

Supporting Information

Surface photochemistry of the herbicide napropamide. The role of the media and environmental factors in directing the fates of intermediates.

José P. Da Silva; Edgar V. Bastos; Luis F.V. Ferreira; Richard G. Weiss

Experimental details:

Diffuse reflectance absorption spectra. Absorption spectra on silica were recorded using a Cintra 40 GCB Scientific Equipment spectrophotometer with a diffuse reflectance attachment. The measured reflectance, R , was used to calculate the remission function $F(R)$ using the Kubelka-Munk equation (eq. 1) (15) where $K=2\epsilon C$ and S are the absorption and scattering coefficients, respectively, and ϵ is the Napierian absorption coefficient and C is the concentration of absorbing species.

$$F(R) = \frac{(1-R)^2}{2R} = \frac{K}{S} \quad (1)$$

This equation applies to optically thick samples and an ideal diffuser, where the radiation has the same intensity in all directions. Since the support usually absorbs at the excitation wavelength, $F(R)_{probe} = F(R) - F(R)_{support} = \Sigma_i 2\epsilon_i C_i / S$, where $F(R)_{support}$ is obtained with a cell containing only the powdered solid support. This equation predicts a linear relationship for the remission function of the probe as function of the concentration when the only form present is the monomer (for a constant scattering coefficient).

HPLC. The samples were analyzed by HPLC using a Merck-Hitachi 655A-11 liquid chromatograph equipped with 655A-22 UV (detection at 220 nm or 300 nm) and Shimadzu SPD-M6A photodiode array detectors. A Merck LiChroCART 125-4 (12.5

cm length, 4 mm internal diameter, RP-18, 5 μm) column and a gradient elution of water, methanol and acetonitrile was employed.

GC-MS. The GC-MS analyses, using Chrompack CP-WAX 58CB (25 m length, 0.25 mm I.D. and 0.25 μm film thickness) and J&W Scientific DB-35MS (30 m length, 0.25 mm I.D. and 0.25 μm film thickness) capillary columns, were performed on a Agilent Technologies 6890N gas chromatograph with a 5973 inert mass selective detector (E.I. 70 eV). The initial temperature, 70 $^{\circ}\text{C}$, was maintained during 5 min and then a heating rate of 5 $^{\circ}\text{C}/\text{min}$ was used until a final temperature of 250 $^{\circ}\text{C}$ was reached.

Diffuse-reflectance laser flash photolysis (DRLFP) and laser-induced luminescence (LIL). Schematic diagrams of the DRLFP and LIL systems are presented in reference (15). Laser flash photolysis experiments were carried out with the third harmonic of a Nd:YAG laser (266 nm, *ca.* 6 ns FWHM, \sim 10-30 mJ/pulse) from B. M. Industries (Thomson-CSF, model Saga 12-10), in the diffuse reflectance mode. The excitation source for the LIL experiments was an N_2 laser (337 nm; PTI model 2000, *ca.* 600 ps FWHM, \sim 1.0 mJ/ pulse). Emission from the solid samples was collected by a collimating beam probe coupled to an optical fiber (fused silica) and detected by a gated intensified charge coupled device (and/or ICCD detector, based on the Hamamatsu S5769-0907). The ICCD was coupled to a fixed imaging compact spectrograph (Oriel, model FICS 77440). The system can be used either by capturing all light emitted by the sample or in a time-resolved mode by using a delay box (Stanford Research Systems, model D6535). Time-resolved absorption and emission spectra are available in the nanosecond to second time range, between 200 and 900 nm. The data are reported as percent of transient absorbance changes, $\Delta\% = 100\Delta J_t/J_o = (1 - J_t/J_o)100$ (where J_o and J_t are diffuse reflected light intensities at a specific wavelength before and at time t after excitation, respectively).

