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Collection of Ion-trap Mass Spectra of Sulfonylurea Pyrolysis Products

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The pyrograms of 14 sulfonylureas, i.e. herbicides characterized by high biological activity and low application dose are discussed and the mass spectra of over 30 relevant pyrolysis products as obtained with a heated filament pyrolyzer interfaced to a capillary gas chromatograph/ion-trap detector mass spectrometer are presented. Such a data compilation is useful for diagnostic purposes for both intact sulfonylureas and their metabolites after degradation in soil, because metabolites and pyrolysis products are often identical and most of their mass spectra are lacking in commercially available mass spectral libraries. The performance of the ion-trap detector based on the quality of the mass spectra is briefly discussed.

INTRODUCTION

Sulfonylureas are a class of herbicides characterized by high biological activity in controlling weeds. This results in application doses typically three orders of magnitude lower than those of *s*-triazine-like molecules. Such a feature, coupled to a relatively low human toxicity, is very important in reducing the impact of herbicides on the environment.[1]

Determinations of sulfonylureas in soil and water samples have included various methods, such as high-performance liquid chromatography, capillary electrophoresis, bioassays and immunoassays.[2–4] Gas chromatography (GC) is generally inapplicable owing to the thermal instability of sulfonylureas, although the formation of stable derivatives for the GC analysis of sulfonylureas has been reported.[5,6]

A number of neutral fragments are produced when sulfonylureas are pyrolyzed for a few seconds at 600–800 °C in an inert atmosphere.[7] Many of the fragments are identical with those observed by mass spectrometry after electron impact, except that the former are neutral molecules and the latter are ionic species.[7] Not surprisingly, the same chemical structures are found in many metabolites of sulfonylureas after hydrolytic or microbial degradation in soils,[8–15] suggesting that heat, electron impact and environment share common pathways for the degradation of sulfonylureas.

As part of our studies on sulfonylurea analysis and application in agronomic practice, we exploited the thermal instability of sulfonylureas in pyrolysis/gas chromatography/mass spectrometry (PY/GC/MS) to obtain a 'fingerprint' of pyrolysis fragments diagnostic of the original molecules and a compilation of gas chromatographic and mass spectral data of molecules which are useful for the identification of sulfonylurea metabolities.

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EXPERIMENTAL

Samples

Pure sulfonylureas (Fig. 1) were obtained by Soxhlet extraction with dichloromethane for 4 h of commercial samples kindly provided by Professor Pietro Catizone and Dr A. Vicari (Department of Agronomy, University of Bologna). The organic extract was dried with anhydrous sodium sulfate and the solvent was evaporated in a rotary evaporator under reduced pressure. An aliquot of the residue in the flask was dissolved in dichloromethane and subjected to pyrolysis without further purification.

PY/GC/MS

A few microliters of the sulfonylurea solution were slowly syringed into the quartz capillary tube used as a sample holder for pyrolysis, while the tube was manually rotated in a warm stream of air from a hair-drier. The sulfonylurea formed a film the inner wall of the tube, thus avoiding overloading or undesirable thermal gradients due to large or irregularly sized samples.

Analyses were performed in an integrated PY/GC/MS system consisting in the CDS Pyroprobe 100 heated filament pyrolyzer (Chemical Data Systems,

