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Chromatography and High-Resolution Mass Spectrometry for the Characterization of the Degradation Products of the Photodegradation of Amidosulfuron: An Analytical Approach

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ABSTRACT: Simulated sunlight irradiation causing degradation of amidosulfuron, a pyrimidinylsulfonylurea herbicide, has been investigated in aqueous solution. The main degradation products were followed up by ultrahigh-pressure liquid chromatography with a UV detector (UHPLC-UV) and identified by combining ultrahigh-pressure liquid chromatography−mass spectrometry (UHPLC-MS) and Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS). On the basis of the retrosynthetic analysis, the most identified degradation products were mainly due to the losses of methylsulfamic acid (CH_5NO_3S), sulfocarbamic acid (CH_3NO_5S), carbamic acid (CH_3NO_2), methyl(methylsulfonyl)sulfamic acid ($C_2H_7NO_5S_2$), *N*-methylmethanesulfonamide ($C_2H_7NO_2S$), and sulfonic acid (H_2SO_4) molecules. Accordingly, O and S-demethylation as well as hydroxylation processes were also observed. Sum formulas of the main degradation products were assigned, and a mechanical pathway is proposed.

KEYWORDS: *amidosulfuron, degradation products, UHPLC-UV, UHPLC-MS, FT-ICR-MS*

INTRODUCTION

The use of herbicides in agriculture is the most effective way to control weed growth and increase agricultural crop yields.[1,2] However, the presence of herbicides even in trace levels in nature is hazardous for human and mammal health. Furthermore, due to their slow biodegradation, the herbicides could easily reach surface water and groundwater. Thus, information on biochemical and chemical degradation of these substances is of great interest, and laboratory setups are necessary to follow-up and understand their fate in the environment.

Amidosulfuron (IUPAC 1-(4,6-dimethoxypyrimidin-2-yl)-3-mesyl(methyl)sulfamoylurea) is a herbicide that belongs to the sulfonylurea family of pesticides and is used worldwide in agronomic crops, rangeland/pasture, and forestry as well as plant organization.[3−5] Upon application, sulfonylurea inhibits the activity of acetolactase synthase (ALS), which is well-known as a first enzyme liable to the biosynthesis of amino acids, for example, valine and isoleucine.

The degradation of sulfonylurea herbicides has been widely conducted in several matrices, for example, waters,[6−10] humic acids and organic amendments in soils,[11,12] clay minerals,[13] and strains of bacteria from contaminated soils.[14] Among the sulfonylurea herbicides, the photolysis of chlorsulfuron, tribenuron-methyl, thifensulfuronmethyl, metsulfuron-methyl, and ethametsulfuron-methyl is already reported in different water matrices.[15−20] Several mass spectrometric tools such as LC-MS and LC-MS-MS, as well as different ionization sources such as electrospray (ESI) and atmospheric pressure chemical ionization (APCI), were employed to identify the degradation products of sulfonylurea herbicides,[15,21] but analyses based on Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry have not been performed for this type of compound yet. In a previous work, we showed that high-resolution mass spectrometry (FT-ICR-MS) could also be used as an efficient technique for the identification of the photolysis, photocatalytic, and hydrolysis products.[22−25]

To date there is no published work that discusses the degradation of amidosulfuron under simulated sunlight irradiation. In the present study, we used both UHPLC-MS and FT-ICR-MS to identify the main degradation products of amidosulfuron. Accordingly, a scheme showing the main pathways of the degradation products of amidosulfuron is provided.

MATERIALS AND METHODS

Chemicals. Amidusulfuron (Figure 1), purity > 97%, was purchased from Sigma-Aldrich (Augsburg, Germany). Solvents for UHPLC analysis were of UPLC-MS grade (Biosolve, Walkenswaard, The Netherlands), and all other chemicals were of analytical grade. All chemicals were used without further purification. Ultrapure water was produced with a Milli-Q system (Millipore, Billerica, MA, USA).

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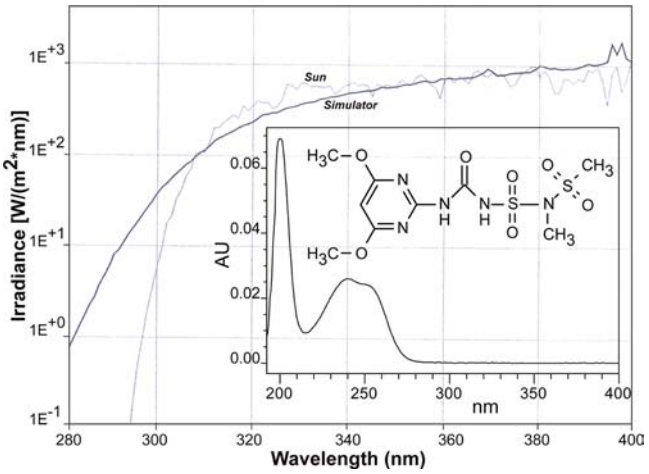

Figure 1. Emission spectral distribution of the sun and xenon arc lamp simulator (only wavelengths ranging from 280 to 400 nm are shown). (Inset) Absorption spectrum of amidosulfuron and its chemical structure.