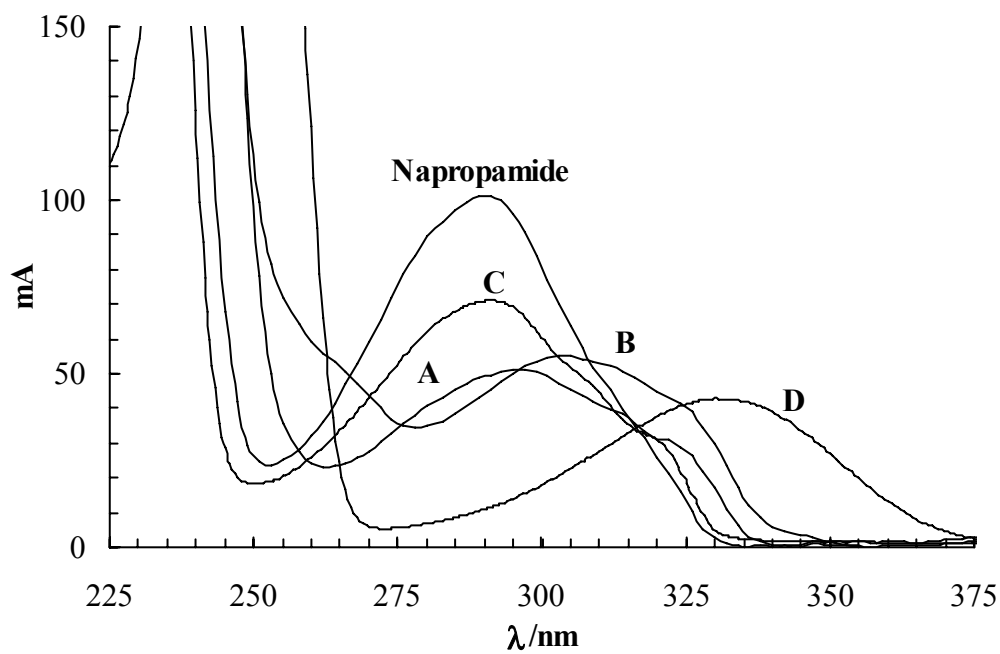


Figure S-1: UV-vis absorption spectra (relative absorbances) of napropamide, its photo-Claisen products (**A** and **B**), naphthol (**C**) and 1,4-naphthoquinone (**D**), shown in Figure 5 of the main text.

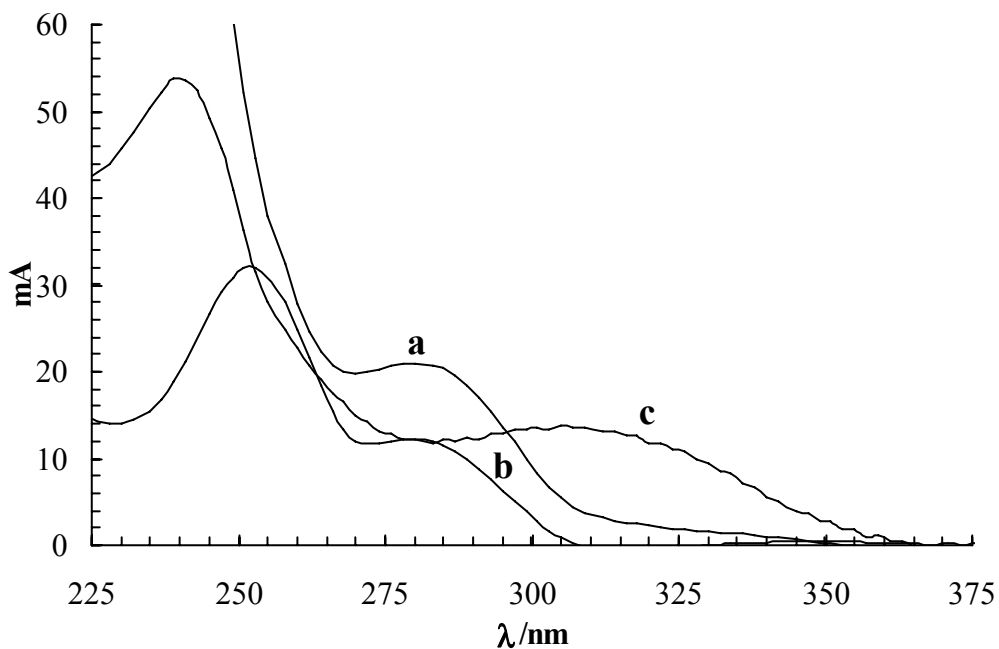


Figure S-2: UV-vis absorption spectra (relative absorbances) of some minor unidentified photoproducts (**a**, **b** and **c**) shown in Figure 5 of the main text.