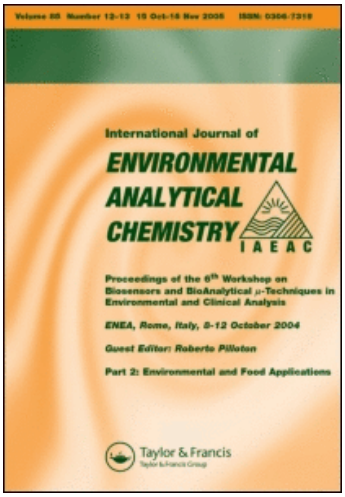

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Photodegradation of bensulphuron methyl in aqueous solution

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Photodegradation of bensulphuron methyl, (methyl α-(4,6-dimethoxypyrimidin-2-carbamoyl-sulphamoyl)-*o*-toluate ester) was carried out in aqueous solution under UV light. The rate of photolysis followed first-order kinetics, with a half-life of 31.7 min at $\lambda = 254$ nm and 41.3 h at $\lambda \geq 290$ nm, with significant correlation coefficients (0.9898 and 0.9625, respectively). The main photoproducts in distilled water were identified with a diode array detector and mass spectrometry. The results indicate that different reaction pathways are followed: cleavage of the sulphonylurea bridge, desulphonylation, which can proceed either by a carbon–sulphur cleavage or a nitrogen–sulphur cleavage and contraction of the sulphonylurea bridge. A mechanism which accounts for the formation of the photoproducts is proposed

Keywords: Sulphonylurea herbicides; Bensulphuron methyl; Photolysis; Degradation products

1. Introduction

One of the most important aspects in our understanding of the fate of pesticides in the environment is knowledge of their degradation mechanism. Such processes may lead to the formation of new chemicals with reduced toxicity or, in some cases, increased toxicity, to aquatic biota.

Sulphonylurea herbicides are used extensively by cereal farmers to control broad-leaved weeds and some grasses. Some of the reasons for the rapid and good acceptance of sulphonylureas include low application rates (2–100 g ha^{-1}), good crop selectivity, and favourable environmental and toxicological properties. Bensulphuron methyl, methyl α-(4,6-dimethoxypyrimidin-2-ylcarbamoylsulphamoyl)-*o*-toluate ester is a selective systemic sulphonylurea herbicide, absorbed by foliage and roots, with rapid translocation to the meristematic tissues. It acts by inhibiting synthesis of the essential amino acids valine and isoleucine, hence stopping cell division and plant growth. This herbicide is a broad-spectrum product for pre-emergence or early post-emergence control

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of most broad-leaved grasses and sedges in transplanted or direct-seeded paddy rice. Despite these advantages, its use in agriculture is constrained by its rapid decomposition [1]. It undergoes degradation even on storage at ambient temperature and chemical hydrolysis, is strongly depending on the pH [2]. Bensulphuron methyl is rapidly detoxified in rice by hydroxylation of one of the two methoxy groups substuted in the in the pyrimidine heterocycle [3]. The persistence in rice paddy water has been examined [4–6].

Photolysis is considered as only a minor degradation process for pesticides. Nevertheless, for this class of herbicides, several reports indicate that photodegradation is an alternative pathway to chemical hydrolysis [7]. The photodegradation of several sulphonylureas by sunlight and UV has been studied on soil, in water, and in organic solvents [8–14]. Generally, photodegradation follows first-order kinetics, with the process being much faster upon UV irradiation than upon sunlight irradiation. The main processes taking place in photodegradation are cleavage of the sulphonylurea bridge, scission of the SO_2-NH bond, and de-esterification and contraction of the sulphonylurea bridge. Recent studies have reported the influence of pH and irradiation wavelength on photodegradation of sulphonylureas [15, 16]. Photolysis of bensulphuron methyl on soil surfaces under UV light and sunlight has been investigated [17, 18].

As part of a research project looking at the environmental fate of sulphonylurea herbicides [14, 19–21], the present study evaluates the rate of photodegradation of bensulphuron methyl in distilled water under UV light ($\lambda = 254$ nm) and under simulated sunlight conditions ($\lambda \geq 290$ nm).

Chemical hydrolysis is often considered to be secondary at pH and temperature values typical of the aquatic environment (5.5–8.0 and 10–15°C, respectively) [2], but its occurrence must not be completely neglected. The aim of the study is to characterize the final photoproducts of bensulphuron methyl and to verify if the degradation pathway also involves photo-assisted hydrolysis.

