

## Urban Trees' Terpenoids: plant-host interactions in a challenging and

### changing environment

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## «Secondary» plant metabolites belong to three main groups:

- Phenols
- Alkaloids
- Terpenoids





## About terpenoids.....

.....also called **isoprenoids**, because they contain repetitions of the 5-C isoprene unit.



- Monoterpenes C<sub>10</sub> **VOLATILE!**
- Sesquiterpenes C<sub>15</sub>
- Diterpenes  $-C_{20}$
- Triterpenes C<sub>30</sub>
- Tetraterpeni C<sub>40</sub>





NOI AMIAMO LA NOSTRA TERRA

Besides being precursors of phyotohormones, photosynthetic pigments, electron carriers and membrane components, isoprenoids are also deeply involved in eco-physiological interactions:



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## Volatile isoprenoids are thought to be involved in defence and chemical communication....





...non-volatile isoprenoids (oleoresins) are not only bioactive molecules, but also valuable raw materials for the chemical and pharmaceutical industry, cosmetics, nutraceuticals and biofuels





#### AGRICOLTURA | FORESTE, AREE VERDI, AMBIENTE | ALIMENTI, GASTRONOMIA, RISTORAZIONE

#### NOI AMIAMO LA NOSTRA TERRA





Emission profiles of volatile terpenoids have been studied in two populations of Calabrian pine infested by the pine processionary moth (PPM)











Plant plots were within the premises of the Aspromonte National Park, in the southmost part of continental Italy



• 1st sampling in February

• 2nd and 3rd samplings in March





Collection of pine needles was matched with the biological cycle of the PPM

• 4th and 5th samplings in April



• 6th sampling in August





### GC-MS analysis - 1

- Sample preparation (head space):
  - Equilibration



- Adsorption on SPME fiber





 $\triangle$ 

• GC-MS analysis - 2



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Twenty-one volatile terpenoids were identified in the head space of Calabrian pine needles

Of these, bornyl acetate [(4,7,7trimethyl-3bicyclo[2.2.1]heptany 1) acetate] was the most frequently and selectively associated with the PPM infestation

| Common name         | IUPAC name                                                                                                    | Type of terpen | RT    | KI   | Structural formula |
|---------------------|---------------------------------------------------------------------------------------------------------------|----------------|-------|------|--------------------|
| Pinene alpha*       | (15,55)-2,6,6-Trimethylbicyclo[3.1.1]hept-2-ene ((-)-α-Pinene)                                                | monoterpenoid  | 7,38  | 939  | <u>S</u>           |
| Pinene beta*        | 6.6-Dimethyl-2-methylidenebic yclo[3.1.1]heptane                                                              | monoterpenoid  | 8,35  | 982  |                    |
| Myrcene beta        | 7-Methyl-3-methylene-1,6-octadiene                                                                            | monoterpenoid  | 8,75  | 1000 |                    |
| Phellandrene alpha  | 2-Methyl-5-(1-methylethyl)-1,3-cyclohexadiene                                                                 | monoterpenoid  | 9,61  | 1035 |                    |
| Limonene*           | 1-Methyl-4-(prop-1-en-2-yl)cyclohex-1-ene                                                                     | monoterpenoid  | 9,8   | 1043 |                    |
| Ocimene beta*       | (Z)-3,7-Dimethyl-1,3,6-octatriene                                                                             | monoterpenoid  | 10,06 | 1053 | H <sub>3</sub> C   |
| Terpinolene*        | 4-Methyl-1-(1-methylethyl)-1,3-cyclohexadiene                                                                 | monoterpenoid  | 11,09 | 1095 |                    |
| Thymol methyl ether | 2-methoxy-4-methyl-1-propan-2-ylbenzene                                                                       | monoterpenoid  | 11,98 | 1131 |                    |
| Camphor*            | 1,7,7-Trimethylbicyclo[2.2.1]heptan-2-one                                                                     | monoterpenoid  | 12,48 | 1152 | Ă,Ă                |
| Bornyl acetate      | 4,7,7-Trimethyl-3-bicyclo[2.2.1]heptanyl) acetate                                                             | monoterpenoid  | 15,82 | 1292 | Ar .               |
| Gurjunene gamma     | (1R,3aR,4R,7R)-1,4-dimethyl-7-prop-1-en-2-yl-1,2,3,3a,4,5,6,7-octahydroazulene                                | Sesquiterpenes | 16,4  | 1318 | 60                 |
| Elemene delta       | (3R , $4R$ ) -1-Isopropil-4-metil-3- (prop-1-en- 2-il) -4-vinylcyclohex-1-ene                                 | Sesquiterpenes | 16,99 | 1344 |                    |
| Cubebene alpha*     | (1R,5S,6R,7S,10R)-10-methyl-4-methylidene-7-(propan-2-yl)tricyclo[4.4.0.0 <sup>1</sup> , <sup>5</sup> ]decane | Sesquiterpenes | 17,27 | 1357 |                    |
| Copaene alpha*      | (1S,6S,7S,8S)-1,3-dimethyl-8-(propan-2-yl)tricyclo[4.4.0.0 <sup>2</sup> , <sup>7</sup> ]dec-3-ene             | Sesquiterpenes | 17,89 | 1384 |                    |
| Bourbonene beta     | 1-methyl-5-methylidene-8-(propan-2-yl)tricyclo[5.3.0.0 <sup>2</sup> , <sup>6</sup> ]decane                    | Sesquiterpenes | 18,82 | 1427 |                    |
| Caryophyllene*      | (1R,4E,9S)-4,11,11-Trimethyl-8-methylidenebicyclo[7.2.0]undec-4-ene                                           | Sesquiterpenes | 18,88 | 1430 | H <sub>0</sub> C H |
| Bisabolene alpha    | (E)-1-Methyl-4-(6-methylhepta-2,5-dien-2-yl)cyclohex-1-ene                                                    | Sesquiterpenes | 19,63 | 1466 |                    |
| Humulene*           | 2,6,6,9-Tetramethyl-1,4-8-cycloundecatriene                                                                   | Sesquiterpenes | 19,93 | 1480 | $\leq$             |
| Murolene gamma*     | (1S,4aS,8aR)-7-methyl-4-methylidene-1-propan-2-yl-2,3,4a,5,6,8a-hexahydro-1H-naphthal                         | Sesquiterpenes | 20,4  | 1492 |                    |
| Germacrene D*       | (1E,5E,8S)-1,5-dimethyl-8-(prop-1-en-2-yl)cyclodeca-1,5-diene                                                 | Sesquiterpenes | 20,18 | 1502 |                    |
| Candinene gamma*    | (1S,4aR,8aR)-7-methyl-4-methylidene-1-propan-2-yl-2,3,4a,5,6,8a-hexahydro-1H-naphtha                          | Sesquiterpenes | 20,89 | 1526 |                    |



