# **Electronic Supplementary Information for:**

# Elucidating nuclear motions in a plant sunscreen during photoisomerization, through solvent viscosity effects

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A. Steady-state difference absorption spectra



**Fig. S1** Transient absorption spectrum of sinapoyl malate in ethylene glycol (green) at a pump-probe timedelay,  $\Delta t = 2$  ns. Overlaid is the  $\Delta UV/vis$  spectrum (black).



**Fig. S2** Transient absorption spectrum of sinapoyl malate in glycerol (orange) at a pump-probe time-delay,  $\Delta t = 2$  ns. Overlaid is the  $\Delta UV/vis$  spectrum (black). Clearly evident is the persistent excited state signal in the 2 ns transient absorption spectrum due to the significant increase in the photoisomerization time-constant.

## **B.** Sequential Fitting Residuals



**Fig. S3** Residuals between the fits returned by the sequential global fitter and the raw data, for sinapoyl malate in a) ethanol, b) ethylene glycol and c) glycerol.

#### **C.** Power Dependence Measurements



Fig. S4 Power dependence of signal intensity at 365 nm for sinapoyl malate in ethanol following photoexcitation at 332 nm at a pump-probe time-delay,  $\Delta t = 2$  ns.

Equivalent power dependency measurements were attempted in sinapoyl malate in ethylene glycol and sinapoyl malate in glycerol. However, for sinapoyl malate in ethylene glycol, no discernible photoproduct above the signal-to-noise could be measured, precluding any power dependence measurements. For sinapoyl malate in glycerol, the extended lifetime of the  $1^{1}\pi\pi^{*}$  state once again prohibited the observation of any photoproduct and thus power dependency measurements at  $\Delta t = 2$  ns.

## D. <sup>1</sup>H NMR



Fig. S5 <sup>1</sup>H NMR spectrum of *trans*-sinapoyl malate in ethanol-*d*<sub>6</sub>, pre-irradiation with assigned peaks.



**Fig. S6** <sup>1</sup>H NMR spectrum of *trans*-sinapoyl malate in ethanol- $d_6$ , post-irradiation, with assigned peaks. Additional peaks are present that are attributed to the *cis*-sinapoyl malate.

#### E. Methyl Sinapate

Additional femtosecond transient electronic (UV/visible) absorption spectroscopy was carried out on methyl sinapate in ethanol, ethylene glycol and glycerol; at 1 mM. These measurements were taken using the same experimental setup as for sinapoyl malate, however, the excitation wavelengths were 329 nm in ethanol, 330 nm in ethylene glycol and 328 nm in glycerol to reflect the changes in absorption band maxima of methyl sinapate in these solvents. The dynamical information in the transient absorption spectra was recovered using the same sequential fitting technique applied to sinapoyl malate. The resulting time-constants and solvent viscosity dependence are shown in Table S1. For the interest of the reader we note that the values of  $\tau_3$  for methyl sinapate are half of the values (within error) of  $\tau_3$  for sinapoyl malate. This is likely due reduced bulk of the methyl tail compared to the malate tail, which directly impacts the rotation about the carbon 3 and 4 C=C bond.

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	$\tau_1$	$\tau_2$	$\tau_3$	$\tau_4$
Ethanol	$330 \pm 40 \text{ fs}$	$3.6 \pm 0.3 \text{ ps}$	$27 \pm 1 \text{ ps}$	>> 2 ns
Ethylene Glycol	$300 \pm 40 \text{ fs}$	$4.8\pm0.3\ ps$	$90 \pm 3 \text{ ps}$	>> 2 ns
Glycerol	$240 \pm 45 \text{ fs}$	$6.4 \pm 0.3 \text{ ps}$	$280 \pm 20 \text{ ps}$	>> 2 ns

**Table S1**: The time-constants along with the viscosity dependence.



**Fig. S7** Plot of the viscosity dependence for each of the rate-constant, with their corresponding linear fits:  $k_1$  (purple),  $k_2$  (green) and  $k_3$  (orange).



Fig. S8 Transient absorption spectra of methyl sinapate in a) ethanol, b) ethylene glycol and c) glycerol.



**Fig. S9** Resulting evolution associate difference spectra from the sequential global fit of methyl sinapate in a) ethanol, b) ethylene glycol and c) glycerol.



**Fig. S10** Residuals between the fits returned by the sequential global fitter and the raw data, for methyl sinapate in a) ethanol, b) ethylene glycol and c) glycerol.