Photoreactor. A cylindrical Pyrex glass vessel of 250 mL is used horizontally as a batch reactor. Solar irradiation was simulated by using a Suntest apparatus from Heraeus (Hanau, Germany) equipped with a xenon lamp; UV-B (280−320 nm), 2.71 W/m^2; and UV-A (320−400 nm), 58.0 W/m^2. The total radiation in the wavelength range between 300 and 830 nm is 820 W/m^2. Exposure area was about 500 cm^2. UV radiation is limited at 280 nm using a filter restricting transmission of light below this value. The illuminance is approximately 150 klx. The temperature was maintained at approximately 30 °C by unbroken cooling and internal water recirculating systems. The emission spectral distribution of the sun and xenon arc lamp simulator in the wavelength range from 280 to 400 nm is shown in Figure 1.

UHPLC-MS. The LC-MS analysis was performed using a Maxis instrument (Bruker Daltonics, Bremen, Germany) in combination with an UPLC system (Acquity, Waters, Eschborn, Germany) equipped with a PDA detector (photodiode array) and an ACQUITY BEH C18 column (1.7 μm, 2.1 × 100 mm, Germany). A gradient of methanol/water (A, 10% methanol, 0.1% formic acid in water; B, methanol) was used for the chromatographic separation. The gradient used was increased from 50% (B) to 70% (B) in 2 min and then was kept stable to 70% of B for 1 min and decreased to 50% until 3.5 min. A total time of 3.5 min was reached for each measurement. The column oven temperature, the injection volume at partial loop with needle overfills, and the flow rates were 313K, 5 μL, and 0.4 mL min^{-1}, respectively. Mass spectra were acquired using Maxis TOF-MS in both negative and positive ion modes. Samples were introduced into the electrospray source at a nitrogen flow rate of 12 L/min (350 °C) with a nebulizer gas pressure of 50 psi, capillary voltage of 4000 V, and acquisition rate of 10 Hz. Data processing was done by the use of Compass DataAnalysis 4.0 (Bruker, Bremen, Germany).

FT-ICR-MS. High-resolution mass spectra for sum formula assignment were acquired on a Bruker APEX Qe Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR-MS) equipped with a 12 T superconducting magnet and an Apollo II electrospray ionization source. The samples were diluted in methanol to a final concentration of 2.7 × 10^{-6} M. For negative and positive electrospray ionization modes, methanol was used. Samples were introduced into the electrospray source at a flow rate of 120 μL/h with a nebulizer gas pressure of 20 psi and a drying gas pressure of 15 psi. The spectra were acquired with a time domain of one-megaword over a mass range of m/z100−500, and the spectra were internally calibrated using appropriate reference lists. The plausible elemental formulas were calculated for each peak in batch mode using homemade software.

RESULTS AND DISCUSSION

Degradation Products. Offline ultrahigh-performance liquid chromatography with UV detector (UHPLC-UV) is used to follow the disappearance of amidosulfuran as well as the formation of its degradation products. Five main degradation products were detected by UHPLC-UV. Figure 2A shows the UHPLC-UV chromatogram after the end of the degradation (20 h), whereas Figure 2B shows the changes of the peak areas of the amidosulfuran and its degradation products during the time of irradiation. In addition, the half-life ($t_{1/2}$) of amidosulfuron was 6.3 h.

Online UHPLC-UV coupled to an electrospray ionization quadrupole time-of-flight (ESI Q-TOF) is used to extract ion mass spectra of the main degradation products of the

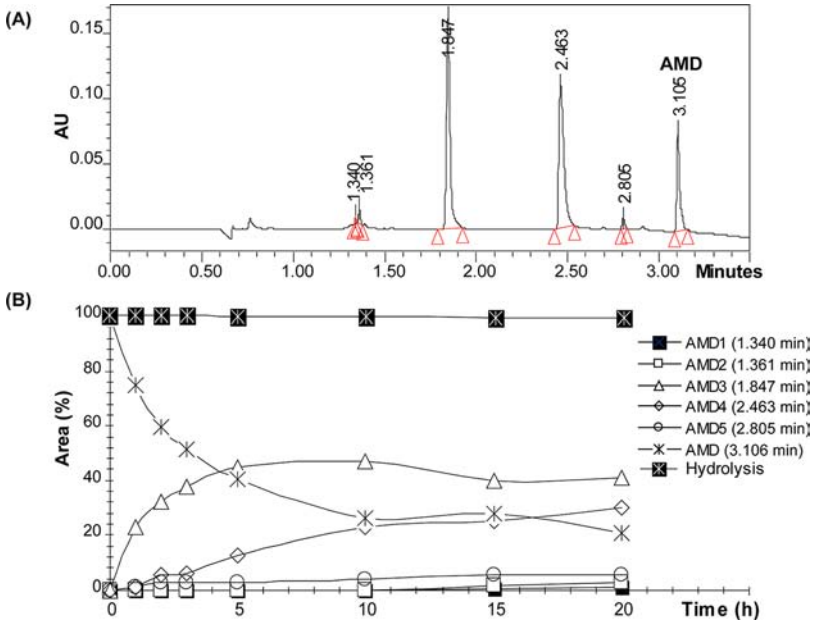

Figure 2. (A) UPHLC chromatogram. (B) Peak area changes of amidosulfuron and its degradation products. Conditions: [AMD] = 2.71 × 10^{-5} M in ultrapure water at ≈30 °C.