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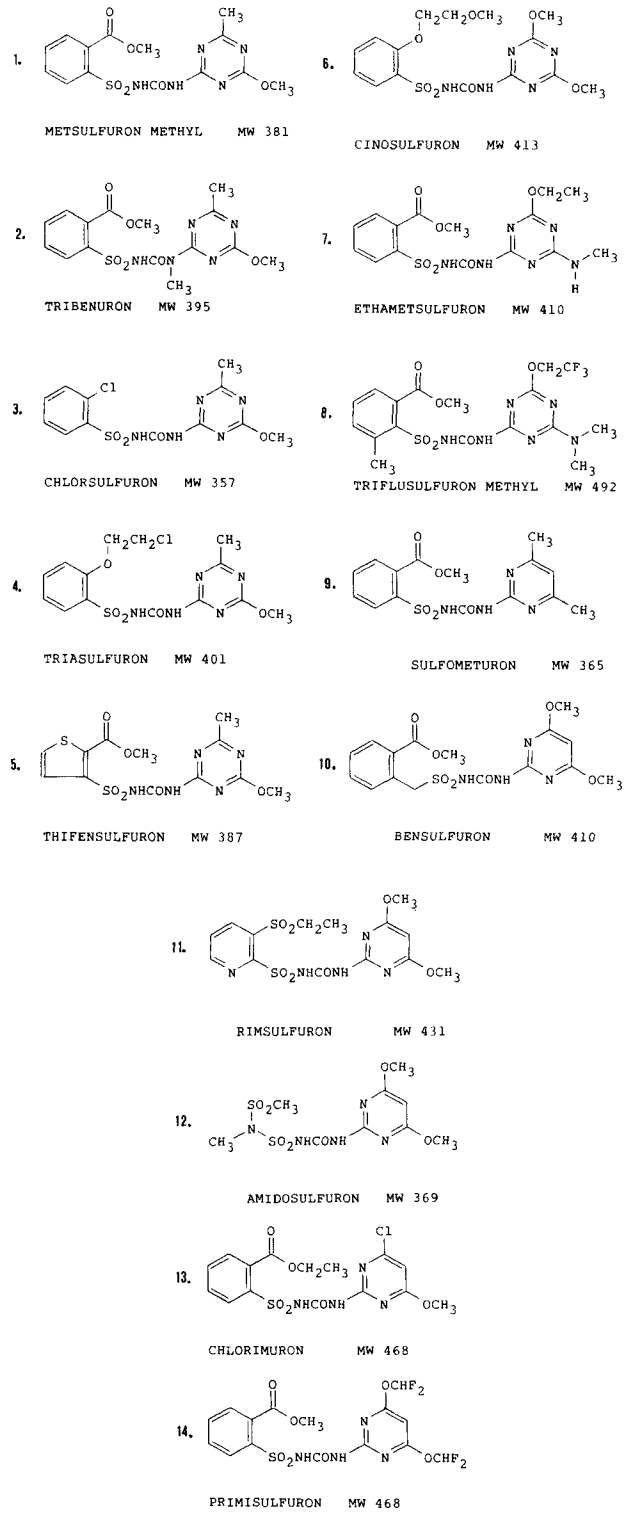


Figure 1. Structural formulae, common names and molecular masses of sulfonylureas.

Oxford, PA, USA), a Varian Model 3400 gas chromatograph (Varian Analytical Instruments, Walnut Creek, CA, USA) and a Finnigan MAT ion-trap detector (ITD) mass spectrometer (Finnigan MAT, San Jose, CA, USA) (Software Release 4.0). Pyrolyses were performed at 800 °C for 5 s with the PY/GC interface heated at 180 °C. The gas chromatograph was equipped with a Supelco SPB-5 (95% methyl, 4% phenyl, 1% vinyl silicone) fused-silica column (30 m × 0.32 mm i.d., 0.25 μm film thickness) (Supelco, Bellefonte, PA, USA) programmed from 50 to 300 °C at 10 °C min^{-1}. The split injection mode was used with an approximate splitting ratio of 1:100 and the injector port was heated at 220 °C. Mass spectra were recorded under electron impact ionization at 70 eV from *m/z* 34 to 400 (1 scan s^{-1}), the GC/MS transfer line was maintained at 220 °C and the ion-trap manifold at 230 °C.

RESULTS AND DISCUSSION

For completeness, the 14 sulfonylureas considered included four compounds, namely **1**, **3**, **5** and **13**, which had been studied previously.[7]

As shown in Fig. 1, all the sulfonylurea structures can be subdivided into three substructures, namely (i) a triazine or diazine ring with various substituents (hereinafter called moiety 1), (ii) the sulphonylurea bridge and (iii) an *ortho*-monosubstituted benzene ring (exclusive of compounds **5**, **8**, **10**, **11** and **12**) (hereinafter called moiety 2).

All the sulfonylureas pyrolyzed at 800 °C yielded two to five main compounds detectable under the GC conditions adopted. Figure 2 shows a typical pyrogram. The temperature of pyrolysis was chosen on the basis of a previous study on a limited set of sulfonylureas.[7] The pyrolysis conditions were kept as constant as possible in terms of time, heating rate and temperature in order to achieve the optimum reproducibility and comparability of results with a view to compiling a large database of pyrograms. However, the relative quantities of pyrolysis products from the sulfonylureas did not appear to vary significantly with pyrolysis temperatures in the range 400–900 °C.

