Nuclear Magnetic Resonance Identification of New Sulfonic Acid Metabolites of Chloroacetanilide Herbicides

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The detection of the sulfonic acid metabolites of the chloroacetanilide herbicides acetochlor, alachlor, butachlor, propachlor, and, more recently, metolachlor in surface and ground water suggests that a common mechanism for dechlorination exists via the glutathione conjugation pathway. The identification of these herbicides and their metabolites is important due to growing public awareness and concern about pesticide levels in drinking water. Although these herbicides are regulated, little is known about the fate of their metabolites in soil. The sulfonic acid metabolites were synthesized by reaction of the parent compounds with an excess of sodium sulfite. Acetochlor, alachlor, butachlor, metolachlor, and propachlor and their sulfonic acid metabolites were studied by nuclear magnetic resonance spectroscopy and fast atom bombardment mass spectrometry. This paper provides a direct method for the preparation and characterization of these compounds that will be useful in the analysis and study of chloroacetanilide herbicides and their metabolites.

Keywords: *Chloroacetanilide metabolites; acetochlor; alachlor; metolachlor; propachlor*

INTRODUCTION

The use of chloroacetanilide herbicides for the control of some annual grasses and broadleaf weeds in crop and noncrop areas has increased in the United States since 1980 (Hogue, 1986). Although alachlor has had the most frequent use on corn and soybeans, the use of the other chloroacetanilide herbicides has increased, especially acetochlor and metolachlor. Recent pesticide monitoring studies have revealed the occurrence of alachlor sulfonic acid (alachlor ESA) in rural ground water at concentrations of 1.2−74 μg/L (Baker et al., 1993). The sulfonic acid derivatives of acetochlor (Breaux et al., 1987), alachlor (Feng, 1991), and propachlor (Sharp, 1988) are also major soil metabolites (Lebaron et al., 1988). Both alachlor and metolachlor are detoxified rapidly by nonsensitive plants via conjugation with glutathione and/or homoglutathione (Lamoreaux and Rusness, 1989). The glutathione conjugate degrades further to the sulfonic acid derivative of the herbicide as a metabolite. Although only a small fraction of the parent herbicide is actually transformed into these metabolites, a recent paper has shown that the sulfonic acid derivatives are highly leachable to ground water (Baker et al., 1993) and very persistent in surface waters (Goolsby et al., 1993). Although the herbicides are regulated in drinking water, their metabolites are not and, therefore, are a concern. Because the sulfonic acid derivatives are not commercially available for standards, this paper reports a straightforward method for the synthesis of the sulfonic acid derivatives from the parent herbicides and the characterization of these derivatives by nuclear magnetic resonance (NMR) spectroscopy and fast atom bombardment mass spectrometry (FAB MS).

MATERIALS AND METHODS

Acetochlor, alachlor, butachlor, metolachlor, and propachlor were purchased from Chem Services, West Chester, PA. All NMR experiments were performed on a GE QE-Plus (300.65 MHz ^{1}H operating frequency) or on a Bruker AM-500 NMR spectrometer (500.13 MHz ^{1}H operating frequency). Deuterated solvents were purchased from Sigma, St. Louis, MO (DMSO and D_2O) and Cambridge Isotope Laboratories, Andover, MA ($CDCl_3$). The NMR spectra were referenced against the residual proton signal of the deuterated solvent. ^{1}H−^{1}H chemical shift-correlated spectroscopy (COSY) was used to assign ^{1}H shifts and couplings. ^{13}C spectra were recorded with broadband proton decoupling at 75.6 MHz (GE QE-Plus) or 125.7 MHz (Bruker AM-500). ^{13}C−^{1}H heteronuclear chemical shift-correlated spectroscopy (HETCOR) was employed to assign the ^{13}C resonances via their attached protons. ^{1}H, ^{13}C, COSY, and HETCOR spectra were measured for all of the herbicides and their sulfonic acid metabolites. In some spectra multiple resonances are observed and attributed to the presence of rotamers. The ratio of rotamers reported for these compounds represents an average calculated from the ratios of relative integrals of all resolved proton pairs.

