Supplementary Materials for

Absolute optical chiral analysis using cavity-enhanced polarimetry

Lykourgos Bougas et al.

Corresponding author: Lykourgos Bougas, bougas.lykourgos@gmail.com

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S1. Optical activity
Electromagnetic radiation propagating through a chiral medium experiences a complex index of refraction that differs in both its real and imaginary parts for right-circular (RCP) and left-circular polarization (LCP). Optical activity, i.e., the ability of a chiral medium to rotate and absorb linearly polarized light travelling through it, can be described by introducing a general form for the refractive index of the chiral medium that differs for RCP and LCP:

$$\varphi = \frac{\pi l}{\lambda} (n_L - n_R),$$

with \(\lambda\) being the wavelength of light and \(l\) being the length of the chiral medium. The (complex) indices of refraction \(n_{R/L}\) of the chiral medium for RCP and LCP, respectively, can be expressed as \(n_{R/L} = n_e \mp \kappa\), with \(n_e\) the average (background) refractive index and \(\kappa\) the chirality (‘Pasteur’) parameter. The real part of \(\kappa\) \([\text{Re}(\kappa)]\) is associated with effects of circular birefringence, while its imaginary part \([\text{Im}(\kappa)]\) with effects of circular dichroism. The SOR values shown in Fig.2A, reflect the value of \(\text{Re}(\kappa)\), in the gas phase, for each presented compound. Our experimental approach allows for the precise measurement of both \(n_e\) and \(\kappa\). Specifically for the chirality measurements presented here (Figs. 2-4), all results are proportional to \(\text{Re}(\kappa)\).

S2. CCP experiment
We employ a frequency metrology scheme\(^3-6\) for the measurement of the central frequencies of each cavity mode (\(R_{CW}, L_{CW}, R_{CCW}, L_{CCW}\)), and, hence, of \(f_c\). In particular, in Fig. S1A we present a schematic of our experimental setup, showing the CCP device that consists of a ring (four-mirror) optical cavity with the mirrors arranged in a bowtie configuration\(^1,2\). We split the laser beam into two parts which are then coupled, through separate optical paths, to the CW and CCW propagation modes of the cavity. We use two separate acousto-optic modulators (AOM) (Gooch & Housego 3270) to independently control and servo-lock the frequency of each of the CW and CCW laser beams into a corresponding cavity mode pair, i.e., \(R_{CW}/R_{CCW}\) or \(L_{CW}/L_{CCW}\). The frequency stabilization/servo-locking is achieved using the Pound-Drever-Hall technique. Both AOMs are driven by a double-channel RF synthesizer (Moglabs Agile XRF421). Measurement of the servo-controlled frequency outputs (possible via the measurement of the supplied RF frequencies to the AOMs), provides us the central frequency of each mode. By resonantly coupling light into the \(R_{CW}/R_{CCW}\) mode pair we can record directly a frequency difference equal to \(2f_c\) only in the presence of a chiral signal (Fig.S1B). Similarly, resonantly coupling light into the \(L_{CW}/L_{CCW}\) mode pair yields a frequency difference equal to \(-2f_c\). The measurements of the AOM RF frequencies are performed using frequency counters (Stanford Research Systems; SR620) that allow us to control the measurement integration time (typically \(~1s\)).

In Fig.S1C we present a time record of the measured frequency difference between the \(R_{CW}/R_{CCW}\) modes, i.e., \(\Delta f = f_{CW} - f_{CCW}\), and in Fig.S1D the associated Allan deviation. Our current CCP-based measurement sensitivity is \(~3.4 \times 10^{-7}\text{rad}/\sqrt{\text{Hz}}\), ultimately limited by photon shot noise at the \(~1.3 \times 10^{-9}\text{rad}/\sqrt{\text{Hz}}\) level.

Finally, measurements of the average refractive index are possible through the direct measurement of the central frequencies of the cavity modes. To do so accurately, we additionally servo-lock the emission frequency of the laser to a cavity resonance. In this case, the laser’s wavelength is fixed while its frequency tracks the changes in refractive index, since: \(\frac{\delta f}{f} = -\frac{\delta n}{n}\). From the gas optical refractivity measurements, we can then extract the gas density of each compound\(^9\).
S3. **Specific optical rotation of chiral compounds**
In Table 1 we provide the values for the specific optical rotation (SOR) \([\alpha]^{21}_D\) of all the different chiral compounds we present and are relevant to our work.

