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Identification of a Soil Metabolite of Bis(trichloromethyl) Sulfone by HPLC/Thermospray Mass Spectrometry

B. Y. Giang, L. L. Chang

Zeneca Inc., Western Research Center, Box 4023, 1200 South 47th Street, Richmond, California 94804-0023, USA

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Bis(trichloromethyl) sulfone (N-1386) is a biocide used in controlling the formation of slimes in industrial water (Sherma et al. 1972). High performance liquid chromatograph (HPLC)/UV/radioactivity monitor (RAM) analysis of extracts of soil samples that were treated with this compound detected the presence of two unknown peaks in the UV chromatogram while only the first of these appeared in the RAM trace. The earlier unknown eluted one minute prior to the N-1386 peak, and the second eluted about seven minutes after the N-1386 peak. The purpose of this work was to identify these unknowns by HPLC/mass spectrometry (HPLC/MS) and to confirm the identification with authentic standards. A thermospray (TSP) HPLC/MS interface (Yergey et al. 1990) was used to mediate between the two seemingly incompatible techniques.

MATERIALS AND METHODS

The HPLC used was a Perkin-Elmer Series 410 LC pump equipped with a Rheodyne Model 7125 injector and a Perkin-Elmer Model 95 UV/Visible detector. The column used was an Alltech 25 cm x 4.5 mm stainless steel column packed with 5 µm ODS. The mobile phase used was a mixture of acetonitrile/water (85/15 v/v) flowing at a rate of 0.8 mL/min. The RAM used was a Radiomatic Flo-one-beta Model IC radioactivity flow detector.

The HPLC was coupled to a Finnigan-MAT model 4021 mass spectrometer via a Vestec thermospray (TSP) LC/MS interface. A shorter second column, a Perkin-Elmer 3 cm x 4.5 mm stainless steel column packed with 3 µm ODS, was used in order to shorten the analysis time. No other detector was attached to the HPLC when the instrument was used for LC/MS work. All other mass spectrometric data were obtained on a VG 7070EHF gas chromatograph/mass spectrometer (GC/MS).

Proton and carbon-13 nuclear magnetic resonance (NMR) spectra were obtained on a Varian EM-360 spectrometer and a Varian XL-200 spectrometer, respectively. All spectra were measured in deuterated chloroform.

Correspondence to: B. Y. Giang

Table 1. Summary of HPLC/ TSP/ NI-MS data for N-1386 and its soil metabolites.

Peak No.	Retention Time*, min	Mass spectral data m/z	Intensity	Interpretation	Identification
1	4.2	147	100	Cl_2-SO_2^-	
		149	70	(P+2) for 147	
		151	10	(P+4) for 147	
		181	8	Cl_3C-SO2-	
		183	10	(P+2) for 181	
		264	0	M-	Cl_2CH-SO_2-CCl_3 Pentachloro-dimethylsulfone
2	5.0	117	1	CCl_3^-	
		119	1	(P+2) for 117	
		181	80	$CCl_3SO_2^-$	
		183	100	(P+2) for 181	
		185	20	(P+4) for 181	
		298	0	M-	Cl_3C-SO_2-CCl_3 N-1386
3	15.8	128	100	S_4^-	
		130	10	(P+2) for 128	
		256	0	M-	S_8

* Data obtained using HPLC/UV equipped with Alltech column.

The N-1386 standard was obtained from the ZENECA reference standards collection. Pentachlorodimethyl sulfone was prepared by the hydrolysis of N-1386 in 2.5% aqueous NaOH solution. The structure of the product was confirmed by negative-ion chemical ionization (NICI) mass spectrometry [m/z (relative intensity) 185(5), 183(24), 181(24, Cl_3SO_2), 151(8), 149(67), 147(100, $CHCl_2SO_2$)], proton NMR (in $CDCl_3$; 7.10-CH), and carbon-13 NMR (in $CDCl_3$; 76.48-$CHCl_2$, 102.45-CCl_3).

A soil sample, which had been treated with carbon-14 labeled N-1386, was extracted twice with a 9:1 (v:v) mixture of acetonitrile:0.01 M KOH and then with 10 mL of acetonitrile. The extracts were combined, and aliquots of the combined solution were used for analysis.

RESULTS AND DISCUSSION

The positive-ion (PI) electron ionization (EI) and methane-chemical ionization (CH_4-CI) mass spectra of N-1386 resemble that of hexachloroethane and suggest the ejection of sulfur dioxide from the molecule. Such behavior makes it impossible to use PI mass spectrometry for the positive identification of this compound. Negative-ion chemical-ionization (NICI) spectrum of N-1386 shows fragments

which contain the SO_2 functional group. Since HPLC is the current method for the assay of this compound, HPLC/ thermospray (TSP)/ MS operated in the NI mode was used for the identification of the unknown metabolites.

Table 1 shows the retention data from the HPLC/ UV/ RAM analysis and the mass spectral data from the HPLC/ TSP/ NI-MS analysis of the extract of the soil sample containing N-1386 metabolites. The mass spectrum of the first peak suggested the structure of pentachlorodimethyl sulfone. This identity was further subtantiated by the good match when comparing its HPLC retention time, NI mass spectrum, and its GC retention time against those of the standard compound prepared as described in the meterials and methods section. The second peak was found to be N-1386 itself. The third peak was found to be elemental sulfur. GC/PI-EIMS results supported the presence of sulfur. Therefore, the two unknown soil metabolites of N1386 have been identified by HPLC/ TSP-MS to be pentachlorodimethyl sulfone and sulfur.

REFERENCES

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