Positive-ion FAB MS analyses of the parent herbicides and negative-ion FAB MS analyses of the deuterated sulfonic acid derivatives were conducted on a Fisons/VG AUTOSPEC-Q tandem mass spectrometer. The sulfonic acid derivatives were prepared from deuterated solvents for the convenience of the NMR analysis and therefore give rise to a deuterated molecular ion. This deuteration is nonspecific and attributable to the exchangeable protons of the ESA derivatives.

Routine syntheses of the sulfonic acid derivatives in essentially quantitative yields were performed in two ways.

Method 1. This method was used for the preparation of the alachlor and metolachlor ESA derivatives as described previously (Aga et al., 1996). The parent herbicide was refluxed with an excess of Na_2SO_3 in 10% ethanol in water for 3−4 h or until a homogeneous mixture was obtained. The solution was acidified with concentrated H_2SO_4, and the product was extracted into methylene chloride. Following evaporation of the methylene chloride, the isolated crude product was recrystallized from hot ethanol. One problem encountered with this method for some of the ESA derivatives was the formation of an emulsion following pH adjustment to form and extract the sulfonic acid derivative. Another of the major drawbacks to this method was the demethylation of the ether moiety during the acidification with H_2SO_4.

Method 2. The second method eliminates the extraction step by synthesizing the sulfonic acid derivative using a slight

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excess of Na_2SO_3 in deuterated DMSO/D_2O (1:5) or in aqueous solution containing 10% of an organic modifier such as ethanol, methanol, or acetonitrile. The herbicide was refluxed in the solvent mixture for 5−24 h, after which time the reaction was complete. This procedure differs from method 1 described previously in that compounds were not desalted before NMR and FAB MS data were acquired. In the case of the deuterated DMSO/D_2O solution, the reaction mixture was analyzed directly. For the ESA derivatives prepared in aqueous solutions, the solvent was evaporated to dryness, and the residue was reconstituted in deuterated DMSO prior to NMR analysis.

Purified solid synthesized using method 2 may be obtained using the procedure described by Aga et al. (1996). Briefly, the crude reaction mixture is applied to a C_{18} Sep-Pak cartridge (Waters, Milford, MA) for the separation of the parent herbicides from their sulfonic acid derivatives. Any residue from the unreacted parent herbicide is eluted from the C_{18} cartridge with 3 mL of ethyl acetate. The Sep-Pak is then washed with methanol (3 mL) to recover the sulfonic acid reaction product. The purified sulfonic acid product can be recovered from the methanol fraction on evaporation of the solvent.

Acetochlor [2-Chloro-*N*-(ethoxymethyl)-*N*-(2-ethyl-6-methylphenyl)acetamide, Figure 1a]. The molecular ion by FAB MS is at 270 (M + 1). ^{1}H NMR ($CDCl_3$) δ 7.22−7.15 (m, H-3, 4, 5), 4.99 (dd, 2H, J = 9.5, H-12), 3.71 (q, 2H, J = 6.9, H-13), 3.68 (s, 2H, H-8), 2.54 (m, 2H, H-9), 2.22 (s, 3H, H-11), 1.22 (t, 3H, J = 7.7, H-10), 1.16 (t, 3H, J = 6.9, H-14); ^{13}C NMR ($CDCl_3$) δ 168.2 (C-7), 142.3 (C-1), 138.4, 136.6 (C-2,6), 129.6 (C-3,5), 127.6 (C-4), 79.1 (C-12), 66.4 (C-13), 42.5 (C-8), 24.0 (C-9), 18.8 (C-11), 15.6 (C-14), 14.8 (C-10).

Alachlor [2-Chloro-*N*-(2,6-diethylphenyl)-*N*-(methoxymethyl)acetamide, Figure 1b]. The molecular ion by FAB MS is at 270 (M + 1). ^{1}H NMR ($CDCl_3$) δ 7.30 (t, J = 7.6, 1H, H-4), 7.18 (d, J = 7.6, 2H, H-3,5), 4.90 (s, 2H, H-13), 3.66 (s, 2H, H-8), 3.46 (s, 3H, H-14), 2.54 (m, 4H, H-9,11), 1.20 (t, 6H, J = 8.1, H-10,12); ^{13}C NMR ($CDCl_3$) δ 168.4 (C-7), 142.1 (C-1), 137.7 (C-2,6), 129.7 (C-4), 127.4 (C-3,5), 80.9 (C-13), 58.4 (C-14), 42.5 (C-8), 24.2 (C-9,11), 14.8 (C-10,12).