2. Experimental

2.1 *Reagents*

Bensulphuron methyl (BSM) was supplied by Riedel de Haën; its limit of solubility in water was 120 mg Lat^{-1} pH 7 and 25°C. 2-Amino-4,6-dimethoxypyrimidine was purchased from Sigma-Aldrich (Milan); methyl 2-[(aminosulphonyl)methyl]benzoate was purchased from ChemPacific (Baltimore, MD); 2-ureido-4,6-dimetoxypyrimidine was synthesized in our laboratory and had a purity of 98%. Water, a super-purity solvent of pesticide grade, and the other solvents of pure analytical high-performance liquid chromatography (HPLC) grade used were from Carlo Erba (Milan).

2.2 *Analytical procedure*

A reverse-phase HPLC equipped with UV detection has been used to monitor the disappearance of bensulphuron methyl and the formation of its photoproducts in aqueous solution samples. The irradiated and dark control samples were analysed by a Waters HPLC system (Model 600 pump, 486 UV detector operating at 238 nm; Milford, MA) and a computing integrator chromatography workstation (Model PU 4810; Philips, USA), equipped with a Luna C-8 reverse-phase column

(250 × 4.6 mm, particle size 5 μm) from Phenomenex (Torrance, CA). A Security Guard column (Phenomenex) was used as a pre-column.

For kinetic studies, the mobile phase was a 60 : 40 mixture of acetonitrile: 0.1% aqueous acetic acid (pH 3.5). The flow rate was 1.0 mL min^{-1}. Under these conditions, the retention time of bensulphuron methyl was 6.30 min. Calibration curves for bensulphuron methyl ($r^2 > 0.9999$) were obtained, injecting 20 μL samples of solutions at a concentration within the range 0.025–2.500 μg mL^{-1}. The detection limit (LOD) (estimated to be three times the background noise) and the limit of quantitation (LOQ) (estimated to be 10 times the background noise) were 0.036 μg mL^{-1} and 0.12 μg mL^{-1}, respectively. No significant difference in background noise was observed between the analyses of the standards in acetonitrile and those of the matrices analysed. Therefore, LOQ limits for the analyses on matrices can be assumed to be the same as those observed for standards.

To monitor the formation of photoproducts, a mobile gradient was used. The mobile-phase gradient consisted of acetic acid 0.1% by volume in water (solvent A), and acetonitrile (solvent B) was used. The gradient used was 60% (A) at $t = 0$–40% (A) at $t = 9$ min, and 40% (A) during 5 min. The flow rate was 1.0 mL min^{-1}. Table 1 lists the typical HPLC retention times, under these conditions, for bensulphuron methyl and its products of photodegradation.

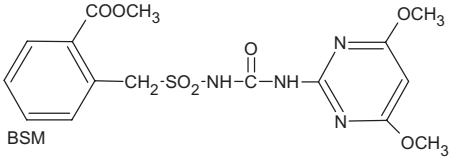
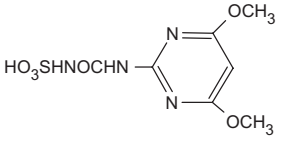
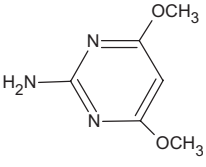
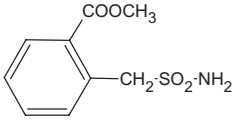
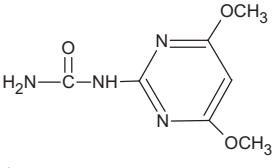
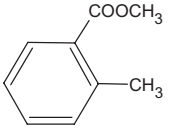
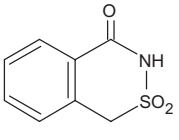
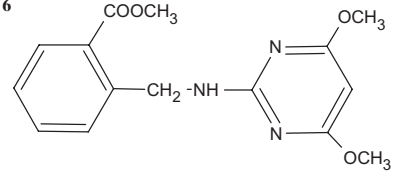
2.3 *Photoproduct identification*

For the identification of the main photoproducts, a more concentrated solution (50 mg L^{-1}) was irradiated at λ 254 nm up to twice the half-life $t_{1/2}$ and analysed by HPLC/diode array detector (DAD) (Waters 996 Photodiode Array Detector, Milford, MA) and by HPLC/mass spectrometry (MS) (LCQ FINNIGAN, Finnigan Corporation, San Jose, CA). MS detection was performed with electrospray ionization (ESI), in positive mode. The operating conditions for ESI were nebulizer gas (N_2); drying gas (N_2) flow 1.0 L min^{-1}; capillary voltage 3500 V and gas temperature 300°C. The structures of bensulphuron methyl and main photoproducts, the chromatographic, and the UV and mass spectrometric data used for their identification are listed in table 1.