S4. **GC/CCP analysis of enantiopure (±)-limonene**
In Fig.S2 we present GC/CCP-based analysis of enantiopure (+) and (-)-limonene. For our analysis we use splitless injection (Agilent HP 6890A GC, Agilent Technologies, USA) of mixture solutions in ethanol (1μL of solution injected). The chiral separations were achieved using a 30m β-DEX™ 120 column (Sigma-Aldrich GmbH, Germany) with 0.25 mm internal diameter and a 0.25 μm film thickness. The column flow was chosen to be 8ml/min and the temperature programme to be 40 °C for 2 minutes then 40 °C to 210 °C at 12 °C min⁻¹. We use these results, under the ‘GC’ label, in our comparison with direct total sample measurements of enantiopure limonene in Fig.2C of the main text.

S5. **Offline chiral analysis of perfumes using GC-MS**
We select the commercially available low-cost fragrance clones according to advertised information provided by their respective production companies, in connection to publicly available information concerning fragrance clones. In the following figures we present the GC/MS analysis of all the perfumes used in this work, both the authentic and the low-cost fragrance clones. We use an identical separation method for all perfumes, designed specifically for the optimal separation of chiral monoterpenes and monoterpenoids. The chiral separations were achieved using a 30m β-DEX™ 120 column (Sigma-Aldrich GmbH, Germany) with 0.25mm internal diameter and a 0.25 μm film thickness. The column flow was chosen to be 1ml/min and the temperature programme consists of an initial 5min step where the oven temperature is held at 40 °C, after which it was increased at a rate of 4 °C/min from 40 °C to 220 °C and then held again for 5 minutes. In Figs.S3-S5, the presented labelled peaks correspond to: 1 (-)-α-pinene; 2 (+)-α-pinene; 3 (-)-β-pinene; 4 (+)-limonene; 5 (-)-limonene; 6 (-)-linalool followed by (+)-linalool (retention times of 23.54 min and 23.79 min, respectively, for the chromatogram of ‘CM’ shown in Fig. S3); and 7 linalyl acetate (achiral).

S6. **Chiral analysis of volatile emissions of a coniferous plant**

a. **Temperature and humidity measurements**
We use a 25L Tedlar® sampling bag (ANALYT-MTC GmbH, Germany) secured around the tree stem to create an open-bottom sampling chamber that encloses the plant’s upper branches. This open-bottom design allows air to move between the interior and exterior of the enclosed space to avoid possible suffocation of the plant during sampling (we do not implement any active mixing of both air volumes). A heating tape supported around the sampling bag allows us to actively control the temperature within the sampling chamber. We use a temperature and humidity logger device (TSP01, Thorlabs GmbH) to record the relative humidity in the laboratory and the temperature inside and outside the sampling chamber. We present our recordings for the whole

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3 www.duftzwillinge.eu; www.parfumo.net/Parfums/Dupes; duft-check.de.
duration of our measurements in Fig. S6, showing an overall stability of the laboratory humidity and the temperature inside the chamber during the measurements.

b. Estimation of overall concentration changes and effective specific optical rotation signal from GC/MS analysis

To sample the plant emissions, we use a ¼ inch teflon sampling line placed inside the sampling chamber (Fig. 4 main text). Samples are collected onto sorbent cartridges at 200 ml min\(^{-1}\) using a GilAir Plus Personal Air Sampling Pump (Sensidyne\textsuperscript{®}, USA). We collect four samples before the mechanical wounding, i.e., branch cut, with a sampling time of ~10 min. Following wounding, we collect two or three consecutive samples approximately every hour for 11 hrs, and two additional samples after 24 hrs (sampling time ~10 min). For the resin data, we collect two samples directly from the exposed wounding site (sampling time ~5 min). In Fig. S7 we reproduce the chromatogram of a sample collected before wounding (as shown also in Fig. 4 of the main text).

We analyze the samples using the offline GC/MS analysis procedure described in the main text. We use a non-linear, least-square minimization method to fit the observed time-dependent behavior of the concentration of each of the dominant monoterpene VOCs observed (pre- and post-wounding), as this extracted from the GC/MS analysis, using the following model function:

\[
C_i(t) = \frac{A}{2} \times \left( \exp \left( \frac{1}{2} \cdot \left( \frac{\sigma}{\tau} \right)^2 - \frac{t - t_0}{\tau} \right) \right) + c \times \text{erfc} \left( \frac{1}{\sqrt{2}} \left( \frac{\sigma}{\tau} - \frac{t - t_0}{\sigma} \right) \right),
\]

where \(C_i\) is the concentration of the \(i\)th chiral VOC \((i = \{1, 7\})\) and \(t\) is the time (independent) variable. This model results from the convolution of a mono-exponential decaying function (characteristic decay constant \(\tau\)) starting at \(t = t_0\), \(H(t - t_0) \times A \exp(-\frac{t - t_0}{\tau})\) [\(H(t - t_0)\) is the Heaviside step function], with a normalized Gaussian function of standard deviation \(\sigma\), which accounts for the sampling time. In addition, \(\text{erfc}\) is the complementary error function, \(A\) a proportionality constant and \(c\) an offset parameter accounting for the observed plateau.