Butachlor [*N*-(Butoxymethyl)-2-chloro-*N*-(2,6-diethylphenyl)acetamide, Figure 1c]. The molecular ion by FAB MS is at 312 (M + 1). ^{1}H NMR ($CDCl_3$) δ 7.28 (t, 1H, J = 7.7, H-4), 7.18 (d, 2H, J = 7.7, H-3, 5), 4.96 (s, 2H, H-13), 3.66 (s, 2H, H-8), 3.63 (t, 2H, J = 6.5, H-14), 2.54 (m, 4H, H-9,11), 1.49 (m, 2H, H-15), 1.31 (m, 2H, H-16), 1.19 (t, 6H, J = 8.1, H-10,12), 0.86 (t, 3H, J = 7.7, H-17); ^{13}C NMR ($CDCl_3$) δ 168.3 (C-7), 142.1 (C-1), 137.8 (C-2,6), 129.7 (C-4), 127.4 (C-3,5), 79.7 (C-13), 70.9 (C-14), 42.6 (C-8), 32.2 (C-15), 24.1 (C-9, 11), 19.6 (C-16), 14.8 (C-10, 12), 14.3 (C-17).

Metolachlor [2-Chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl)acetamide, Figure 1d]. The molecular ion by FAB MS is at 284 (M + 1). Rotamers (65:35) were observed in ^{13}C and ^{1}H NMR spectra at 20 °C. ^{1}H NMR ($CDCl_3$, 20 °C) δ 7.21 (t, 1H, H-4), 7.15 (d, 1H, H-3), 7.09 (d, 1H, H-5), 4.18 (m, 1H, H-12), 3.67−3.44 (2m, 2H, H-13a, 13b), 3.57 (35%), 3.56 (65%) (2s, 2H, H-8), 3.23 (65%), 3.20 (35%) (2s, 2H, H-14), 2.54 (m, 2H, H-9), 2.22 (35%), 2.18 (65%) (2s, 3H, H-11), 1.20 (t, 3H, J = 7.7, H-10), 1.09 (35%), 1.08-(65%) (2d, 3H, J = 7.7, H-15); ^{13}C NMR ($CDCl_3$) δ 167.2, 167.2 (C-7), 143.0, 142.9 (C-1), 137.47, 137.4, 137.3 (C-2,6), 129.4, 129.3, 129.3 (C-3,5), 127.3, 127.2 (C-4), 75.0 (C-13), 58.9 (C-14), 55.8, 55.7 (C-12), 43.2, 43.2 (C-8), 24.3, 24.0 (C-9), 19.3 (C-11), 15.9, 15.8 (C-15), 14.6, 14.3 (C-10).

Propachlor [2-Chloro-*N*-(1-methylethyl)-*N*-phenylacetamide, Figure 1e]. The molecular ion by FAB MS is at 212 (M + 1). ^{1}H NMR ($CDCl_3$) δ 7.45 (m, 3H, H-3, 4, 5), 7.15 (m, 2H, H-2, 6), 4.94 (sept, 1H, H-9), 3.67 (s, 2H, H-8), 1.05 (d, 6H, J = 7.5, H-10,11); ^{13}C NMR ($CDCl_3$) δ 165.9 (C-7), 137.4 (C-1), 130.6 (C-2,6), 129.9 (C-3,5), 129.4 (C-4), 47.6 (C-9), 43.1 (C-8), 21.1 (C-10,11).