2.4 *Photolysis studies*

A stock solution of pure standard in acetonitrile (400 mg L^{-1}) was prepared. This solution was mantained in the dark at 4°C and used to prepare a working solution (11 mg L^{-1}). The working solution was divided into two parts. One of these portions was used for the irradiation experiment, the other as a control, kept in the dark. To avoid microbial degradation, all glass apparatus was heat-sterilized by autoclaving for 60 min (Tecnoclav 50, Fedegon, Pavia, Italy) at 121°C before use, and the aqueous solution was sterilized by filtration (Millex GS/AP 0.22 μm, Millipore, Bedford, MA). Aseptic techniques were adopted throughout the study to maintain sterility. The photodegradation of the samples was carried out in quartz cylindrical tubes (20 mm × 40 mm; ~12.6 mL) using a low-pressure mercury lamp emitting at 254 nm (20W) (Helios, Italquarz, Milan) and a water-cooled filter. For irradiation at $\lambda \geq 290$ nm, a fluorescent lamp (Philips, Eindhoven, Netherlands) that simulated the UV output of sunlight and 5 mL capped borosilicate tubes were used. The lamps

Table 1. Retention times, UV data and mass spectra of the main photoproducts of bensulfuron methyl.

Compounds	T_r (min)	UV data (nm)	Mass (m/z)
 BSM	10.97	238	411 $(M+H)^+$
 **1**	3.02	274, 232	278 $(M+H)^+$
 **2**	3.97	260, 227	156 $(M+H)^+$
 **3**	4.11	231	230 $(M+H)^+$
 **4**	5.94	260, 225	199 $(M+H)^+$
 **5**	6.66	280, 230	151 $(M+H)^+$
 **6**	7.81	247	198 $(M+H)^+$
 **7**	9.97	234	304 $(M+H)^+$

did not emit light at wavelengths below 290 nm [22]. The temperature was controlled at $28 \pm 3^{\circ}C$. For both conditions of irradiation, the photon flux received by the solutions, using ferrioxalate actinometry, was found to be 6.7×10^{15} photons/cm^2 s^{-1} and 2.5×10^{16} photons/cm^2 s^{-1}, respectively. At various time intervals, samples were withdrawn in triplicate and analysed by HPLC.

Control samples were analysed by HPLC at the same intervals as the irradiated samples to monitor hydrolytic disappearance or to confirm that the degradation process was only the result of photochemical reactions. The observed rate constants, k, were calculated by regression analysis of recovered bensulphuron methyl concentration vs. time. The half-life was calculated using the equation $t_{1/2} = \ln 2/k$.

3. Results and discussion

3.1 *Spectrometric results*

The UV spectrum of bensulphuron methyl in CH_3CN/H_2O 1 : 20 (v/v) shows an adsorption maximum below 290 nm (234 nm) but also a measurable absorption tail at $\lambda \geq 290$ nm. According to an EC directive (94/37/CE), phototransformation must be taken into account if the molar extinction coefficients > 10 L mol cm^{-1} for $\lambda \geq 290$ nm, for bensulphuron methyl $\varepsilon = 683$ L mol cm^{-1} at $\lambda = 290$ nm, meaning that the photolitic degradation pathway should not be neglected.

3.2 *Kinetics studies*

The photolysis of bensulphuron methyl at various illumination times and at different wavelengths ($\lambda = 254$ nm and $\lambda \geq 290$ nm) followed pseudo-first-order kinetics with a high r^2 value, thus indicating that the half-life was independent of initial herbicide concentration. Bensulphuron methyl disappeared from the aqueous solution (after irradiation at 254 nm) under laboratory conditions with an estimated $t_{1/2}$ of 31.7 min; the estimated $t_{1/2}$ of bensulphuron methyl after irradiation at $\lambda \geq 290$ nm was 41.3 h (table 2). The transformation of bensulphuron methyl in aqueous solutions irradiated at $\lambda \geq 290$ nm was significantly slower than at 254 nm. This is mainly due to the weaker absorption of bensulphuron methyl at the longer wavelength range. The observed rate constants (2.2×10^{-2} min^{-1} at $\lambda = 254$ nm and 2.8×10^{-4} min^{-1} at $\lambda \geq 290$ nm) correspond to the sum of the photolysis and hydrolysis ($k_h \approx 1 \times 10^{-5}$ min^{-1} at pH 6.0) rate constants [2], but the latter can be discounted.

