies, though, are needed to assess the effect of the other metals influence on these metabolic pathways, as well as their simultaneous presence in the soil, and to evaluate which organs are more affected, as well as the type and extent of influence they have on different species.

Another interesting *I. lutescens* aspect to investigate is the correlation between its two colour morphs and their headspace emission. Flowers scent emission is subjected to the selective pressure of the pollinators availability, but also to the plant community emission, thus making it an even more natural selection character than floral traits (Parachnowitsch et al. 2012). The volatile emission and the floral color are determined by compounds sharing the same biosynthetic pathways: thus, interfering with genes involved in one of the metabolic pathways might influence both (Dötterl et al. 2011; Milet-Pinheiro et al. 2012). Carotenoids, which confer yellow-to-red color to the flowers, share the same biosynthetic precursors (IPP and DMAPP) of terpenes (Dudareva 2004). Flavonoids and anthocyanins are responsible for pale yellow-to-yellow and orange-to-blue floral colors, respectively: they are biosynthesized along the phenylpropanoids metabolic pathway, together with volatile benzenoids (Zvi et al. 2008). Volatiles are produced in earlier stages of these metabolisms, whilst pigments are developed later (Wang et al. 2013). Wang et al. (2013) reported an anthocyanins content 18- to 28-fold higher in purple *Iris lutescens* flowers compared to the yellow ones; their qualitative profile, though, was not different. Moreover, the anthocyanin content of the leaves did not differ, suggesting a tissue-specific regulation of the biosynthetic pathway. The flavonoids and carotenoids contents were, instead, comparable in all the organs (Wang et al. 2013). As emerged from the statistical analysis, flower was indeed the organ whose VOCs emission between the two morphs differed the most: 7 out of the 10 compounds accounting for at least 1.00% of the dissimilarity between the headspaces showed statistically relevant differences in their relative abundances in the two colour morphs. No significant differences between the two colours, instead, were reported for the emissions of specimens grown on calcareous soil (Wang et al. 2013). This might suggest the more important role of VOCs in ultramafic crops, in which the fauna is scarcer: they can attract pollinators from longer distances, thus overcoming the general less-coloured environment minor attraction capability of the serpentine soil. The VOCs variation between the two morphs might ensure the attraction of pollinators from at least one of the two colours.

Another interesting pattern of the analysed specimens is the greater similarity of the flower and rhizome VOCs emissions compared to those of the leaves, in both the colour morphs.

**Conclusion**

Although the calcareous and serpentine growing *Iris lutescens* are (yet) not botanically defined as different ecotypes, the volatile emission of the specimens in this study differed, at least for the flowers, from the headspaces reported in the literature for their calcareous soil-growing counterparts in both the colour morphs.

Moreover, the differences in the emitted VOCs were more evident between the flowers of the two morphs, compared to the leaves and the rhizomes. This could be due to shared biosynthetic pathways of VOCs and floral pigments, and/or to the vessillary function of these organs in the economy of the plant. This behaviour is different for what is reported for the two morphs growing on calcareous soil, where the VOCs emitted by the yellow and purple flowers are not statistically significantly different. This could be explained as an even more important role of the colour in the pollinators attraction in an ultramafic environment, where the fauna is scarcer and the overall "background colour" is darker.

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**Tables**

**Table 1.** Complete headspace compositions for the flower, leaf and rhizome samples of the two morphotypes of *Iris lutescens* Lam.