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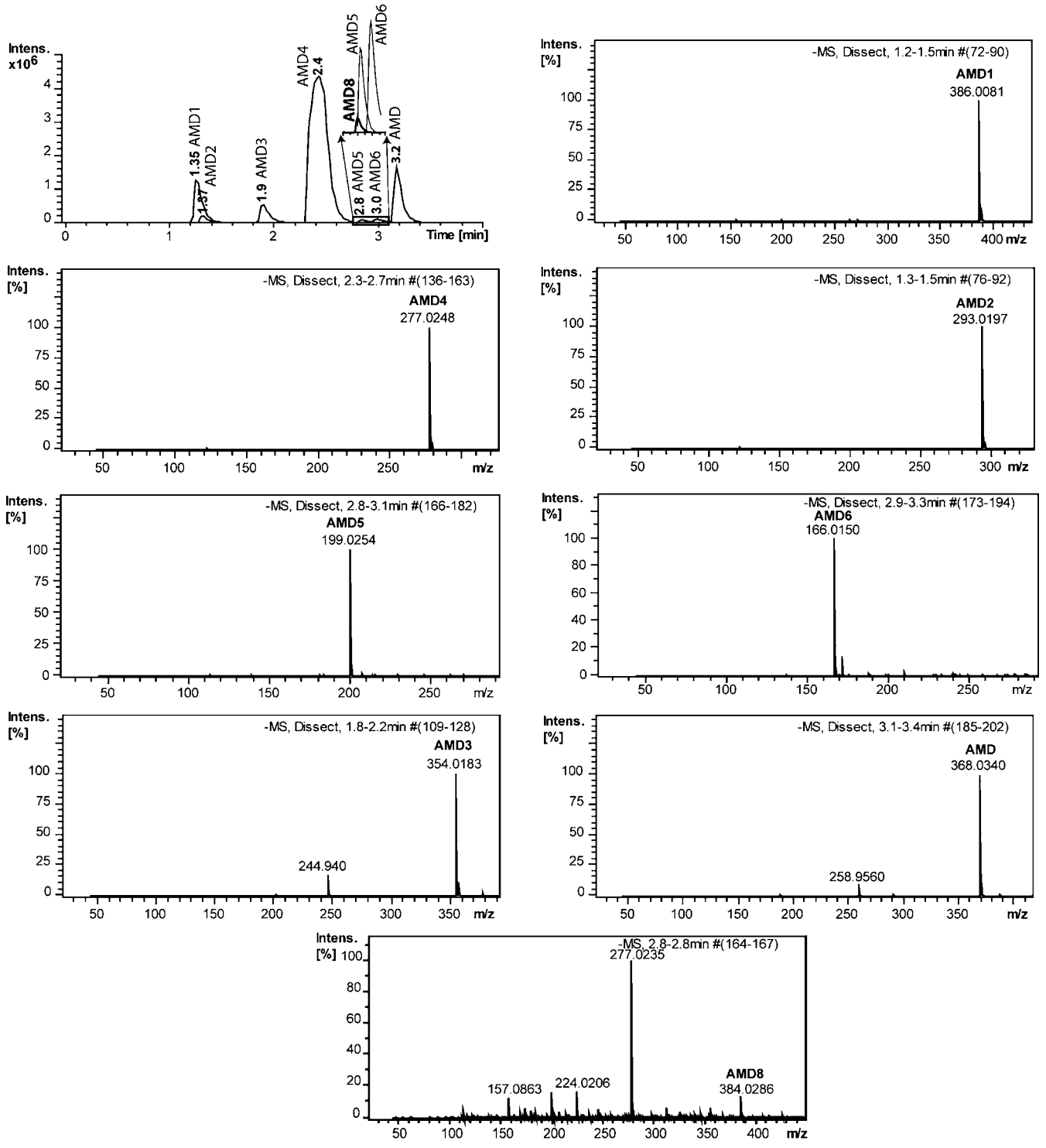

Figure 3. (Top left) Extracted ion chromatogram of amidosulfuron (AMD; 3.2 min) and its degradation products (AMD1−6 and AMD8) in negative ion mode (the chromatogram's inset reveals the presence of three degradation products with very low UV absorbance (AMD5, AMD6, and AMD8). The extracted ion mass spectra of the $[M - H]^-$ of amidosulforon and its degradation products AMD1, AMD2, AMD3, AMD4, AMD5, AMD6, and AMD8 are also shown.

degradation of amidosulfuran. The extracted negative ions mass spectra (Figure 3) showed the presence of seven degradation products with their characterized retention times and sum formulas of the $[M - H]^-$ ions: AMD1 (1.35 min; m/z 386.0081; $C_8H_{12}N_5O_9S_2$); AMD2 (1.37 min; m/z 293.0197; $C_7H_9N_4O_7S$); AMD3 (1.9 min; m/z 354.0183; $C_8H_{12}N_5O_7S_2$); AMD4 (2.4 min; m/z 277.0248; $C_7H_9N_4O_6S$); AMD5 (2.8 min; m/z 199.054; $C_7H_{11}N_4O_3$); AMD6 (3.0 min; m/z 166.0150; $C_7H_8N_3O_2$); and AMD8 (2.78 min; m/z 385.0362; $C_9H_{15}N_5O_8S_2$).

