Supplementary material

1. Time courses for the photodegradation of the herbicides

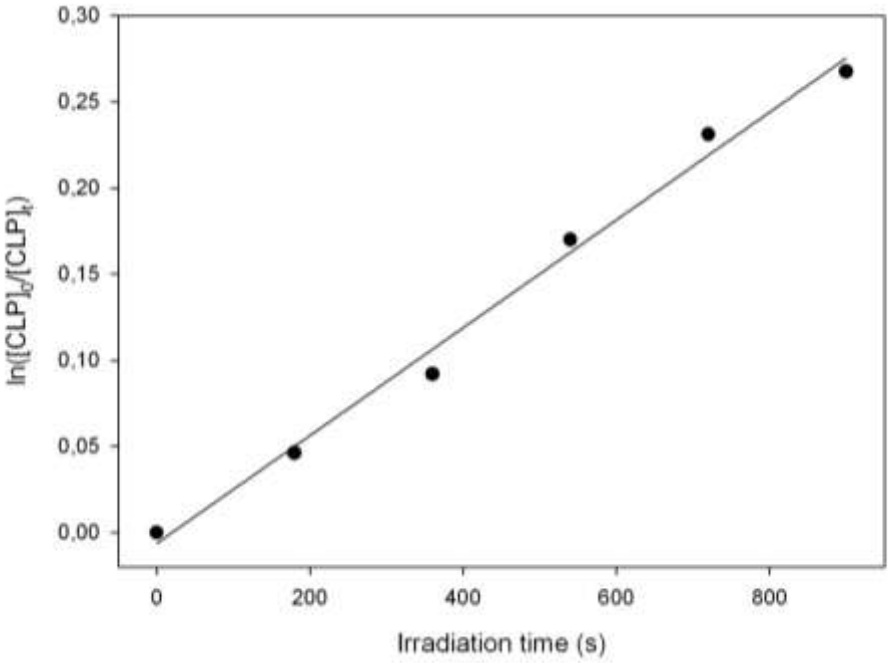

Fig.1SM. Photodegradation of chlorpropham

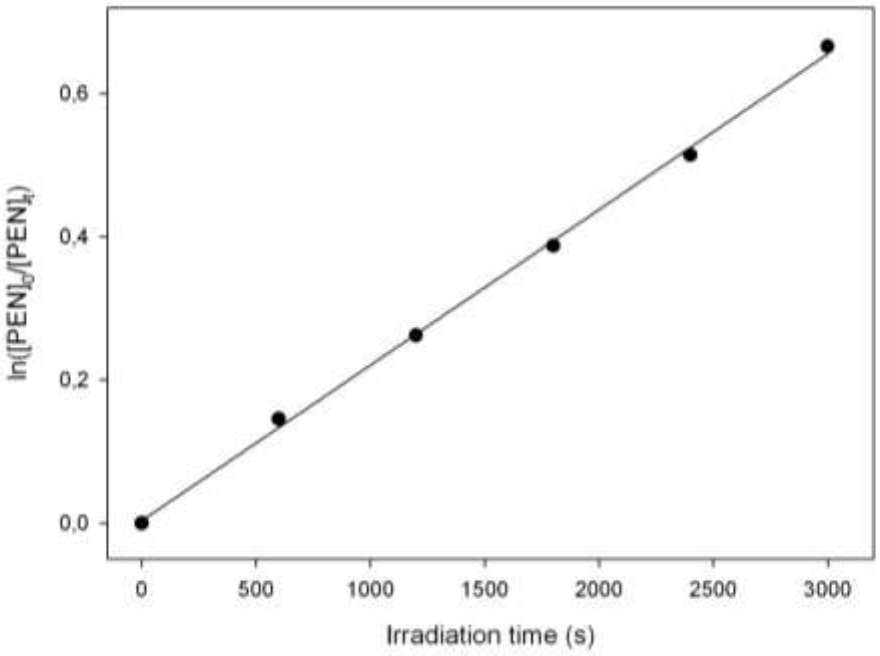

Fig.2SM. Photodegradation of phenisopham

2. Isolation and identification of photoproducts

Procedures for isolation and characterization of phototransformation products from chlorpropham (**1a**)