| Constituents | l.r.i.[a] | Relative abundance (%) ± SD | | | | | |
|---|---|---|---|---|---|---|---|
| | | Flower | | Leaf | | Rhizome | |
| | | Yellow | Purple | Yellow | Purple | Yellow | Purple |
| (*E*)-3-hexen-1-ol | 853 | -[b] | - | 1.59±0.23 | 3.72±0.93 | - | - |
| 1-hexanol | 871 | - | - | 0.08±0.11 | 0.38±0.53 | - | - |
| 2-heptanone | 891 | - | - | - | - | 0.06±0.08 | - |
| α-thujene | 931 | 0.59±0.09 | 0.28±0.02 | - | - | 0.63±0.11 | 0.31±0.05 |
| α-pinene | 941 | 9.60±1.29 | 51.21±1.55 | 0.20±0.02 | 0.76±0.30 | 3.50±0.34 | 8.16±0.82 |
| sabinene | 976 | 0.87±0.23 | 0.45±0.03 | - | - | 3.10±0.45 | 1.04±0.19 |
| β-pinene | 982 | 7.35±0.71 | 3.11±0.01 | 0.13±0.02 | 0.50±0.11 | 1.15±0.06 | 2.75±0.04 |
| 6-methyl-5-hepten-2-one | 985 | - | 0.65±0.10 | - | 0.19±0.06 | - | - |
| 3-octanone | 987 | - | - | - | - | 0.28±0.02 | 0.42±0.05 |
| myrcene | 993 | 6.19±0.88 | 3.16±0.13 | 0.26±0.06 | 0.16±0.01 | 3.49±0.30 | 2.08±0.23 |
| *p*-mentha-1(7),8-diene | 1004 | 0.12±0.01 | - | - | - | - | - |
| α-phellandrene | 1005 | - | 0.40±0.01 | - | - | 0.27±0.06 | 0.09±0.12 |
| (*Z*)-3-hexenol acetate | 1009 | - | - | 27.69±0.96 | 59.97±14.11 | - | - |
| *n*-hexyl acetate | 1010 | - | - | 0.76±0.63 | 0.54±0.07 | - | - |
| α-terpinene | 1018 | 0.92±0.12 | - | 0.58±0.33 | - | 9.52±1.03 | 6.54±0.69 |
| *p*-cymene | 1027 | - | - | 0.24±0.11 | - | 4.03±0.37 | 1.21±0.21 |
| limonene | 1032 | 65.09±2.51 | 17.91±0.41 | - | 0.15±0.21 | - | 0.99±1.40 |
| 1,8-cineole | 1034 | - | 10.27±0.60 | 1.47±0.06 | 2.23±0.93 | 6.64±1.11 | 13.88±0.25 |
| (*Z*)-β-ocimene | 1042 | - | - | 0.36±0.06 | 0.11±0.16 | - | - |
| phenyl acetaldehyde | 1045 | - | 0.82±0.31 | - | - | - | - |
| (*E*)-β-ocimene | 1052 | - | - | 5.29±0.39 | 2.29±1.92 | 1.01±0.07 | 1.07±0.08 |
| γ-terpinene | 1062 | 0.22±0.03 | 0.15±0.01 | - | - | 0.17±0.04 | 0.11±0.01 |
| *cis*-sabinene hydrate | 1070 | 0.32±0.01 | 2.46±0.18 | - | 0.13±0.01 | 0.43±0.01 | - |
| dihydro myrcenol | 1074 | - | - | - | - | 0.15±0.01 | - |
| terpinolene | 1088 | 2.91±4.12 | - | - | - | 0.93±0.11 | 0.81±0.10 |
| 6-camphenone | 1093 | - | - | - | - | 0.09±0.12 | 0.23±0.01 |
| 2-nonanone | 1094 | - | - | - | - | 0.61±0.13 | 0.30±0.01 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| linalool | 1101 | - | - | - | - | 2.12±0.05 | 0.57±0.02 |
| nonanal | 1102 | - | 0.37±0.04 | - | 1.24±0.36 | 0.53±0.01 | 0.20±0.28 |
| dipropyl disulfide | 1110 | - | - | - | - | - | 1.09±0.29 |
| (*E*)-4,8-dimethylnona-1,3,7-triene | 1116 | - | - | - | - | 3.12±0.25 | - |
| (*E*)-1-(prop-1-en-1-yl)-2-propyl disulfane | 1118 | - | - | - | - | - | 0.17±0.00 |
| *cis*-limonene oxide | 1134 | 0.08±0.11 | - | - | - | - | - |
| *trans*-pinocarveol | 1139 | - | - | - | - | - | 0.16±0.01 |
| *cis*-verbenol | 1142 | - | - | - | - | - | 0.07±0.09 |
| camphor | 1143 | - | - | - | - | 0.07±0.09 | 0.50±0.02 |
| *cis*-β-terpineol | 1145 | 0.05±0.07 | - | - | - | - | - |
| pinocarvone | 1163 | - | - | - | - | 0.09±0.13 | 0.27±0.01 |
| 3-thujanol | 1169 | - | - | - | - | - | 0.22±0.03 |
| menthol | 1173 | - | - | - | - | 0.19±0.10 | - |
| *cis*-pinocamphone | 1175 | - | - | - | - | - | 0.05±0.07 |
| 4-terpineol | 1178 | 0.15±0.00 | 0.12±0.01 | - | - | 0.09±0.12 | 0.41±0.15 |
| α-terpineol | 1191 | 0.22±0.01 | - | - | - | 0.06±0.08 | 0.25±0.01 |
| dihydro carveol | 1192 | 0.06±0.08 | - | - | - | - | - |
| myrtenol | 1193 | - | - | - | - | 0.44±0.01 | 2.03±0.77 |
| myrtenal | 1194 | 0.07±0.09 | - | - | - | 0.06±0.08 | 0.15±0.21 |
| *n*-dodecane | 1200 | - | - | 0.23±0.01 | - | - | - |