Acetochlor ESA [2-[(2-Ethyl-6-methylphenyl)(ethoxymethyl)amino]-2-oxoethanesulfonic Acid]. Acetochlor (0.13 g, 0.48 mmol) and Na_2SO_3 (0.09 g, 0.7 mmol) were refluxed in 5 mL of D_2O and 0.5 mL of DMSO-d_6 for 4 h until a clear yellow solution was formed. The solution was allowed to cool to room temperature. The molecular ion by FAB MS of deuterated sulfonic acid was at 316 (M + 1). Rotamers (72:28) were observed in the ^{13}C and ^{1}H NMR spectra at 20 °C. ^{1}H NMR (D_2O) δ 7.47−7.24 (m, 3H, H-3, 4, 5), 5.20 (28%), 5.08 (72%) (2q, 2H, J = 11.5, H-12), 4.32 (28%), 3.71 (72%) (2s, 2H, H-8), 3.75 (72%), 3.64 (28%) (2q, 2H, J = 7.0 and 7.1, respectively, H-13), 2.43 (m, 2H, H-9), 2.27 (72%), 2.22 (28%) (2s, 3H, H-11), 1.24, 1.18 (28%) (m, 3H, H-14), 1.18 (m, 3H, H-10); ^{13}C NMR (D_2O) δ 171.0, 170.1 (C-7), 145.0, 144.6 (C-1), 140.8, 139.4, 138.9 (C-2,6), 132.3, 132.0, 131.9, 131.6, 130.1, 130.0 (C-3,4,5), 84.3, 80.6 (C-12), 69.4, 68.6 (C-13), 57.4, 56.3 (C-8), 26.4, 25.9 (C-9), 20.5, 20.2 (C-11), 17.1, 17.1, 17.0, 16.5 (C-10,14).

Alachlor ESA [2-[(2,6-Diethylphenyl)(methoxymethyl)amino]-2-oxoethanesulfonic Acid]. Alachlor (0.23 g, 1.0 mmol) and Na_2SO_3 (2.62g, 20.8 mmol) were refluxed in H_2O/EtOH (250 mL:25 mL) overnight until a clear solution was formed. The pH of the solution was reduced to approximately 1.5 by adding concentrated H_2SO_4. The resulting solution was extracted four times with approximately 100 mL of CH_2Cl_2. The CH_2Cl_2 was evaporated to dryness, and the product was recrystallized from CH_2Cl_2 layered with EtOH. The molecular ion by FAB MS of deuterated sulfonic acid was at 316 (M + 1). Rotamers (62:38) were observed in the ^{13}C and ^{1}H NMR spectra at 20 °C. ^{1}H NMR (DMSO/D_2O) δ 7.46−7.28 (m, 3H, H-3, 4, 5), 5.09 (38%), 4.98 (62%) (2s, 2H, H-13), 4.28 (38%), 3.64 (62%) (s, 2H, H-8), 3.44 (62%), 3.37 (38%) (2s, 3H, H-14), 2.43 (m, 4H, H-9,11), 1.11 (62%), 1.04 (38%) (2t, 6H, J = 7.5, H-10,12); ^{13}C NMR (DMSO/D_2O) δ 169.1, 168.4 (C-7), 142.8, 142.5 (C-1), 138.1, 137.9 (C-2,6), 130.4, 130.0 (C-3,5), 127.8, 127.8 (C-4), 83.9, 80.6 (C-13), 58.1, 57.3 (C-14), 55.2, 54.2 (C-8) , 24.4, 24.0 (C-9,11), 14.9, 14.4 (C-10,12).

Butachlor ESA [2-[(2,6-Diethylphenyl)(butoxymethyl)-amino]-2-oxoethanesulfonic Acid]. Butachlor (0.50 g, 1.6 mmol) and Na_2SO_3 (0.30 g, 2.4 mmol) were refluxed in H_2O/MeOH (9 mL:1mL) for 6 h until a clear solution was formed. The solution was evaporated to dryness and reconsituted in deuterated DMSO for NMR analysis. The molecular ion by FAB MS of deuterated sulfonic acid was at 358 (M + 1). Rotamers (55:45) were observed in the ^{13}C and ^{1}H NMR spectra at 20 °C. ^{1}H NMR (DMSO/D_2O) δ 7.36−7.05 (m, 3H, H-3, 4, 5), 5.10 (55%), 4.99 (45%) (2s, 2H, H-13), 4.24 (55%), 3.62 (45%) (2s, 2H, H-8), 3.58, 3.42 (2q, 4H, H-14), 2.60 (m, 4H, H-9,11), 1.50 (m, 2H, H-15), 1.25 (m, 2H, H-16), 1.22 (45%), 1.10 (55%) (2t, 6H, H-10,12), 0.84 (m, 3H, H-17); ^{13}C NMR (DMSO/D_2O) δ 168.9, 168.2 (C-7), 142.7, 142.4 (C-1), 138.1, 138.0 (C-2,6), 130.4, 129.9 (C-3,5), 127.8, 127.7 (C-4), 82.6, 79.3 (C-13), 71.4, 70.4 (C-14), 56.2, 55.3,(C-8), 31.6, 31.5 (C-15), 24.3, 24.0 (C-9,11), 22.0, 19.3 (C-16), 14.8, 14.3 (C-10,12), 13.8, 13.8 (C-17).