A 1 x 10^{-3} M solution of chlorpropham (30 mg) in 140 mL of H_2O/CH_3CN (9:1 v/v) was irradiated with UV-B lamps for 1 h. Then, the solvents were evaporated under vacuum and the residue was separated by preparative TLC. Elution with CH_2Cl_2/AcOEt (9:1 v/v) gave **1a** (5 mg) and photoproduct **2a** (22 mg) at decreasing Rfs. Compound **2a** was identified by spectroscopic data.[23]

Isopropyl 3-hydroxyphenylcarbamate (**2a**): UV λ_{max} (H_2O/CH_3CN 9:1 v/v) nm 235 (log ε 3.7), 280 nm (log ε 3.1); EI-MS *m/z* 195, 153, 136, 109; IR ν_{max} ($CHCl_3$) 3576, 3425, 1719, 1519, 1214 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.33 (1H, br s), 7.13, (1H, t, J=8.1 Hz), 6.65 (1H, d, J=8.1 Hz), 6.63 (1H, s), 6.56 (1H, d, J=8.0 Hz), 6.38 (1H, br s), 5.01 (1H, sept, J=6.5 Hz), 1.30 (6H, d, J=6.5 Hz); ^{13}C NMR ($CDCl_3$) δ 157.1, 153.7, 139.2, 130.2, 110.8, 110.6, 106.0, 69.4, 22.3.

Procedures for isolation and characterization of phototransformation products from phenisopham(**1b**)

A 1 x 10^{-3} M solution of phenisopham (50 mg) in 146 mL of H_2O/CH_3CN (7:3 v/v) was irradiated in open quartz tubes with UV-B lamps for 2 h. Then, the solvents were evaporated under vacuum and the residue was separated by preparative TLC. Elution with CH_2Cl_2/AcOEt (9:1 v/v) gave phenisopham **1b** (15 mg), photoproducts **5b** (2 mg), **2b** (<1 mg),**6b** (4 mg) and **4b** (25 mg) at decreasing Rfs. Product **2b** (=**2a**) was identified as above. Products **4b**-**6b** were spectroscopically characterized.

Isopropyl 2-(ethyl(phenyl)carbamoyl)-3-hydroxyphenylcarbamate (**4b**):UVλ_{max} (H_2O/CH_3CN 9:1 v/v) nm 230 (log ε 3.0), 270 nm (log ε 2.4); EI-MS *m/z* 342, 180, 162, 121, 106; IRν_{max} ($CHCl_3$) 3561, 3411, 1731, 1685, 1635, 1627, 1210 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.19-7.17 (4H, m), 7.07 (1H, t, J=8.0 Hz), 7.01 (2H, d, J=9.0 Hz), 6.90 (1H, brs), 6.81 (1H, brs), 6.50 (1H, d, J=8.0 Hz), 4.96 (1H, sept, J=6.5 Hz), 4.10 (1H, m), 3.86 (1H, m), 1.31 (6H, m), 1.20 (3H, t, J=7.1 Hz). ^{13}C NMR ($CDCl_3$) δ 171.0, 154.8, 154.7, 152.6, 141.1, 135.5, 131.5, 128.6, 127.3, 126.6, 112.3, 111.4, 68.9, 45.2, 22.1, 14.15.