The main scheme of the thermal degradation entailed the cleavage of the two N—C ureic bonds with the formation of neutral molecules through reciprocal proton transfer, the latter being a common occurrence in pyrolysis.[16] As a result of such fission, a heterocyclic (triazine or diazine) amine was formed from moiety 1 and a sulfonamide derived from moiety 2. Figure 3 shows all the structures proposed as pyrolysis fragments of the 14 sulfonylureas. It should be mentioned that the heterocyclic amine, the sulfonamide and the isocyanates, (compounds **A**, **B**, **C** and **D**, respectively in Fig. 3) are the main fragments produced by electron impact mass spectrometry of intact sulfonylureas.[1,7] This correspon-

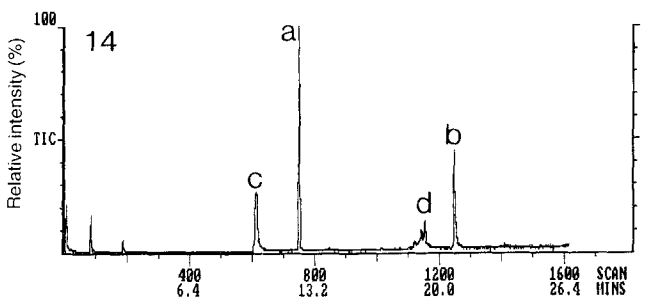
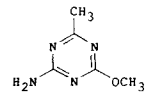


Figure 2. Pyrogram of primisulfuron. For peak identification, see Table 1 and Fig. 3.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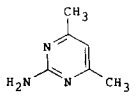
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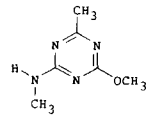
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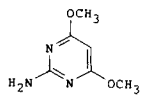
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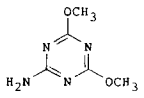
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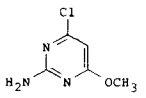
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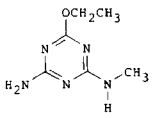
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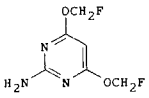
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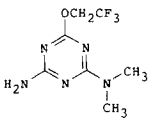
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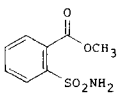
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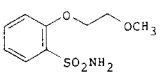
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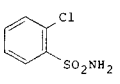
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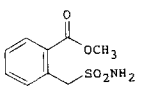
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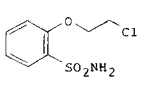
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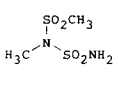
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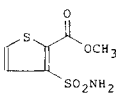
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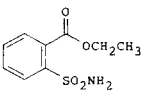
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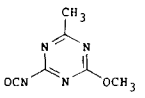
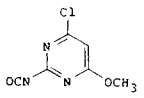

1C,3C,4C, MW 166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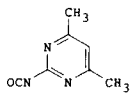
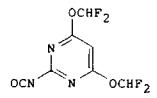

9C, MW 149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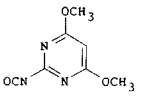
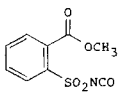

10C,11C,12C, MW 181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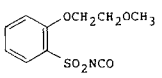
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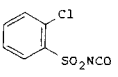
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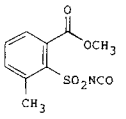
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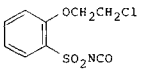
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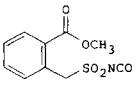
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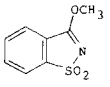
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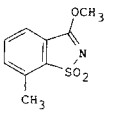
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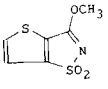
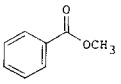
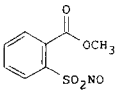
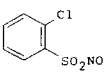

5E, MW 203


1X', MW 136


5X, MW 112


1X", MW 229


11X', MW 94


3X, MW 205

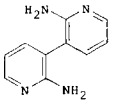

11X", MW 186

Figure 3. Structures proposed for the sulfonylurea pyrolysis fragments. Numbers refer to the original sulfonylurea (see Fig. 1).

dence corroborated the identification of such structures in the pyrograms. Compounds **A** and **B** were the main fragments from the standpoint of sulfonylurea characterization and also represent the two most important metabolities of sulfonylureas in the environment.[8–15] Whereas the heterocyclic amine **A** was invariably present as one of the most abundant fragments in all pyrograms (Table 1), the sulfonamide **B** was not produced at all from sulfonylureas **8** and **11**, and was only a minor peak in the pyrogram of sulfonylureas **5**, **10** and **12**. Although such an observation is difficult to explain, it is interesting that all the sulfonylureas in question do not have the usual monosubstituted benzene ring as moiety 2. The stability of the sulfonamide might therefore be affected by the structure of moiety 2, monosubstituted benzene rings showing high stability.