| decanal | 1204 | - | 0.19±0.05 | 0.17±0.01 | 0.89±0.64 | 0.29±0.04 | 0.50±0.06 |
| verbenone | 1205 | - | 0.31±0.09 | - | - | - | 0.24±0.03 |
| methyl thymol | 1235 | - | - | 1.03±0.01 | 0.74±0.33 | 5.62±0.06 | 0.60±0.01 |
| methyl carvacrol | 1241 | - | - | 1.56±0.06 | 0.08±0.11 | 7.38±0.25 | 2.61±0.16 |
| *p*-anisaldehyde | 1256 | - | 0.07±0.09 | - | - | - | - |
| 2-undecanone | 1294 | - | - | - | - | 0.06±0.08 | - |
| *n*-tridecane | 1300 | - | - | 0.82±0.01 | - | 0.07±0.10 | 0.18±0.03 |
| methyl myrtenate | 1301 | 0.20±0.02 | - | - | - | - | 0.21±0.03 |
| panaxene | 1313 | - | - | - | - | 0.38±0.08 | 0.35±0.01 |
| silphiperfol-5-ene | 1328 | - | - | - | - | 0.76±0.02 | 6.09±0.13 |
| presilphiperfol-7-ene | 1334 | - | - | - | - | - | 2.97±0.28 |
| 7-*epi*-silphiperfol-5-ene | 1345 | - | - | - | - | 2.16±0.09 | 6.74±0.21 |
| α-longipinene | 1351 | - | - | - | - | - | 0.43±0.03 |
| α-terpinyl acetate | 1352 | - | - | - | - | 0.14±0.03 | - |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| (*E*)-2-undecenal | 1357 | - | - | - | - | 0.20±0.03 | - |
| silphiperfola-4,7(14)-diene | 1362 | - | - | - | - | - | 0.28±0.02 |
| cyclosativene | 1368 | - | 0.29±0.08 | - | 0.20±0.05 | 0.28±0.04 | 3.27±0.13 |
| longicyclene | 1373 | - | 0.07±0.10 | - | - | 0.42±0.14 | 1.90±0.37 |
| α-copaene | 1376 | - | 0.21±0.04 | 4.39±0.04 | 1.28±0.48 | 2.23±0.20 | - |
| silphiperfol-6-ene | 1377 | - | - | - | - | 0.22±0.06 | 0.17±0.01 |
| β-patchoulene | 1380 | - | - | - | - | 0.16±0.22 | - |
| β-panasinsene | 1383 | - | - | - | - | - | 4.77±0.64 |
| β-bourbonene | 1384 | - | - | 0.48±0.02 | 0.66±0.54 | - | - |
| α-isocomene | 1388 | - | - | - | - | 0.20±0.02 | 0.39±0.04 |
| β-cubebene | 1390 | - | - | 0.73±0.04 | 0.50±0.21 | 0.15±0.01 | - |
| β-elemene | 1392 | - | - | 1.09±0.05 | 0.15±0.21 | 0.43±0.01 | 0.17±0.02 |
| sativene | 1395 | - | - | - | - | - | 0.31±0.04 |
| *n*-tetradecane | 1400 | - | 0.06±0.08 | - | - | 0.21±0.04 | - |
| β-maaliene | 1401 | - | - | - | - | - | 0.28±0.15 |
| longifolene | 1403 | - | - | - | - | - | 1.09±0.26 |
| dodecanal | 1408 | - | - | - | - | 0.10±0.14 | - |
| α-gurjunene | 1410 | - | - | - | - | 0.08±0.11 | 0.08±0.11 |
| 1,7-*di*-*epi*-β-cedrene | 1415 | - | - | - | - | - | 0.29±0.04 |
| β-caryophyllene | 1420 | 0.06±0.08 | 0.52±0.05 | 11.96±0.52 | 9.2±6.12 | 7.79±1.91 | 3.18±0.88 |
| 2,5-dimethoxy-*p*-cymene | 1424 | - | - | - | - | - | 0.19±0.03 |
| β-copaene | 1429 | - | - | 0.40±0.01 | 0.21±0.08 | - | - |
| β-gurjunene | 1432 | - | - | 0.06±0.08 | - | - | - |
| γ-elemene | 1433 | - | - | - | - | - | 0.06±0.08 |
| *trans*-α-bergamotene | 1438 | - | - | - | - | 1.86±0.10 | - |
| α-himachalene | 1448 | - | 0.46±0.01 | - | - | - | 3.11±0.30 |
| *epi*-β-santalene | 1449 | - | - | - | - | 0.72±0.02 | 0.47±0.01 |
| α-*neo*clovene | 1454 | - | - | - | 0.12±0.16 | - | - |
| (*E*)-geranyl acetone | 1455 | - | 0.10±0.13 | - | 0.98±0.89 | 0.69±0.00 | 0.29±0.01 |
| α-humulene | 1456 | 0.14±0.00 | 0.51±0.02 | 0.62±0.04 | 0.19±0.27 | 1.31±0.08 | 0.38±0.01 |
| (*E*)-β-farnesene | 1460 | - | 0.38±0.15 | - | - | - | - |
| *allo*aromadendrene | 1461 | - | - | 0.16±0.04 | - | 0.10±0.13 | 0.36±0.02 |
| *cis*-muurola-4(14),5-diene | 1462 | - | - | 0.20±0.02 | - | - | - |
| β-santalene | 1463 | - | - | - | - | 1.15±0.27 | - |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| α-acoradiene | 1463 | - | - | - | - | - | 0.07±0.09 |
| 9-*epi*-(*E*)-caryophyllene | 1467 | - | 0.06±0.08 | 0.18±0.02 | - | - | - |
| γ-himachalene | 1475 | - | 0.46±0.03 | - | - | - | 2.14±0.04 |