Isopropyl 4-(ethyl(phenyl)carbamoyl)-3-hydroxyphenylcarbamate (**5b**)*:*UVλ_{max} (H_2O/CH_3CN 9:1 v/v) 232 nm (log ε 1.9), 273 nm (log ε 2.4); EI-MS *m/z* 342, 222, 180, 148, 121; IR ν_{max} ($CHCl_3$) 3628, 3424, 1730, 1630, 1626, 1209 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 11.57 (1H, s), 7.33 (2H, t, J=9.0 Hz), 7.27 (1H, m), 7.10 (2H, d, J=9.0 Hz), 6.86 (1H, d, J=2.0 Hz), 6.54 (1H, d, J=9.0 Hz), 6.43-6.35 (2H, brs), 4.96 (1H, sept, J=6.5 Hz), 3.93 (2H, q, J=7.0 Hz), 1.25 (6H, d, J=6.5 Hz), 1.21 (3H, t, J=7.0 Hz); ^{13}C NMR ($CDCl_3$) δ 170.7, 162.5, 152.9, 152.7, 152.4, 141.9, 131.5, 129.6, 127.5, 127.2, 107.5, 106.1, 69.0, 46.5, 21.9, 12.5.

Isopropyl 2-(ethyl(phenyl)carbamoyl)-5-hydroxyphenylcarbamate (**6b**)*:*UVλ_{max} (H_2O/CH_3CN 9:1 v/v) nm 233 (log ε 3.3), 278 nm (log ε 2.7); EI-MS *m/z* 342, 180, 162, 121, 106; IR ν_{max} ($CHCl_3$) 3583, 3300, 1722, 1648, 1627, 1214 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 9.29 (1H, s), 7.78 (1H, d, J=1.5Hz), 7.26-7.22 (2H, m), 7.16 (1H, t, J=8.0 Hz), 6.99 (2H, d, J=8.0 Hz), 6.74 (1H, d, J=8.0 Hz), 6.09 (1H, dd, J=8.0, 1.5Hz), 6.01 (1H, br s), 4.99 (1H, sept, J=6.5 Hz), 3.98 (2H, q, J=7.0 Hz), 1.31 (6H, d, J=6.5 Hz), 1.24 (3H, t, J=7.0 Hz). ^{13}C NMR ($CDCl_3$) δ 170.4, 158.4, 156.9, 153.7, 143.9, 140.9, 132.4, 129.7, 127.6, 126.9, 108.9, 106.4, 69.4, 46.0, 22.5, 13.4.

3. HPLC chromatograms

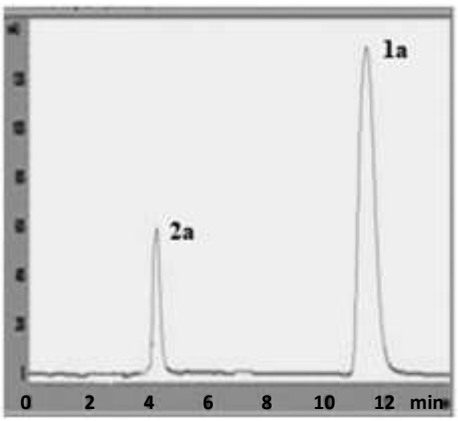

Fig.3SM HPLC profile of the irradiation mixture of chlorpropham (**1a**) in H_2O/CH_3CN (9 : 1 v/v, 5 x 10^{-5} M) after 15 min of UV-B irradiation.

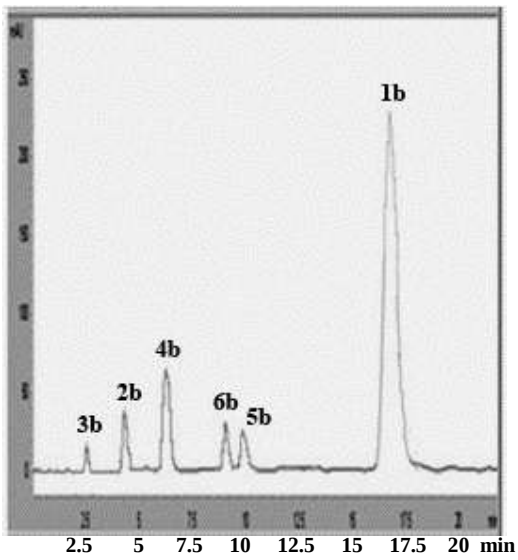

Fig.4SM HPLC profile of the irradiation mixture of phenisopham (**1b**) in H_2O/CH_3CN (9:1 v/v, 5 x 10^{-5} M) after 30 min of UV-B irradiation.