Control samples show that bensulphuron methyl persists in distilled water. So, we can confirm that the degradation process could be attributed to photolysis only.

Table 2. Photolysis kinetic parameters of bensulfuron methyl.

Bensulfuron methyl	λ	K_{obs}	$t_{1/2}$[a]	r^2
Distilled water	254	0.0219 min^{-1}	31.7 min	0.9898
Distilled water	≥290	0.0168 h^{-1}	41.3 h	0.9625

[a]The varibility of the triplicate samples was no more than 5%.

3.3 *Photoproduct identification*

Bensulphuron methyl, when photoirradiated at $\lambda = 254$ nm and $\lambda \geq 290$ nm, gave the same photoproducts. For their identification, a more concentrated solution (50 mg L^{-1}) was irradiated at λ 254 nm up to three times the half-life $t_{1/2}$ and analysed by HPLC-DAD analysis (figure 1). The retention times are listed in table 1. Photoproducts with t_r 3.97 (2) and t_r 4.11 (3), identified by comparison of their chromatographic features with those of analytical standards 2-amino-4,6-dimethoxypyrimidine and methyl 2-[(aminosulphonyl)methyl]benzoate, are representative of the

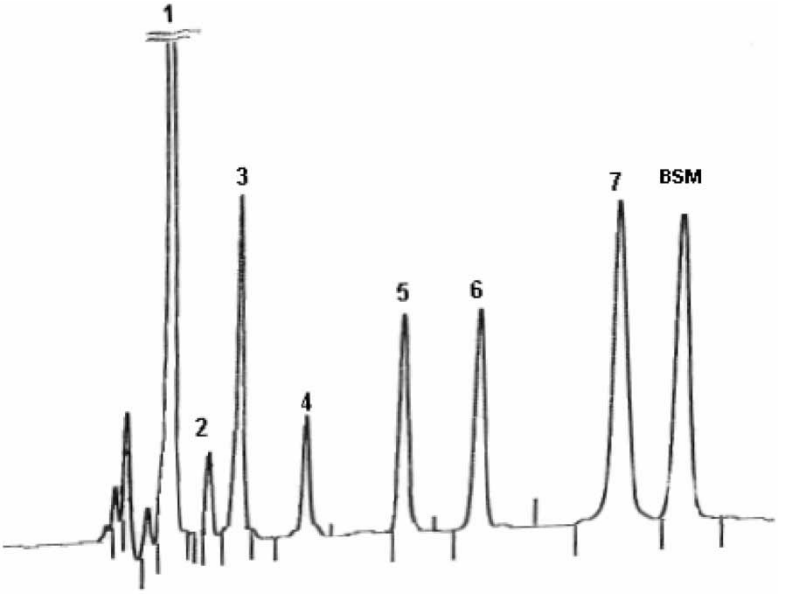


Figure 1. HPLC chromatogram of irradiated solution of bensulfuron methyl at $\lambda = 254$ nm after three times the half-life.

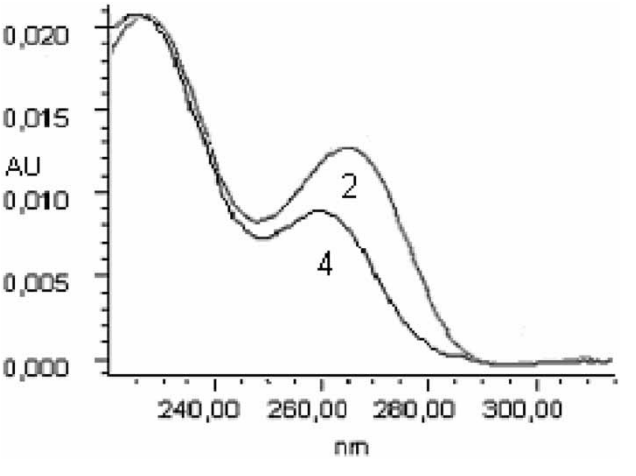


Figure 2. DAD analysis of 2-amino-4,6-dimethoxypyrimidine (2) and of the photoproduct with t_r 5.94 (4).