In positive ionization mode, the extracted ion chromatogram shows the presence of only three degradation products, namely, AMD4, AMD6, and AMD7, with their retention times (2.4, 2.9, and 1.8 min), respectively (Figure 4). The extracted positive

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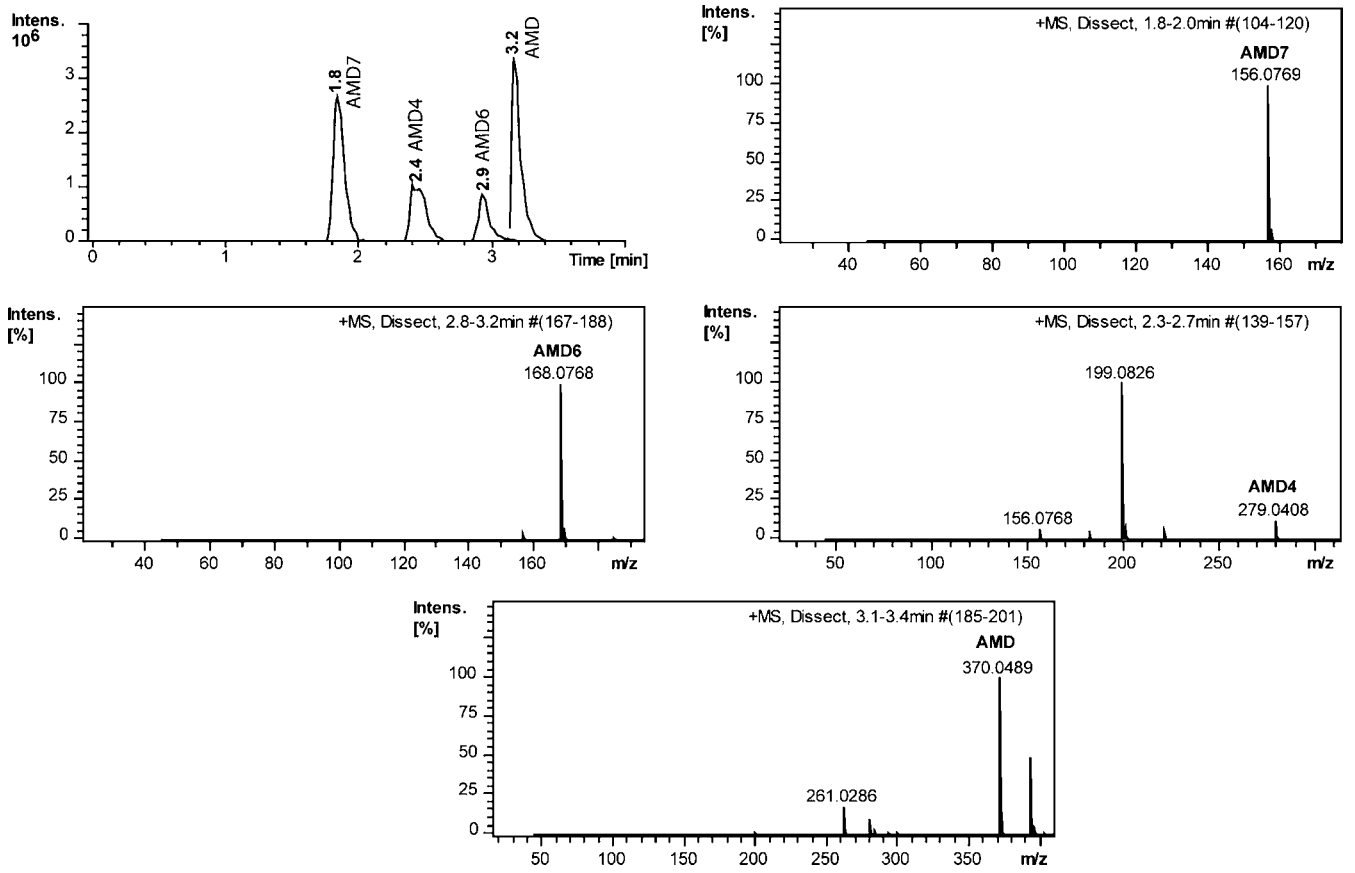

Figure 4. (Top left) Extracted ion chromatogram of amidosulfuron (AMD; 3.2 min) and its degradation products (AMD7, 1.8 min; AMD6, 2.9 min; and AMD4, 2.4 min) in positive mode. Extracted ion mass spectra of AMD7, AMD6, AMD4, and AMD are also shown.