Compounds **C** and **D** (Fig. 3) are related to the above-discussed main fragments, because they are the isocyano derivatives of moiety 1 and moiety 2 of the original sulfonylurea. In other words, the isocyano fragments **C** and **D** complement fragments **B** and **A**, respectively, representing the other 'half' of the original sulfonylurea after pyrolytic degradation. Although such isocyano derivatives were a less constant presence than the previous two main fragments, their occurrence and relative abundances followed the general trend observed for fragments **A** and **B**. In particular, fragment **D** was small or totally lacking when the corresponding sulfonamide was small or absent (Table 1).

A third category of pyrolysis fragments, namely compounds **E** (Fig. 3), was that generated on moiety 2 by cyclization between the sulfonamidic chain and the other substituent, with loss of water from the latter. These structures are only tentatively identified, since no standard molecule was available for confirmation. Such a fragment was seldom observed and, of course, was not found when the substituent could not lose water. Nevertheless, this cyclization was interesting since a similar mechanistic route is observed in metabolism, except that the latter entails loss of methanol instead of water.[1]

Finally, a few minor compounds (compounds **X**, Fig. 3) were observed in some pyrograms. Such compounds (**11X′** and **11X″** are only suppositions) are related to the above-described main fragments by modifications of the substituents on moiety 2 or by a possible dimerization in the case of **11X″**. The dimer might be a secondary product of pyrolysis, i.e. produced by recombination of two thermally reactive fragments present in large excess in the pyrolysis probe.

The main ions in the mass spectra of the pyrolysis fragments are listed in Table 2. All the mass spectra of the heterocyclic amines (compounds **A**) were very diagnostic, showing abundant molecular ions (often >40%, base peak for compounds **10A**, **11A**, **12A** and **13A**) and characteristic fragmentations. The sulfonamides **B** were also identified from their molecular ions or diagnostic fragmentations. The isocyano derivatives **C** and **D** were differentiated from the amine derivatives by means of their molecular ions, when these were present in at least one of the two related compounds. Otherwise, the GC behavior (isocyano derivatives always eluted earlier than the corresponding sulfonamides under the conditions adopted, except for the heterocyclic derivatives of sulfonylurea **9**) and other diagnostic ions were used as discriminating factors.

Finally, singly and sometimes doubly protonated molecular ions were evident when relatively large quantities of sulfonylureas were pyrolyzed and especially when the analyte was a strong proton acceptor, such as triazine or diazine amines, as a consequence of saturation and space-charging effects.[17,18]

CONCLUSION

Table 3 offers a means of identifying sulfonylureas on the basis of the most significant ions in the mass spectra

Table 1. Sulfonylurea pyrolysis products[a]

No.	A	B	C	D	E	X
1	L(140)	L(215)	S(166)	S(241)	L(197)	X′ S(136) X″ S(229)
2	L(154)	L(215)	—	L(241)	L(197)	—
3	L(140)	L(191)	L(166)	L(217)	—	S(205)
4	L(140)	L(235)	L(166)	L(261)	—	—
5	L(140)	S(221)	—	—	S(203)	S(112)
6	L(156)	L(231)	—	L(257)	—	—
7	L(169)	L(215)	—	L(241)	—	—
8	L(237)	—	—	S(255)	L(211)	—
9	L(123)	L(215)	S(149)	—	—	—
10	L(155)	S(229)	L(181)	S(255)	—	—
11	L(155)	—	L(181)	—	—	X′ S(94)? X″ L(186)?
12	L(155)	S(188)?	L(181)	—	—	—
13	L(159)	L(229)	L(185)	—	—	—
14	L(227)	L(215)	L(253)	S(241)	—	—

[a] Numbers **1–14** refer to the original molecule. **A**, **B**, **C** and **D** indicate the heterocyclic amine (moiety 1), the sulfonamide (moiety 2) and the isocyanates of moieties 1 and 2, respectively. **X** = fragments of various nature. For structures, see Fig. 3. L-large pyrolysis peak; S = small pyrolysis peak (i.e. less than 20% of the largest peak height). Molecular masses are given in parentheses.