two chromophoric groups present on this sulphonylurea (a pyrimidine group and a benzenic group, respectively). Therefore, the presence of the pyrimidine group was easily recognizable in the photoproduct with t_r 5.94 (4) (figure 2), whereas the presence of the benzenic group was recognizable in the photoproduct with t_r 6.66 (5) (figure 3). Photoproduct with t_r 9.97 (7) showed the same spectral feature of the parent compound (figure 4). As can be seen in figure 5, the degradation product with t_r 7.81 (6) shows a spectral feature different from both that of the two chromophoric groups and that of the bensulphuron methyl. All photodegradation products were analysed via

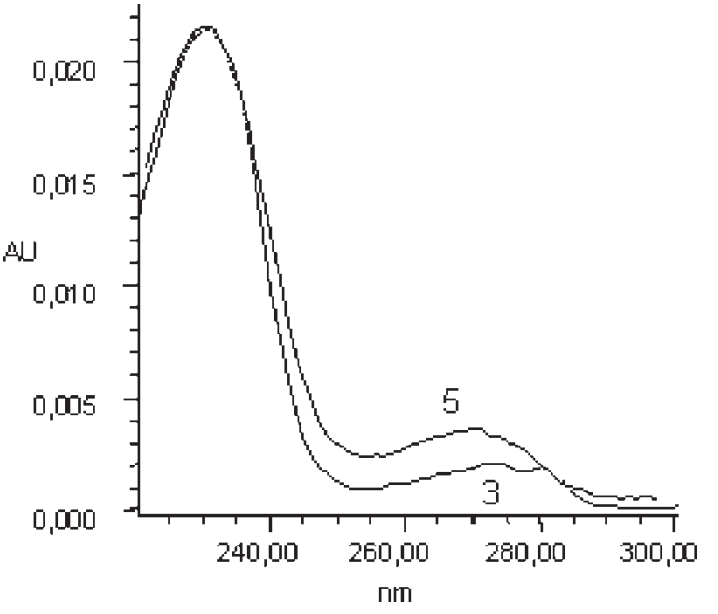


Figure 3. DAD analysis of methyl 2-[(aminosulfonyl)methyl] benzoate (3) and of the photoproduct with t_r 6.66 (5).

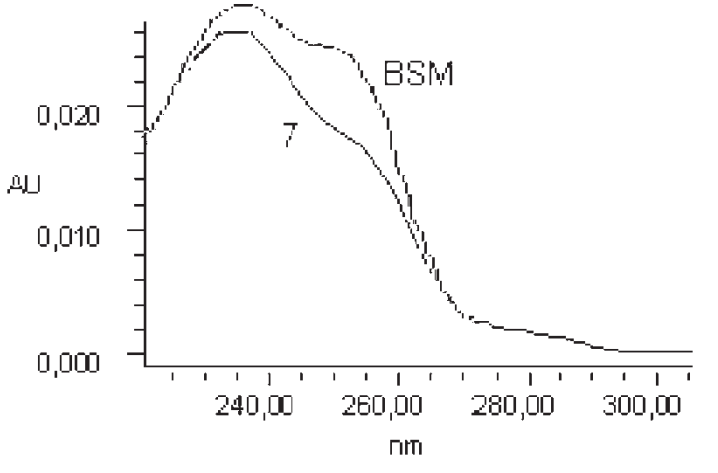


Figure 4. DAD analysis of BSM and of the photoproduct with t_r 9.97 (7).

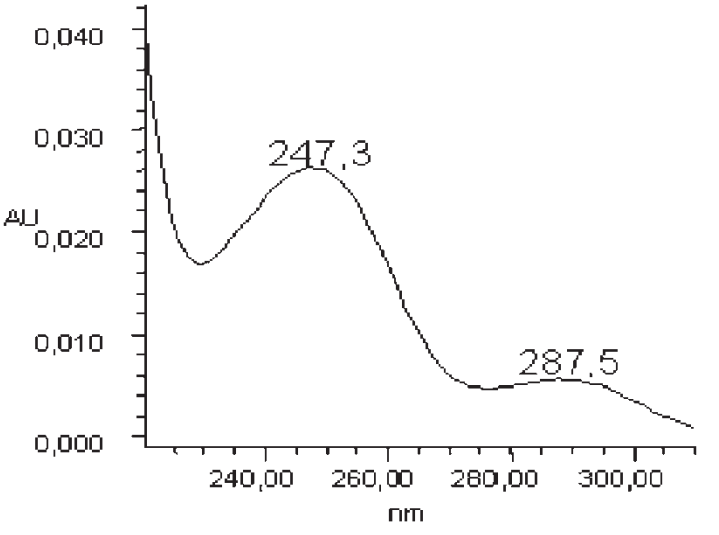


Figure 5. DAD analysis of photoproduct with t_r 7.81 (6).