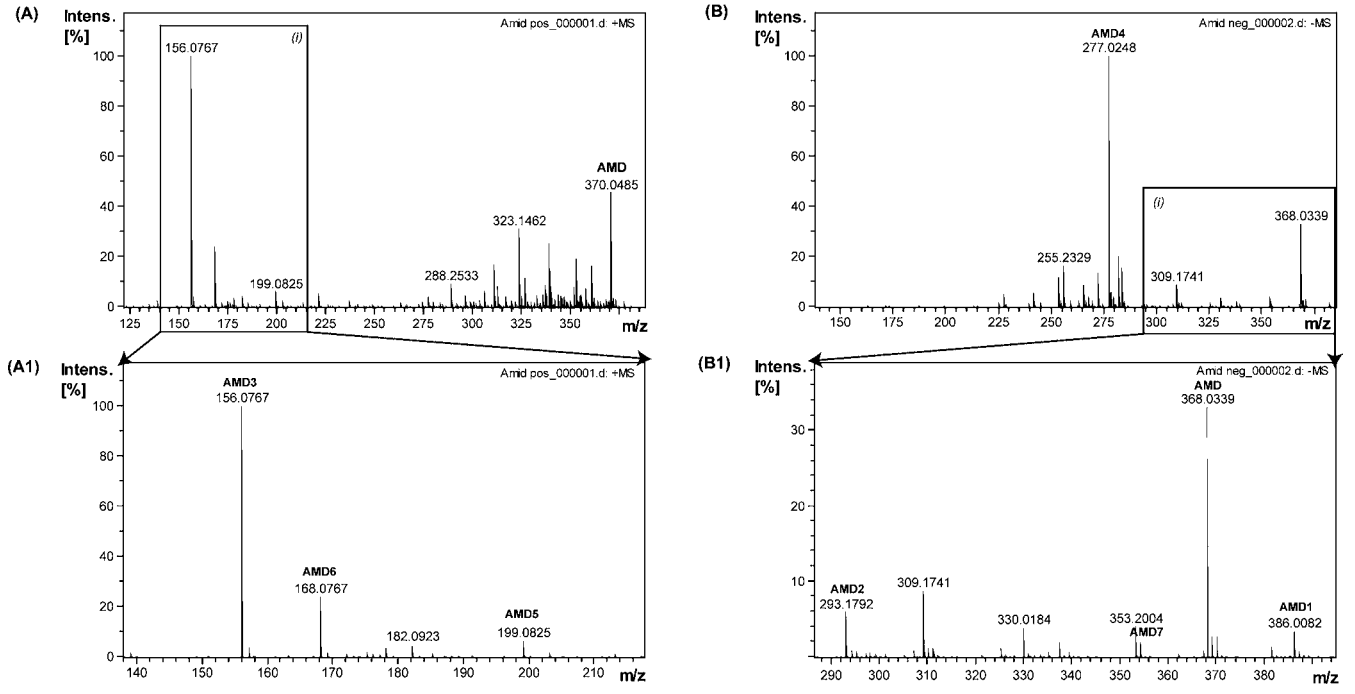

Figure 5. (A) FT-ICR mass spectrum of amidosulfuron degradation in positive mode. (A1) Enlarged mass view that shows the degradation products AMD3, AMD5, and AMD6 at molecular masses of m/z 156.0767, 168.0767, and 199.0825, respectively. (B) FT-ICR mass spectrum of amidosulfuron degradation in negative mode. (B1) Enlarged mass view that shows the degradation products AMD1, AMD2, AMD7, and AMD at molecular masses of m/z 386.0082, 293.1792, 354.01844, and 368.0339, respectively.

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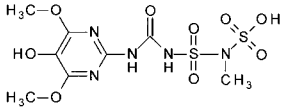
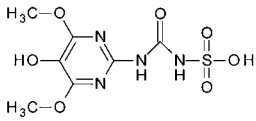
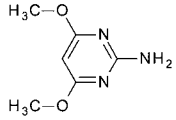
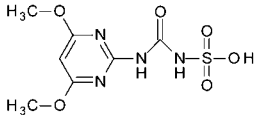
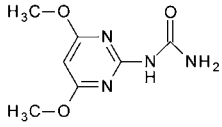
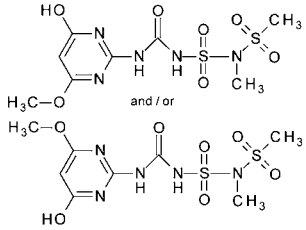
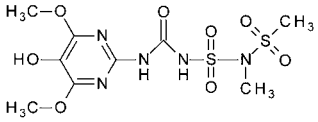
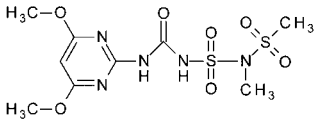
Table 1. Positive and Negative FT-ICR-MS and UPLC-MS Analysis Data of Amidosulfuron and Its Degradation Products