Table 2. Five-peak mass spectra of the sulfonylurea pyrolysis fragments[a]

Fragment	RMM	*m/z* [relative intensity (%)]				
1A, 3A, 4A, 5A	140	69 (100)	42 (90)	140 (46)	110 (37)	58 (26)
2A	154	56 (100)	69 (95)	42 (87)	154 (38)	124 (27)
6A	156	43 (100)	69 (63)	126 (26)	156 (27)	111 (20)
7A	169	43 (100)	125 (70)	169 (58)	170 (47)	112 (45)
8A	237	44 (100)	69 (32)	109 (15)	237 (13)	83 (12)
9A	123 (29)	43 (100)	42 (88)	67 (56)	96 (44)	39 (43)
10A, 11A, 12A	155	155 (100)	68 (84)	69 (47)	43 (45)	154 (42)
13A	159	159 (100)	158 (97)	43 (92)	67 (73)	160 (63)
14A	227 (37)	51 (100)	43 (73)	99 (57)	161 (43)	111 (38)
1B, 2B, 7B, 9B, 14B	215 (0)	199 (100)	92 (47)	103 (43)	77 (32)	184 (29)
3B	191 (32)	111 (100)	75 (90)	50 (52)	128 (46)	127 (46)
4B	235 (54)	64 (100)	63 (94)	156 (75)	92 (72)	80 (60)
5B	221 (13)	157 (100)	190 (65)	125 (58)	126 (53)	45 (49)
6B	231 (3)	59 (100)	60 (35)	45 (32)	173 (10)	215 (7)
10B	229 (0)	91 (100)	149 (40)	92 (30)	119 (26)	34 (23)
12B	188 (0)	110 (100)	44 (17)	79 (15)	65 (12)	94 (8)
13B	229 (0)	184 (100)	213 (86)	65 (58)	50 (43)	121 (43)
1C, 3C, 4C	166 (32)	136 (100)	95 (70)	67 (66)	44 (55)	42 (53)
9C	149	42 (100)	149 (96)	39 (94)	69 (90)	40 (70)
10C, 11C, 12C	181	41 (100)	181 (77)	55 (75)	68 (70)	83 (65)
13C	185	184 (100)	185 (87)	127 (80)	92 (60)	155 (53)
14C	253 (14)	51 (100)	187 (53)	69 (46)	52 (40)	125 (18)
1D, 2D, 7D	241 (1)	210 (100)	90 (40)	50 (32)	77 (30)	199 (21)
3D	217	111 (100)	175 (80)	75 (78)	217 (34)	50 (37)
4D	261	63 (100)	64 (80)	156 (75)	92 (74)	261 (41)
6D	257 (3)	59 (100)	45 (41)	60 (31)	58 (29)	92 (7)
8D	255 (72)	104 (100)	91 (98)	63 (92)	89 (90)	90 (81)
10D	255 (0)	91 (100)	149 (74)	119 (41)	92 (34)	63 (18)
1E, 2E	197 (22)	133 (100)	104 (90)	105 (86)	76 (80)	77 (55)
5E	203 (44)	110 (100)	111 (85)	45 (66)	139 (55)	82 (50)
8E	211 (30)	91 (100)	90 (98)	63 (77)	89 (73)	118 (49)
1X′	136	105 (100)	77 (81)	50 (31)	136 (20)	85 (18)
3X	205 (13)	111 (100)	75 (61)	141 (43)	50 (37)	175 (23)
1X″	229 (0)	105 (100)	77 (93)	50 (63)	133 (60)	92 (58)
5X	112 (20)	56 (100)	111 (60)	68 (25)	41 (24)	42 (22)
11X′	94	67 (100)	94 (90)	41 (86)	40 (51)	39 (38)
11X″	186 (33)	94 (100)	39 (58)	93 (56)	66 (38)	67 (35)

[a] For fragment structures, see Fig. 3.

Table 3. Identification of sulfonylureas based on the most significant ion of the pyrolysis fragment[a]

m/z			
A	B	X″	Sulfonylurea
123			**9**
140	191		**3**
140	199		**1**
140	221		**5**
140	235		**4**
154			**2**
155	110		**12**
155	212		**10**
155		186	**11**
156			**6**
159			**13**
169			**7**
227			**14**
237			**8**

[a] For numbers and letters, see Table 1 and Fig. 1).

of the fragments generated by PY/GC/MS of the original molecule. PY/GC/MS is an attractive tool for the study of sulfonylureas, because it provides a large amount of data with no sample preparation.

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