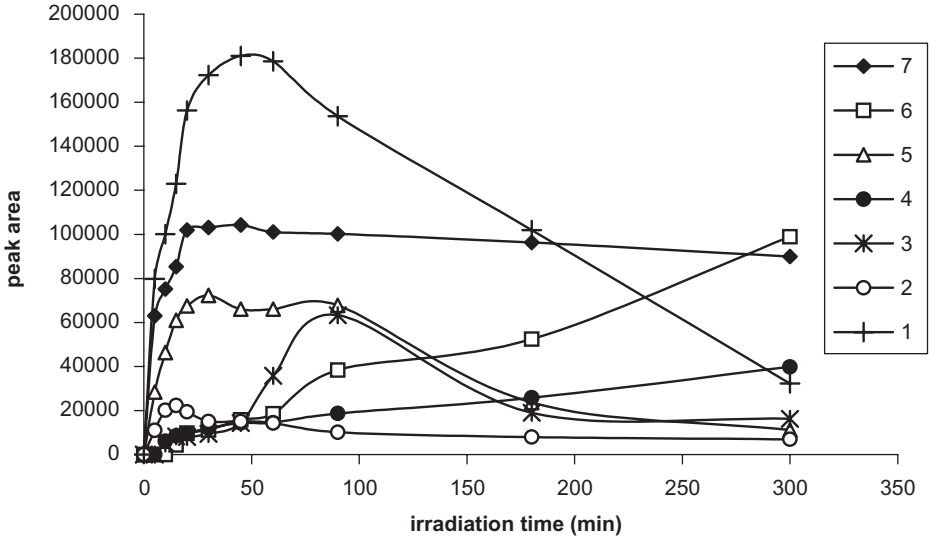


Figure 6. Evolution of the main photoproducts during bensulphuron methyl irradiation at $\lambda = 254$ nm.

HPLC/MS and identified on the basis of pseudomolecular ions $(M + H)^+$. Figure 6 shows the kinetics curves of the main photoproducts in the reaction mixture. Standards were not all available, so data are expressed as peak areas from the UV detector on the HPLC. Degradation products are likely to have different UV absorption characteristics and thus different response factors. Peak areas that we have reported, based on this technique, are likely to be very different from those based on actual mass-balance measurements with standards. However, the technique we used is useful in that it does allow an assessment of the formation and decline of individual degradation products.