| β-chamigrene | 1476 | - | - | - | - | 0.08±0.11 | - |
| γ-muurolene | 1477 | - | - | 0.08±0.11 | - | 2.38±0.20 | - |
| germacrene D | 1478 | - | 0.25±0.00 | 30.13±1.23 | 5.35±3.33 | - | 2.20±0.20 |
| γ-curcumene | 1480 | - | - | - | - | 0.53±0.02 | - |
| β-selinene | 1485 | - | - | - | - | 0.15±0.21 | 0.12±0.16 |
| valencene | 1492 | - | - | - | - | 0.22±0.06 | 0.11±0.15 |
| viridiflorene | 1493 | - | - | - | - | - | 0.09±0.13 |
| bicyclogermacrene | 1495 | - | - | 2.38±0.51 | 0.61±0.37 | 0.55±0.08 | 0.09±0.12 |
| *trans*-β-guaiene | 1499 | - | - | 0.37±0.02 | 0.13±0.18 | - | - |
| *n*-pentadecane | 1500 | - | 0.08±0.11 | - | - | 0.46±0.06 | 0.76±0.19 |
| β-himachalene | 1501 | - | - | - | - | 0.17±0.23 | - |
| γ-patchoulene | 1502 | - | - | - | - | 0.07±0.10 | - |
| cuparene | 1505 | - | - | - | - | 0.08±0.11 | - |
| germacrene A | 1506 | - | - | 0.16±0.05 | - | - | - |
| (*E*,*E*)-α-farnesene | 1507 | - | 1.32±0.43 | 3.04±0.62 | 0.74±0.30 | - | - |
| β-bisabolene | 1509 | - | - | - | 0.11±0.16 | 0.35±0.03 | - |
| cameroonan-7-α-ol | 1512 | - | - | - | - | - | 0.09±0.13 |
| *trans*-γ-cadinene | 1513 | - | - | - | 0.15±0.21 | 0.53±0.04 | - |
| cubebol | 1516 | - | - | - | - | - | 0.43±0.01 |
| δ-cadinene | 1524 | - | 0.16±0.01 | 0.73±0.01 | 0.51±0.03 | 0.54±0.03 | 0.50±0.04 |
| *cis*-α-irone | 1546 | - | - | - | - | - | 0.67±0.06 |
| elemol | 1549 | 3.65±0.71 | 0.78±0.18 | - | - | - | - |
| *di*-*epi*-cedrene-1-oxide | 1551 | - | - | - | 0.14±0.19 | - | 0.17±0.01 |
| germacrene D-4-ol | 1575 | - | - | 0.13±0.00 | - | - | 0.19±0.01 |
| caryophyllene oxide | 1581 | - | - | - | 0.17±0.23 | 4.00±1.05 | 0.79±0.32 |
| guaiol | 1595 | 0.42±0.11 | - | - | - | - | - |
| *n*-hexadecane | 1600 | - | 0.15±0.21 | - | 0.47±0.01 | 0.88±0.16 | 1.54±0.42 |
| 5-*epi*-7-*epi*-α-eudesmol | 1603 | 0.07±0.09 | - | - | - | - | - |
| humulene epoxide II | 1607 | - | - | - | - | 0.47±0.04 | - |
| humulane-1,6-dien-3-ol | 1615 | 0.36±0.13 | - | - | - | - | - |
| hydroxy-neoisolongifolane | 1621 | - | 1.89±0.91 | - | - | - | - |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| caryophylla-4(14),8(15)-dien-5-ol | 1636 | - | - | - | - | 0.07±0.09 | - |
| *epi*-α-cadinol | 1640 | - | - | - | - | 0.07±0.09 | - |
| patchouli alcohol | 1660 | - | - | - | - | - | 0.17±0.00 |
| 3,5,5-trimethyl-2-ethylhexyl hexanoate | 1660 | - | - | - | - | 5.59±1.00 | - |
| cadalene | 1674 | - | - | - | - | - | 0.05±0.07 |
| 8-hydroxy-isobornyl isobutyrate | 1675 | - | - | - | - | 0.10±0.14 | - |
| *n*-heptadecane | 1700 | - | 0.06±0.08 | - | - | 0.06±0.08 | 0.19±0.01 |
| (*E*)-7-octadecene | 1773 | - | - | - | - | - | 0.44±0.04 |
| 1-octadecene | 1786 | - | - | - | - | - | 0.06±0.08 |
| 2-ethylhexyl salicylate | 1815 | 0.30±0.18 | 0.08±0.11 | 0.36±0.22 | 1.97±1.44 | 0.77±0.30 | 0.73±0.16 |
| Monoterpene hydrocarbons | | 93.83±1.75 | 76.65±1.91 | 7.03±0.99 | 3.96±1.85 | 27.80±2.82 | 25.13±3.74 |
| Oxygenated monoterpenes | | 1.13±0.37 | 13.14±0.86 | 4.05±0.00 | 3.18±1.35 | 23.53±0.49 | 22.59±1.02 |
| Sesquiterpene hydrocarbons | | 0.20±0.08 | 4.66±0.45 | 57.10±2.72 | 20.08±11.91 | 25.99±1.35 | 42.66±1.96 |
| Oxygenated sesquiterpenes | | 4.49±1.03 | 2.67±1.09 | 0.13±0.00 | 0.30±0.42 | 4.60±0.91 | 1.83±0.16 |
| Apocarotenoids | | - | 0.10±0.13 | - | 0.98±0.89 | 0.69±0.00 | 0.96±0.05 |
| Sulfur compounds | | - | - | - | - | - | 1.26±0.29 |
| Other non-terpene derivatives | | 0.30±0.18 | 2.51±0.38 | 31.68±1.73 | 69.34±14.35 | 13.34±0.45 | 5.29±0.50 |
| Total identified (%) | | 99.94±0.09 | 99.73±0.02 | 99.99±0.01 | 97.83±0.28 | 95.93±0.38 | 99.7±0.23 |

