Metabolism of Two New Acylanilide Herbicides, Antor Herbicide (H-22234) and Dual (Metolachlor) by the Soil Fungus *Chaetomium globosum*

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We studied the metabolism of Antor herbicide [2-chloro-*N*-(2′,6′-diethylphenyl)-*N*-methyl(ethylcarboxylate)acetamide] and Dual [2-chloro-*N*-(2′-ethyl-6′-methylphenyl)-*N*-(2-methoxy-1-methylethyl)acetamide] by resting cells of *Chaetomium globosum*, a fungus previously shown to degrade the related herbicide, alachlor. Disappearance of the herbicides and production of products were followed by gas–liquid chromatographic analysis of the organic extract. At least ten products were observed with Antor herbicide as the substrate and at least eight with Dual. The products of Antor herbicide, identified by gas chromatography–mass spectrometry using electron and chemical ionization were: 2-chloro-*N*-(2′,6′-diethylphenyl)acetamide, 2-hydroxy-*N*-(2′-ethyl-6′-vinylphenyl)-*N*-methyl(ethylcarboxylate)acetamide, ethyl 7-ethyl-2,3-dihydroindoxyacetate, 2-chloro-*N*-(2′-ethyl-6′-vinylphenyl)-*N*-methyl(ethylcarboxylate)acetamide, and ethyl 2,6-diethylphenyliminoacetate. Compounds produced from Dual were: 2-chloro-*N*-(2′-ethyl-6′-methylphenyl)acetamide and 2-chloro-*N*-(2′-ethyl-6′-methylphenyl)-*N*-(2-hydroxy-1-methylethyl)acetamide. Generally, *C. globosum* removes one or both of the R groups from the nitrogen, dehydrogenates the ethyl substituent, and in some cases forms an indoline ring. It may also remove the chloro, methoxy, or ethoxy substituent from the R groups with subsequent hydroxylation at that position.

Antor herbicide [2-chloro-*N*-(2′,6′-diethylphenyl)-*N*-methyl(ethylcarboxylate)acetamide] and Dual [2-chloro-*N*-(2′-ethyl-6′-methylphenyl)-*N*-(2-methoxy-1-methylethyl)acetamide] are acylanilide herbicides structurally similar to the preemergence herbicide, alachlor (Lasso). Alachlor was previously shown to be degraded in soil (Beestman and Deming, 1974; Chou, 1974) and by a soil fungus, *Chaetomium globosum* (Taylor, 1972). Chou (1974) and Taylor (1972) found that very little of the ring-labeled alachlor was released as $^{14}CO_2$ by soils or *C. globosum*, respectively. Subsequent studies by Tiedje and Hagedorn (1975) showed that *C. globosum* degraded alachlor to six extractable products and released chloride ion. Four of the products were identified as: 2-chloro-*N*-(2′,6′-diethylphenyl)acetamide, 2,6-diethylaniline, *N*-(2-chloracetyl)-2,3-dihydro-7-ethylindole, and 2′,6′-diethyl-*N*-(methoxymethyl)aniline.

In this report, products of Antor herbicide and Dual produced by *C. globosum* were identified and a plausible pathway of breakdown presented. Comparison among the products of the three herbicides revealed similarities in metabolic attack on the herbicides and their intermediates. Dual will henceforth be referred to by its common name, metolachlor.

MATERIALS AND METHODS

Instrumental Analysis. Gas–liquid chromatographic (GLC) analysis was done on a Perkin-Elmer 900 gas chromatograph with a flame-ionization detector. Operating temperatures were: detector and injector, 220 °C; oven, 135–210 °C (3 °C/min) for programmed runs or at 210 °C for isothermal analysis of both compounds. Carrier gas flow rate was 30 mL/min. The column used was 2 m × 2 mm (i.d.) glass column, packed with 3% SP2100 on 100/120 mesh Supelcoport (Supelco, Inc., Bellefonte, Pa.).

Chemical and electron ionization mass spectra of the products were obtained with a Finnegan gas chromatograph–mass spectrometer (GC/MS). Either methane or isobutane was used for chemical ionization mass analysis (CI), while electron ionization (EI) was done with an ionizing voltage of 70 eV. A column comparable to the one described above was also used in the GC/MS units. The oven was programmed 125–250 °C at 4 °C/min.