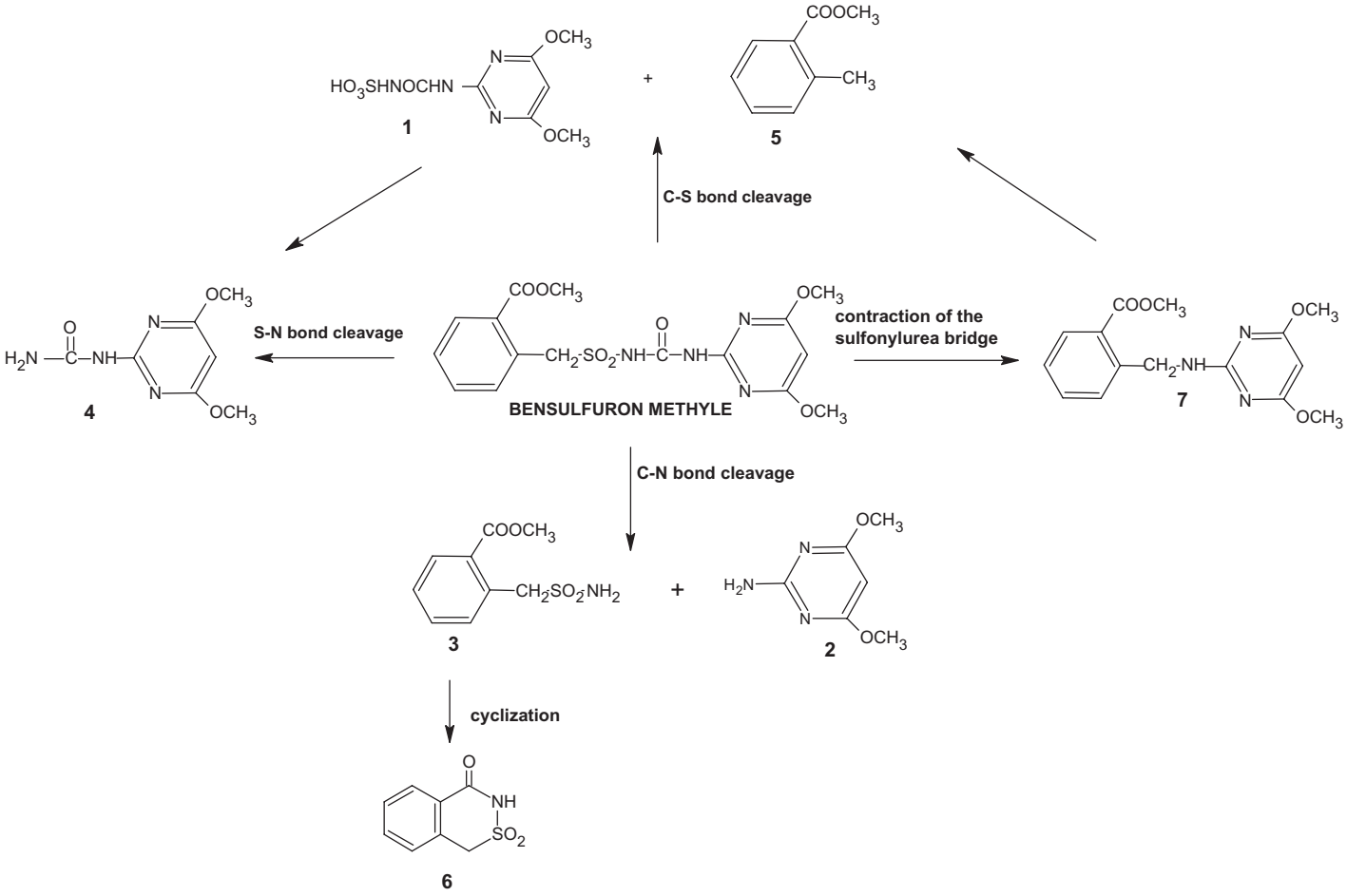


Figure 7. Hypothetic photodegradation pathway of bensulphuron methyl in aqueous solution.

The results obtained, together with literature data [3, 17], regarding different photodegradation mechanisms of sulphanylurea herbicides, allowed us to propose the structures shown in table 1 for these photoproducts, and a tentative pathway for the photolysis of bensulphuron methyl in aqueous solution is proposed in figure 7.

Different routes are proposed:

- Sulphur–nitrogen bond cleavage, a classic homolytic reaction of amine photochemical deprotection [23], followed by H abstraction from water to give the photoproduct 2-ureido-4,6-dimetoxypyrimidine (4).
- Carbon–sulphur bond cleavage to give photoproducts 4,6-dimetoxypyrimidine-2-yl aminocarbonylsulphamic acid (1). In this reaction, the photogenerated sulphonyl radical ($O_2S \cdot R$) is transformed into RSO_3H, which can in turn be transformed in (4). Indeed, figure 6 shows that (1) formation is very fast in the first 30 min of irradiation and then decreases because of its photodesulphonylation.
- Carbon–nitrogen bond cleavage to give photoproducts 2 and 3. The cleavage of the sulphonylurea bridge corresponds to a hydrolysis mechanism occurring also for chemical degradation. Meanwhile, in distilled water, pure chemical degradation occurs very slowly [2], suggesting that this hydrolysis reaction is indeed photoassisted. Photoproduct (3) may be cyclized (transformed into a molecule consisting of two rings), with loss of water, to give photoproduct 2-methylsulphonylbenzoic acid imine (6).

4. Conclusions

The photolysis studies carried out on bensulphuron methyl in distilled water have enabled us to better understand the behaviour of this herbicide in the environment. The data obtained indicate that under these conditions, the photolytic process under simulated sunlight was as important as the hydrolytic effect.

The photodegradation process could contribute to the detoxification of this herbicide in aquatic environments, but further studies regarding degradation photoproducts would be required to evaluate their toxicity.

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