Charl D 11%

STREET.

Genes from Calabrian pine encoding for the biosynthetic major enzymes, namely terpene synthases, are being isolated and characterised, and their expression in response PPM to infestation is being quantified



Fig. 5 Phylogenetic true of terpent synthases (TPSs) in gymnospirms: Cuprosacese (nd diamonda), Pinamar (black), Taxacese (group), Ginkgeneouse (brown) and Cycadacone (heavenly). The Physiconitralis patent est-kaurone synthase (PITPS-entKS; vioist diamond) was used to not the true. Branchus indicated with dots ruptum nt bootstrap support more than 80% (100 repetitions). Modifications in the typical y he-domain architecture of TPS and the presence of functional active sites (a yellow cross indicate loss of function) are illustrated corresponding to the different subfamilies of the TPS plant family and to the different groups within the TPS d3 subfamily. For acronyms denoting plants species, are Table S1. DTPSs diterpone syntheses, MIPSs monoterpone syntheses, SIPSs associterrors without



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REVIEW

## On the Evolution and Functional Diversity of Terpene Synthases in the *Pinus* Species: A Review

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### Terpenoids for biocontrol in UPF: prospective projects - 1



Graphical concept of **UTreeTer** showing the overall objective (i.e. the role of terpenoids in the interactions among major tree species of Italian cities, their arthropod pests and pathogens, and natural enemies of these organisms), the organization in workpackages (WPs), and the involved research units.

## The UTreeTer project: terpenoids in a north-south transect of Italian UPF species and their hosts, in a changing climate

[tree/pathogen/pest/pest's natural enemies]

- (i) Pinus spp. (pine)/Sphaeropsis sapinea/Thaumetopoea pityocampa/Phrixe caudata, Villa brunnea, Calosoma sycophanta;
- (ii) Quercus ilex (holm oak)/Phyllosticta spp., Microsphaera spp./Lymantria dispar dispar, Thaumetopoea processionea, Corythucha arcuata, Coroebus spp./P. caudata, V. brunnea, Oencyrtus pytiocampae;
- (iii) Platanus × acerifolia (plane tree)/Apiognomonia platani/Corythucha ciliata/Anthocoris spp., Orius laticollis.
- (iv) Special attention will be also given to Aesculus hippocastanum (horse chestnut) nand Populus spp (poplar).



## Terpenoids for biocontrol in UPF: prospective projects - 2

TerBioFor -Constitutive and host-inducible terpenoids as prospective biocontrol agents in UPF





# Thank you very much for your consideration!