Degradation products	Chemical structure	Calculated mass	Retention time (min)	Neutral Sum formulas
AMD1		387.0155	1.34	$C_8H_{13}N_5O_9S_2$
AMD2		294.0270	1.36	$C_7H_{10}N_4O_7S$
AMD3		155.0695	1.84	$C_6H_9N_3O_2$
AMD4		278.0321	2.46	$C_7H_{10}N_4O_6S$
AMD5		198.0753	2.8	$C_7H_{11}N_4O_3$
AMD6	*Not proposed*	167.0695	3.0	$C_7H_9N_3O_2$
AMD7		355.0256	1.8	$C_8H_{13}N_5O_7S_2$
AMD8		385.0362	2.78	$C_9H_{15}N_5O_8S_2$
AMD		369.0413	3.2	$C_9H_{16}N_5O_7S_2$

ion mass spectra showed abundant peaks at masses m/z 156.0769, 279.0408, and 168.0768, which were attributed to the following sum formulas: $C_6H_{10}N_3O_2$ (AMD7), $C_7H_{11}N_4O_6S$ (AMD4), and $C_7H_{10}N_3O_2$ (AMD6).

To validate these results, high-resolution mass spectrometry (FT-ICR-MS) is used. Fourier transform mass spectra of the degradation of amidosulfuron in positive and negative ionization modes are shown in Figure 5A,B. Enlarged views for each of these mass spectra in the mass range (m/z 140−220) amu are also provided (Figure 5A1,B1). To summarize, Table 1 shows accurate masses of the neutrals that present amidosulforon and its degradation products together with their detected retention times (in minutes) and sum formulas, as well as chemical structures.

The sum formulas of the neutrals that are provided in Table 1 could be revealed by performing calculations on the measured masses. These calculations took into consideration the presence of carbon, hydrogen, nitrogen, oxygen, and sulfur. A homemade program was used to generate possible sum formulas according to the following criteria: O/C ratio, ≤ 1; H/C ratio, $\leq 2n + 2$; element counts, C $\leq$ 20, H $\leq$ 30, O $\leq$ 6, N $\leq$ 6, and S $\leq$ 2. The nitrogen rule was also checked, and only those sum formulas that adhere to this rule were considered. This was important because all measured masses correspond to ions with a closed

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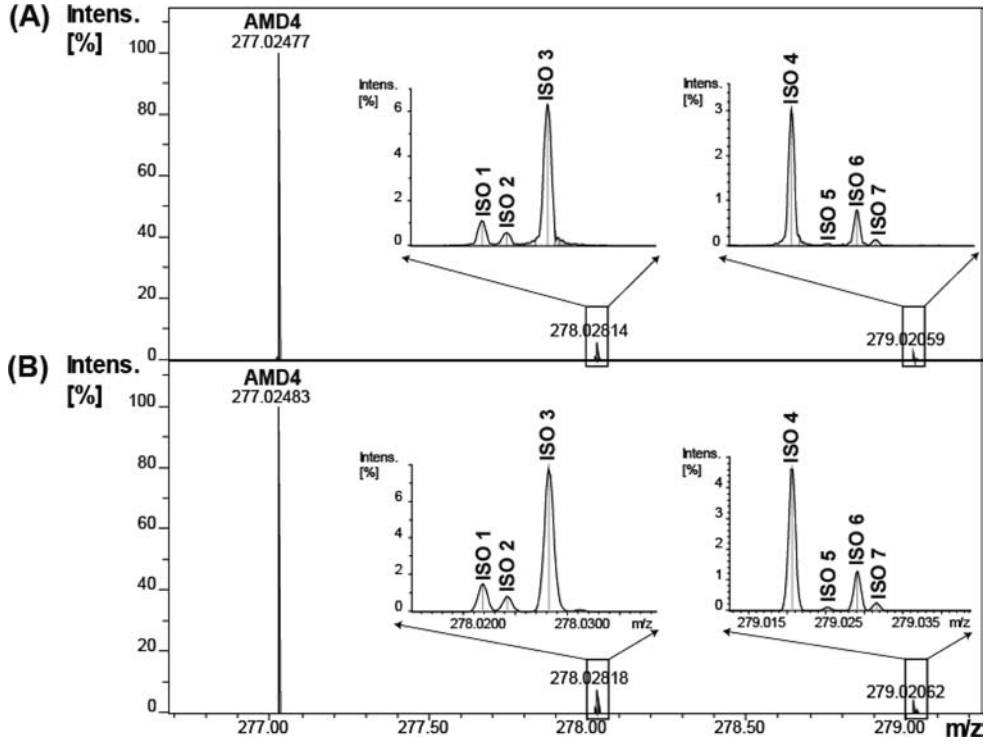

Figure 6. (A) Enlargement of the mass 277.02477 with sum formula $[C_7H_9N_4O_6S]^-$ corresponding to the degradation product AMD4 (see Figure 5B) with its observable isotopologues present in high intensity (see also Table 2, where the assigned formula of each ISO abbreviation is given). (B) Show simulated mass spectrum of the same mass.

electronic shell (even electron species), so that the nitrogen rule should apply. No radical ions can be detected for this type of compounds under the used electrospray conditions.[22−26]