Metolachlor ESA [2-[(2-Ethyl-6-methylphenyl)(2-methoxy-1-methylethyl)amino]-2-oxoethanesulfonic Acid]. Metolachlor (0.54 g, 1.91 mmol) and Na_2SO_3 (2.53g, 20 mmol) were refluxed in H_2O/EtOH (270 mL:30 mL) for 5 h until a clear solution was formed. The pH of the solution was reduced to approximately 1.5 by adding concentrated H_2SO_4. The resulting solution was extracted six times with approximately 65 mL of CH_2Cl_2. The CH_2Cl_2 was evaporated to dryness, and the product was recrystallized from CH_2Cl_2 layered with EtOH. The molecular ion by FAB MS of deuterated sulfonic acid was 330 (M + 1). Rotamers (60:40) were observed in ^{13}C and ^{1}H NMR spectra at 20 °C. ^{1}H NMR (D_2O, 20 °C) δ 7.35 (m, 2H, H-3,5), 7.24 (m, 1H, H-4), 4.32 (m, 1H, H-13a), 3.74 (m, 1H, H-13b), 3.54 (s, 2H, H-8), 3.49 (m, 1H, H-12), 3.28 (60%), 3.25 (40%) (2s, 3H, H-14), 2.54 (m, 2H, H-9), 2.25 (40%), 2.23 (60%) (2s, 3H, H-11), 1.24 (t, 3H, J = 7.5, H-10), 1.12 (40%), 1.10 (60%) (2d, 3H, J = 7.0 and 6.6, respectively, H-15); ^{13}C NMR (D_2O) δ 167.9, 167.7 (C-7), 143.5, 143.4, (C-1), 138.1, 137.9, 137.6 (C-2,6), 129.8, 129.6, 129.5, 129.2 (C-3,5), 127.4, 127.3 (C-4), 75.1, 74.9 (C-13), 58.8, 58.7 (C-8), 55.4, 55.1, 54.9, 54.7 (C-14,12), 24.1, 23.9 (C-9), 18.9, 18.8 (C-11), 15.9, 15.7 (C-15), 13.9, 13.8 (C-10).

Propachlor ESA [2-[(Phenyl)(1-methylethyl)amino]-2-oxoethanesulfonic Acid]. Propachlor (0.50 g, 2.4 mmol) and Na_2SO_3 (0.30 g, 2.4 mmol) were refluxed in H_2O/CH_3CN(8 mL:2 mL) for 3 h until a clear solution was formed. The solution was evaporated to dryness and reconstituted in deuterated DMSO for NMR analysis. The molecular ion by FAB MS was at 256. ^{1}H NMR (DMSO and NaOD) δ 7.38 (m,

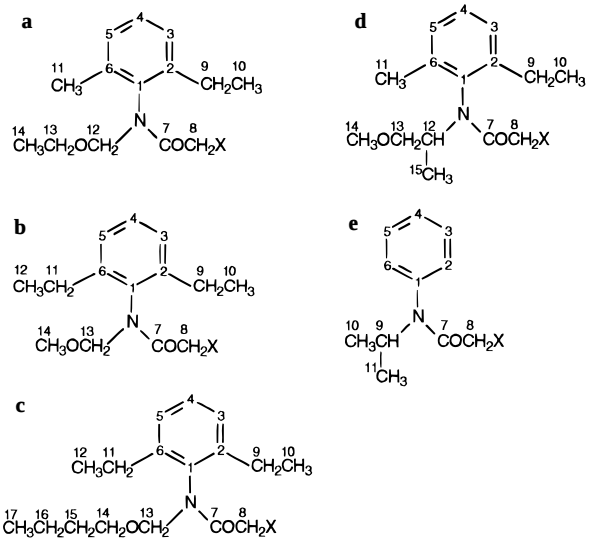

Figure 1. Numbering of proton and carbon atoms of acetochlor (a), alachlor (b), butachlor (c), metolachlor (d), and propachlor (e).