Using the specific optical rotation \([\alpha]_{25^\circ}^{19}\text{mm}^{}\) value (Table I) for each of the dominant chiral monoterpenes observed in the plant emissions, we can then calculate an effective expected specific optical rotation signal from the GC/MS analysis as follows:

\[
\varphi_{GC/MS}(t) [\text{deg} (\text{gr/ml})^{-1} \text{dm}^{-1}] = \frac{1}{\sum_i C_i(t) l_i} \sum_i [\alpha]_i l_i C_i(t).
\]

In Fig. 4C and Fig. 4D of the main text we present the results for \(C_{total}(t) = \sum_i C_i(t)\) and \(\varphi_{GC/MS}(t)\), respectively, that are in agreement with our CCP-based online chiroptical measurements. We reproduce these results in Fig. S8 for clarity.

c. Concentration changes as observed from the CCP-based refractometric measurements

In Fig. S9 we present the CCP-based refractometric raw-data for each online sampling measurement using the thermal desorption unit (TDU, Fig. 4B main text). One of these (for the online sample recorded at \(\Delta t = 0.3 \text{ hr}\)) is presented as an inset in Fig. 4B.

From these data we extract the measurements of the overall concentration of the emitted compounds from the coniferous plant, pre- and post-wounding, as presented in Fig. 4C. CCP measurements combined with our sampling approach, which based on the use of the thermal
desorption unit, allows us to observe directly in the refractometric data differences in dynamics between the dominant (monoterpene) chiral compounds. In particular, in accord with the GC/MS analysis (Fig.S8), the α-pinene/camphene enantiomers decay much faster (blue points Fig.S9) than (-)-limonene (green points Fig.S9) following mechanical wounding.

S7. Photo of the damaged plant branch
In Fig.S10 we present a photo of the damaged branch of the Pinus heldreichii we used for the measurements (shown also in Fig.4 of the main text). The resin covering the wounding site can be clearly seen in the photo. Samples of the emissions of the resin (Fig.4C,D of the main text) are taken directly from the exposed wounding site.
Table S1.
Chemical properties of chiral volatile organic compounds.