Figure 6 shows a further step forward, which has been performed in the case of degradation product AMD4 to show the importance of the fine isotopic structure (FIS) for revealing further validation of the detected sum formula. We performed the mentioned FIS analysis specifically for the degradation product AMD4 (as an example) due to its high abundance. FIS analysis requires very high resolution so that an enlarged mass spectrum of the $[M - H]^-$ of AMD4 at m/z 277.02477 and sum formula $C_7H_9N_4O_6S$, which shows each heavy isotope, should be feasible. This is illustrated in Figure 6, which shows the presence of species with the following sum formulas: ISO 1, $C_7H_9N_3O_6S^{15}\boldsymbol{N}$); ISO 2, $C_7H_9N_4O_6{}^{33}\boldsymbol{S}$; ISO 3, $C_6H_9N_4O_6S^{13}\boldsymbol{C_1}$; ISO 4, $C_7H_9N_4O_6{}^{34}\boldsymbol{S}$; ISO 5, $C_6H_9N_3O_6S^{13}\boldsymbol{C^{15}N}$; ISO 6, $C_7H_9N_4O_5S^{18}\boldsymbol{O}$; and ISO 7, $C_5H_9N_4O_6S^{13}\boldsymbol{C_2}$, which correspond to the natural abundance isotopes of the $[M - H]^-$ of AMD4. These sum formulas, which contain heavy isotopes (Table 2), were also calculated, and a very good match in regard to the isotopic patterns of both experimental and simulated isotope patterns could be achieved. This validates that the ion $[M - H]^-$ with m/z 277.02477 does indeed belong to the sum formula $C_7H_9N_4O_6S$. The same principle can be applied for all other degradation products.

Degradation Pathways. The main proposed pathways of the degradation of amidosulfuron are shown in Figure 7. Most of these pathways involve the following competing process: (i) carbon−nitrogen (C−N) and sulfur−nitrogen (S−N) bond cleaveages; (ii) O or S-demethylation; and (iii) hydroxylation process. Thus, the degradation product AMD8 with mass 385 ($C_9H_{15}N_5O_8S_2$, IUPAC 1-(5-hydroxy-4,6-dimethoxy-pyrimidin-2-yl)-3-[methyl(methylsulfonyl)sulfamoyl]urea) (Figure 7), is

Table 2. High-Accuracy Measurements (FIS Analysis) That Show the Assigned Formulas of the Degradation Product AMD4 (Mass 277.02477) as well as Its Corresponding Heavy Isotopes in Negative Mode FT-ICR-MS (See Also Figure 6)

	assigned formula	measd m/z	calcd m/z	error (ppm)
parent ion				
AMD4	$C_7H_9N_4O_6S$	277.02477	277.02483	0.2
isotope labels				
ISO 1	$C_7H_9N_3O_6S^{15}N$	278.02185	278.02186	0.0
ISO 2	$C_7H_9N_4O_6{}^{33}S$	278.02421	278.02422	0.0
ISO 3	$C_6H_9N_4O_6S^{13}C$	278.02814	278.02818	0.2
ISO 4	$C_7H_9N_4O_6{}^{34}S$	279.02059	279.02062	0.1
ISO 5	$C_6H_9N_3O_6S^{13}C^{15}N$	279.02529	279.02522	0.3
ISO 6	$C_7H_9N_4O_5S^{18}O$	279.02905	279.02907	0.1
ISO 7	$C_5H_9N_4O_6S^{13}C_2$	279.03147	279.03154	0.2

obtained as a result of a hydroxylation process in the para-position of the pyrimidine ring of amidosulfuron. Furthermore, S-demethylation (S−C cleavage bond) of AMD8 can also take place to form AMD1 with a nominal mass of 387 ($C_8H_{13}N_5O_9S_2$, IUPAC (5-hydroxy-4,6-dimethoxypyrimidin-2-yl)carbamoylsulfamoylmethylsulfamic acid).

The degradation product AMD2 with a nominal mass of 294 ($C_7H_{10}N_4O_7S$; IUPAC (5-hydroxy-4,6-dimethoxypyrimidin-2-yl)carbamoylsulfamic acid) can be formed from AMD1 by substitution of one molecule of methylsulfamic acid (CH_5O_3NS) by a hydroxyl group.

O-demethylation of amidosulfuran by loss of one of the two methyl groups in the meta position of the pyrimidinyl group leads to the formation of the degradation product AMD7 with a nominal mass of 355 ($C_8H_{13}N_5O_7S_2$; IUPAC 1-(4-hydroxy-6-