3H, H-3, 4, 5), 7.20 (m, 2H, H-2,6), 4.78 (sept, 1H, H-9), 3.10 (s, 2H, H-8), 0.91 (d, 6H, $J = 7.5$, H-10,11); ^{13}C NMR (DMSO + NaOD) δ 166.2 (C-7), 137.7 (C-1), 130.8 (C-2,6), 129.9 (C-3,5), 129.4 (C-4), 47.7 (C-9), 43.0 (C-8), 21.1 (C-10,11).

DISCUSSION

Figure 1 shows the general numbering scheme for the protons and carbons of the chloroacetanilide herbicides and their sulfonic acid derivatives used in this study. The assignment of the ^{1}H and ^{13}C NMR spectra of acetochlor, alachlor, butachlor, and propachlor was accomplished using one-dimensional and two-dimensional NMR techniques (COSY and HETCOR) to assign and confirm the identity of the proton and the carbon resonances of these compounds. Of the family of chloroacetanilide herbicides examined in this study, metolachlor is the only compound that has a significant population of two rotational isomers or rotamers at room temperature, as evidenced by the doubling of the resonances in the ^{1}H and ^{13}C NMR spectra. NMR is well suited for the detection of rotamers, which differ in their molecular structure but similarly give rise to identical molecular ions in their mass spectra. Moser et al. (1982) established that the rotational energy barrier around the phenyl−nitrogen bond for metolachlor is 154.3 kJ mol^{-1}. This energy barrier is due to the nonbonded pair of electrons of nitrogen that can form a π bond to the phenyl ring, resulting in a somewhat planar structure of the phenyl ring and the other nitrogen substituents. A more sterically favored conformation would place these nitrogen substituents perpendicular to the plane of the phenyl ring. These two conformations are electronically different and can be detected by NMR. In aqueous solutions at ambient pressure, it is not possible to heat metolachlor sufficiently to result in the coalescence of the proton and carbon resonances of the rotamers. An alternative explanation of the doubling of NMR resonances in metolachlor is magnetic inequivalence of the $COCH_2Cl$ protons as a result of the CH chiral center in the nearby isopropyl methyl ether substituent on the nitrogen. However, on the basis of the results we have obtained for the other ESA derivatives described below, we believe that the most likely explanation of these results is the presence of metolachlor rotamers.

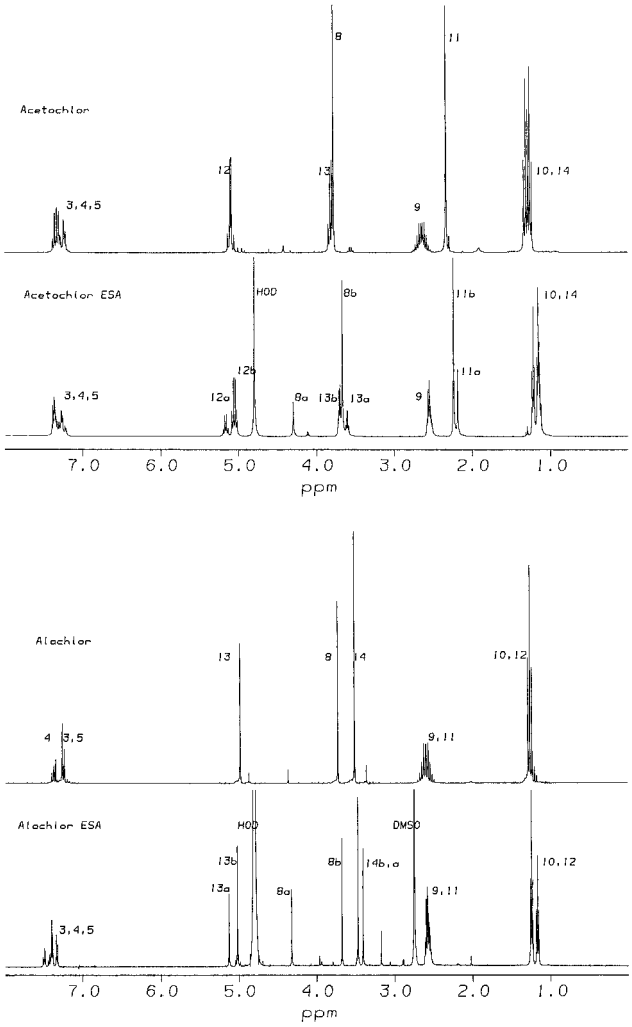

Figure 2. Proton NMR spectra of acetochlor (a), acetochlor ESA (b), alachlor (c), and alachlor ESA (d).