[a] Linear retention indices on a DB5 column; [b] Not detected.

**Table 2.** Compounds detected in the organs of the two morphs headspaces contributing for at least 1.00% to the dissimilarity of the samples.

| Compound | Dissimilarity contribution (%) | Cumulative dissimilarity contribution (%) |
|---|---|---|
| | **Flower** | |
| Limonene* | 37.02 | 37.02 |
| α-Pinene* | 32.65 | 69.67 |
| 1,8-Cineole* | 8.057 | 77.73 |
| β-Pinene* | 3.327 | 81.06 |
| Myrcene* | 2.375 | 83.43 |
| Terpinolene | 2.284 | 85.71 |
| Elemol* | 2.252 | 87.97 |
| *cis*-Sabinene hydrate* | 1.679 | 89.65 |
| Hydroxy-neoisolongifolane | 1.483 | 91.13 |
| (*E*,*E*)-α-Farnesene | 1.033 | 92.16 |
| | **Leaf** | |
| (Z)-3-Hexenol acetate* | 36.10 | 36.10 |
| Germacrene D* | 27.71 | 63.81 |
| β-Caryophyllene | 4.255 | 68.07 |
| α-Copaene | 3.474 | 71.54 |
| (*E*)-β-Ocimene* | 3.355 | 74.89 |
| (*E*,*E*)-α-Farnesene* | 2.572 | 77.47 |
| (*E*)-3-Hexen-1-ol* | 2.385 | 79.85 |
| Bicyclogermacrene* | 1.979 | 81.83 |
| 2-Ethylhexyl salicylate | 1.801 | 83.63 |
| Methyl carvacrol* | 1.655 | 85.29 |
| Nonanal | 1.383 | 86.67 |
| (*E*)-Geranyl acetone | 1.096 | 87.77 |
| β-Elemene* | 1.051 | 88.82 |
| | **Rhizome** | |
| 1,8-Cineole* | 6.582 | 6.582 |
| 3,5,5-Trimethyl-2-ethylhexyl hexanoate | 5.078 | 11.66 |
| Silphiperfol-5-ene* | 4.845 | 16.50 |