| Formula                          | Molar mass [gr/mol] | Boiling point [°C] | Vapour pressure @ 21 °C [mbar] | $[\alpha]^2_{D21\text{nm}}$ [deg. (gr/ml)$^{-1}$dm$^{-1}$] |
|---------------------------------|---------------------|--------------------|--------------------------------|----------------------------------------------------------|
| (R)-(-)-2-butanol               | C$_4$H$_{10}$O      | 74.12              | 100                            | -23.0 ± 0.8                                               |
| (+)-α-pinene                    | C$_{10}$H$_{16}$    | 136.24             |                                | 123.2 ± 1.3                                               |
| (+)-camphene                    |                     |                    |                                | 53.9 ± 1.2                                                |
| (-)-β-pinene                    |                     |                    |                                | 16.2 ± 2.2                                                |
| (R)-(-)-α-phellandrene          |                     |                    |                                | -986.8 ± 1.1                                              |
| (R)-(+)limonene                 |                     |                    |                                | 184.6 ± 1.8                                               |
Fig. S1. Schematic and operation principles for chirality sensing using cavity-enhanced chiral polarimetry and frequency metrology. A. Schematic diagram of the experimental setup. The laser beam is being split into two orthogonal linearly polarized parts, which couple into the four-mirror cavity in opposite directions (CW and CCW). Quarter-wave plates ($\lambda/4$) allow us to convert the linear polarizations of the CW and CCW beams into circular polarized beams and vice versa. AOM: Acousto-optic modulator. The Faraday crystal, generating an intracavity Faraday polarization anisotropy ($\theta_F$), is located on one arm of the cavity while the chiral sample, generating an intracavity chiroptical polarization anisotropy ($\varphi_c$) is located on the other. We analyze the chiroptical signal from gaseous samples using either gas chromatography or direct dynamic air headspace sampling. B. Cavity frequency polarization spectrum of the optical cavity in the absence and presence of an intracavity chiroptical ($\varphi_c$) polarization anisotropy. Measuring the frequency difference between different mode pairs we extract the chiroptical signal ($\varphi_c$) through a direct measurement of $f_c = (\varphi_c \cdot \text{FSR})/\pi$. C. Time record of frequency difference between the R$_{CW}$/R$_{CCW}$ modes ($\Delta f = f_{CW} - f_{CCW}$), and D its associated (overlapping) Allan deviation.
Fig. S2.
CCP-based chromatographic chiral analysis of enantiopure limonene in the gas phase. GC/CCP-based chiral analysis of enantiopure (+)-limonene (left) and (-)-limonene (right). The analysis is performed under identical conditions as for the case of racemic limonene shown in Fig.2C of the main text.
Fig. S3.
**GC/MS analysis of perfume mixtures.** Chromatograms for the perfumes: ‘Coco Mademoiselle’ by Chanel (EdP) (‘CM’ in the main text); ‘Miss Dior’ by Dior (EdP) (‘MD’); ‘Magic’ by Miro (‘AC#1’); ‘Madame Isabelle’ by La Rive (‘AC#2’); and ‘Suddenly Madame Glamour’ by Lidl (‘AC#3’). Samples are collected from the headspace of 20ml scintillation vials that contain ~1mL of perfume. For ease of comparison, we normalize the signals of each spectra to the maximum signal value of (+)-limonene (peak 4) of the first spectrum of ‘Coco Mademoiselle’.
Fig. S4. 
**GC/MS analysis of perfume mixtures.** Chromatograms of the perfumes: ‘*Angel*’ by Thierry Mugler (EdP) (‘Ang’); ‘*River of Love*’ (RoL) by La Rive (EdP) (‘AC#3’ in the main text); ‘*Wish*’ by Chopard (EdP) (‘AC#4’); and ‘*Diable Bleu*’ by Creation Lamis (EdP) (‘AC#5’). Samples are collected from the headspace of 20ml scintillation vials that contain ~1mL of perfume, by sampling into homemade cartridges. For ease of comparison, we normalize the signals of each spectra to the maximum signal value of (+)-limonene (peak 4) of the first spectrum of ‘*Angel*’.
**Fig. S5.**

**GC/MS analysis of perfume mixtures.** Chromatograms of the perfumes: ‘*La vie est belle*’ by Lancôme (EdP) (‘LVeB’), and ‘*Queen of Life*’ (QoL) by La Rive (EdP) (‘AC#6’). Samples are collected from the headspace of 20ml scintillation vials that contain ~1mL of perfume, by sampling into homemade cartridges. For ease of comparison, we normalize the signals of each spectra to the maximum signal value of (+)-limonene (peak 4) of the spectrum of ‘*La vie est belle*’.
Fig. S6.
Lab environmental conditions during measurements of plant emissions. Relative humidity measurements (%) of the laboratory’s environment (A), and temperature measurements within and outside (i.e., laboratory temperature) the chamber that encloses the...
**Fig. S7.**

**GC/MS analysis of plant emissions.** Chromatogram of sample collected before wounding. The labeled monoterpene compounds correspond to: 1 (-)-α-pinene; 2 (+)-α-pinene; 3 (-)-camphene; 4 (+)-camphene; 5 (-)-β-pinene; 6 (-)-limonene; 7 (+)-limonene.
Fig. S8.
Time dependent behavior of the concentration of the dominant monoterpane VOCs in the plant emissions, pre- and post-wounding, obtained through an offline GC/MS analysis. A. (±)-α-pinene and (±)-limonene. B. (±)-camphene and (-)-β-pinene. C. Time dependent behavior of the overall concentration of the emissions as estimated from the measurements in A and B. D. Normalized chiroptical signal (effective specific optical rotation) as predicted from the individual GC/MS concentration measurements.
Fig. S9. CCP-based refractometric measurement of plant emissions pre- and post-wounding. CCP-based refractometric raw-data of the (online) samples showing the changes in the overall concentration of all emitted compounds. The difference in dynamics between the dominant chiral compounds is also discernable from the refractometric data in accord with our (offline) GC/MS analysis (Fig.S8).
Fig. S10.
Photo of the damaged branch of Pinus heldreichii. The resin that hardens to seal the wound site is clearly visible.