Radioactivity was measured on a Packard Tri-Carb Scintillation Spectrometer, Model 3310. All samples were counted in Bray's solution (Bray, 1960) and were corrected for quenching by external standardization. The organic extracts were gently taken to dryness under a stream of dry air. The residue was redissolved in ethanol and counted in Bray's solution due to the high quenching caused by the extractant, Freon 113.

Reagents. Antor herbicide was obtained as formulation from Hercules, Inc., Wilmington, Del., and purified according to the method described for alachlor by Tiedje and Hagedorn (1975). The Antor herbicide was recovered as white needle-shaped crystals after concentrating the hexane extract in a flash evaporator and then freezing it. This procedure was repeated several times until the Antor herbicide was 99.9% pure by GLC analysis. ^{14}C ring- and carbonyl-labeled Antor herbicide were also provided by Hercules, Inc. The carbonyl label was located in the carbonyl of the chloracetyl moiety.

Metolachlor, a clear liquid, was provided as a formulation by Ciba-Geigy Corp., Agricultural Division, Greensboro, N.C. It could only be partially purified using the above extraction procedure. However, purification was achieved by eluting the partially purified metolachlor from Florisil columns. The reagent sequence for column elution was: (1) the column was conditioned with 50 mL of 1% methanol in benzene followed by 50 mL of petroleum ether; (2) 3 to 5 mL of the impure metolachlor sample was added; (3) the sample was eluted with 50 mL of petroleum ether followed by 200 mL of benzene–methylene chloride–acetonitrile (60:30:1). The impurities remained on the column or were largely eluted with the petroleum ether fraction while the last solvent system eluted the metolachlor. This purification procedure was repeated several times to remove most of the impurities. The metolachlor was 95% pure by GLC analysis.

Procedures. The pure culture of *C. globosum* was originally obtained from the culture collection of the late W. G. Fields, Department of Botany and Plant Pathology, Michigan State University. It was maintained by aseptic transfer on potato dextrose agar. This strain has been

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deposited in the American Type Culture Collection, accession number 34507. Mycelial pellets for resting cell experiments were obtained by growing the fungus in 500-mL flasks containing 250 mL of potato dextrose broth, incubated at 28 °C, on a rotary shaker. The pellets were harvested aseptically by vacuum filtration and washed two times with 125 mL of sterile, deionized water. The mycelia were then resuspended in a 500-mL flask containing 300 mL of 0.02 M phosphate buffer, pH 7.2, in which either 0.32 mM Antor herbicide or 0.35 mM metolachlor was dissolved. The herbicide solutions were sterilized by filtration through 0.22 μm Millipore filters prior to addition of the mycelia. Following suspension of the mycelia in the herbicide solution, the resting cells were returned to the rotary shaker and incubated at 28 °C.

Each resting cell experiment was composed of three flasks containing a herbicide solution with mycelia and two flasks containing only the herbicide solution as a control for nonbiological degradation. Another set of three flasks contained only mycelia suspended in a 0.02 M phosphate buffer, pH 7.2; this served as a control for nonherbicide derived products.

Analysis. In experiments using radioactive Antor herbicide, 6-mL samples were periodically removed for the following determinations: 1 mL was analyzed for total ^{14}C content while the remaining 5 mL was reserved for GLC analysis. Samples were frozen until all had been collected before proceeding with extraction and GLC analysis. The 5-mL portion was extracted two times with 2.5 mL of Freon 113 which contained an internal standard for GLC analysis. Antor herbicide was used as an internal standard for metolachlor experiments, while aldrin was used as an internal standard for Antor herbicide experiments. In experiments containing radioactive Antor herbicide, 1 mL each of the Freon and aqueous phases were assayed for ^{14}C content. The remaining portion of the 5-mL Freon extract was analyzed by GLC for disappearance of the Antor herbicide.

The fungus was removed from the remaining solution by vacuum filtration at the conclusion of the experiment, and the combined solutions from the replicates were extracted three times with Freon 113. The extract was concentrated in a flash evaporator and analyzed by GLC and GC/MS.