| | | |
|---|---|---|
| Methyl thymol* | 4.566 | 21.07 |
| Methyl carvacrol* | 4.336 | 25.41 |
| β-Panasinsene | 4.333 | 29.74 |
| α-Pinene* | 4.237 | 33.98 |
| β-Caryophyllene* | 4.193 | 38.17 |
| 7-*epi*-Silphiperfol-5-ene* | 4.163 | 42.33 |
| Caryophyllene oxide* | 2.918 | 45.25 |
| (*E*)-4,8-Dimethylnona-1,3,7-triene* | 2.833 | 48.08 |
| α-Himachalene* | 2.824 | 50.91 |
| Cyclosativene* | 2.721 | 53.63 |
| α-Terpinene* | 2.712 | 56.34 |
| Presilphiperfol-7-ene* | 2.700 | 59.04 |
| *p*-Cymene* | 2.567 | 61.61 |
| γ-Muurolene* | 2.163 | 63.77 |
| α-Copaene* | 2.027 | 65.80 |
| Germacrene D* | 2.000 | 67.80 |
| γ-Himachalene* | 1.945 | 69.74 |
| Sabinene* | 1.876 | 71.62 |
| *trans*-α-Bergamotene* | 1.691 | 73.31 |
| β-Pinene* | 1.454 | 74.76 |
| Myrtenol | 1.442 | 76.20 |
| Linalool* | 1.409 | 77.61 |
| Longicyclene* | 1.345 | 78.96 |
| Myrcene* | 1.285 | 80.24 |
| β-Santalene | 1.045 | 81.29 |

* Indicates compounds for which a statistically significant difference between the two morphotypes has been evidenced by means of the F- or T-test.

**Figure captions**

**Fig. 1**