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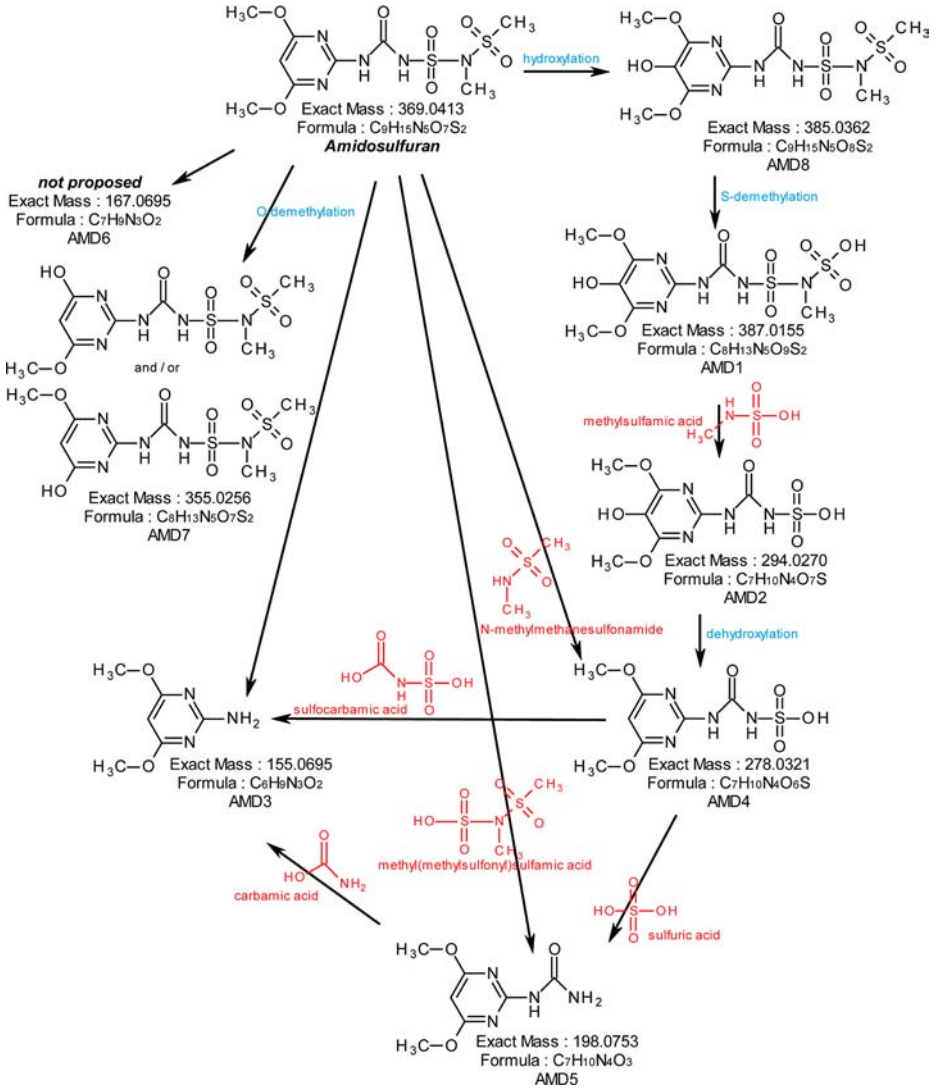

Figure 7. Proposed pathways for the degradation of amidosulfuron in neutral form.

methoxypyrimidin-2-yl)-3-[methyl(methylsulfonyl)sulfamoyl]-urea). This step of the degradation is considered as a first step of the degradation not only for the degradation of amidosulfuron but also for the degradation of bensulfuron-methyl and triasulfuron.[27,28]

The degradation product AMD4 with a nominal mass of 278 ($C_7H_{10}N_4O_6S$; IUPAC (4,6-dimethoxypyrimidin-2-yl)-carbamoylsulfamic acid) can be obtained either by loss of the *N*-methylmethanesulfonamide molecule directly from amidosulfuron (S−N bond cleavage) or by dehydroxylation of AMD2. A similar degradation product was identified in the degradation of imazosulfuron in aqueous medium.[29]

Accordingly, N−S bond cleavage from amidosulfuron by loss of methyl(methylsulfonyl)sulfamic acid and/or N−S bond cleavage from AMD4 by loss of the sulfuric acid (H_2SO_4) molecule can lead to the degradation product AMD5 with a nominal mass of 198 ($C_7H_{10}N_4O_3$; IUPAC (4,6-dimethoxypyrimidin-2-yl)urea). The final AMD3 degradation product can be the result of either −NH−C(O)− cleavage from amidosulfuron, AMD4, or from AMD5 (Figure7).

Accordingly, the degradation of the herbicides, for example, iodosulfuron methyl ester, chlorsulfuron, and tribenuron methyl, in aqueous solution has also been explained as a result of −NH—C═O bond cleavages.[15,21,25] It has been reported that the degradation products AMD3 and AMD5 were identified as degradation products of imazosulfuran, azimsulfuran, [^{14}C]amidosulfuron, pyrazosulfuran-ethyl, and halosulfuran-methyl under abiotic and biotic conditions.[9,19,29−31]

To sum up, the degradation of amidosulfuran under simulated sunlight irradiation is studied and the related degradation products were identified by combining UHPLC-UV, UHPLC-MS, and FT-ICR-MS. This combination allowed us to draw up the most plausible pathways concerning the degradation products of amidosulfuron. It should be noted that the pyrimidine ring existing in the amidosulfuron structure is retained during amidosulfuron degradation. This analytical approach can be used to unequivocally identify the key degradation products of related organic contaminants in the environment without specific separation.

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Notes

The authors declare no competing financial interest.

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