Unlike the parent herbicides, the NMR spectra of all of the sulfonic acid derivatives except for propachlor show evidence of significant populations of two rotamers at room temperature. Variable-temperature NMR studies of these compounds are being conducted to find the relative rates of interconversion. With the exception of propachlor, the observation of rotamers for the sulfonic acid derivatives of chloroacetanilide herbicides can be attributed to the increased bulkiness of the SO_3^- group relative to the chlorine atom in the parent compounds. The activity and the rate of metabolism of these herbicides may be directly affected by this rotational barrier and by chirality (Buser and Müller, 1995a,b). For example, metalaxyl, a related chiral fungicide, also forms rotamers and has one antipode that shows higher activity (Hubele et al., 1988). As in the parent compound, the doubling of resonances in the metolachlor ESA could be explained by magnetic inequivalence of the $COCH_2SO_3^-$ protons as a result of the CH chiral center in the nearby isopropyl methyl ether substituent on the nitrogen. However, this explanation is not possible for the butachlor, alachlor, and acetochlor derivatives, which contain no nearby chiral center. Because propachlor alone lacks substituents on the aromatic ring, the conspicuous absence of additional resonances in the NMR spectra of the propachlor ESA derivative further confirms the hypothesis that the rotamers in the other ESA derivatives arise as a result

of steric hindrance to rotation about the phenyl−nitrogen bond.

The utility of NMR for the molecular characterization of these herbicides and their sulfonic acid metabolites can be discerned by examination of the ^{1}H NMR spectra of alachlor, acetochlor, and their sulfonic acid metabolites shown in Figure 2. Acetochlor and alachlor are positional isomers with the same elemental composition. Therefore, these compounds give rise to identical molecular ions by mass spectrometry. In contrast, because NMR is extremely sensitive to electronic changes, the ^{1}H and ^{13}C spectra of these compounds contain significant differences. The presence of two rotamers in the solutions containing the acetochlor and alachlor ESA metabolites is clearly indicated by the doubling of resonances in the ^{1}H NMR spectra shown in Figure 2.

The current body of research on chloroacetanilide herbicides has used primarily mass spectral analysis and HPLC to identify these herbicides and their metabolites. NMR has not been used mainly due to the low level (parts per million) at which these metabolites are produced. However, Liu et al. (1991) used ^{1}H NMR and nuclear Overhauser effect (NOE) studies to characterize the other metabolites of metolachlor from bacteria cultures and to follow the rate of formation of these metabolites. However, their extraction procedure did not allow the isolation of highly polar metabolites, such as ESA, to be identified because they remained in the aqueous fraction of the culture medium. The combination of a solid-phase extraction procedure described previously (Aga et al., 1994) and the FAB MS and NMR techniques described here allowed us to identify and confirm the presence of ESA metabolites of chloroacetanilide herbicides in surface and ground water. Recently, Ciba Geigy announced introduction of a new herbicide formulation of metolachlor containing only one pair of isomers that provide the majority of herbicidal activity. This new formulation is intended to reduce the field-application rate of metolachlor, and it is expected to be approved for use by the U.S. Environmental Protection Agency in early 1997. The NMR method described here, which allows the measurement of different isomers of metolachlor and its ESA metabolite, will be an important tool in investigating the fate and behavior of this new isomeric form of metolachlor in the environment.

CONCLUSION

The recent detection of alachlor ESA in ground water samples in the midwestern United States and the detection of alachlor ESA in surface water (Thurman et al., 1996) show that this metabolite occurs frequently in water. Furthermore, the recent discovery of the metolachlor ESA (Aga et al., 1996) shows that the process of sulfonation of chloroacetanilide herbicides is an important process in agricultural soils. Because standards for the identification of these compounds are not available for environmental analysis, a method for their synthesis is timely and useful for studies of the environmental fate of chloroacetanilide herbicides in the environment. Although very similar in structure, the ESA derivatives were successfully characterized using NMR and FAB MS.

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