The chromatograms showing the Antor herbicide and metolachlor products were drawn from the total ion current observed following chromatographic separation of the components in the GC/MS unit. These peaks are identified by numbers which correspond to the numbers under the proposed structures in the subsequent figures. In the text the structures are also referred to by these numbers but are preceded by an "A" or "M" prefix to identify Antor herbicide and metolachlor products, respectively. The GC/MS data are presented as m/e followed in parentheses by the intensity of that fragment relative to the base peak (percent of base peak). Background was subtracted from all product data by using the data from scans of areas adjacent to the peaks. Structures were derived from the mass spectral data in accordance with what could be expected from the original herbicide (see Supplementary Material Available paragraph).

RESULTS

Metabolism of Antor Herbicide. There was almost no loss of radioactivity in the resting cell experiments using ^{14}C carbonyl- or ring-labeled Antor herbicide, indicating that very little label was released as CO_2. This agrees with the previous results with this fungus metabolizing ring-labeled alachlor where no $^{14}CO_2$ could be detected (Tiedje and Hagedorn, 1975; Taylor, 1972).

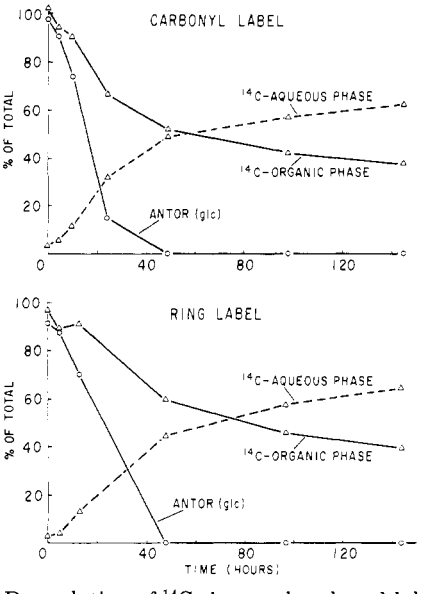

Figure 1. Degradation of ^{14}C ring- and carbonyl-labeled Antor herbicide by *C. globosum* in resting cell experiments. Antor herbicide degradation was also monitored by GLC analysis of the organic extract.

The loss of label from the organic phase and the subsequent increase in label in the aqueous phase is shown in Figure 1. Nearly identical results were obtained with ring- and carbonyl-labeled Antor herbicide. After 144 h of incubation, the organic phases had lost 40% of the ring and 37% of the carbonyl labels, while the aqueous phases had gained 54 and 52%, respectively. Gas–liquid chromatographic results from both ring- and carbonyl-labeled experiments indicated that the parent compound had disappeared after 48 h of incubation. Products were detected by GLC within 24 h. No products or substrate disappearance were noted in concentrated Freon extracts from control flasks containing Antor herbicide only, and no peaks appeared in chromatograms of concentrated extracts of controls where cells had been incubated in buffer without herbicide.

Initial GLC analysis of concentrated extracts of resting cell solutions containing Antor herbicide indicated that there were as many as ten extractable products (Figure 2). Separation of the later-eluting peaks was not adequate to obtain good GC/MS data, so the structures of those compounds were not determined. However, seven of the products could be identified; their structures are presented in Figure 3.

Products AI and AV both had a parent ion at m/e 233, by CI and EI, with no chlorine. Mass spectral data for AI were: 233 (11), 160 (100), 144 (7), 132 (49), 118 (11), 105 (28). Mass spectral data for AV were: 233 (20), 160 (100), 146 (80), 144 (22), 132 (64), 130 (66), 118 (29). At least six different isomers or structures derived from Antor herbicide could yield this parent mass. Three were definitely eliminated because their expected fragmentation patterns could not fit this fragmentation data. The most reasonable structures derived from these data were: ethyl 2,6-diethylphenyliminoacetate ($C_{14}H_{19}O_2N$) and ethyl 7-ethyl-2,3-dihydroindoxyacetate ($C_{14}H_{19}O_2N$). These are considered tentative identifications because the fragmentation evidence does not discount a third possibility, ethyl-*N*-(2′-ethyl-6′-vinylphenyl)glycine. This latter structure would be a logical product from Antor herbicide directly or from structure AVI. The first two structures, the imine and the indoline, were reported to be the correct identi-

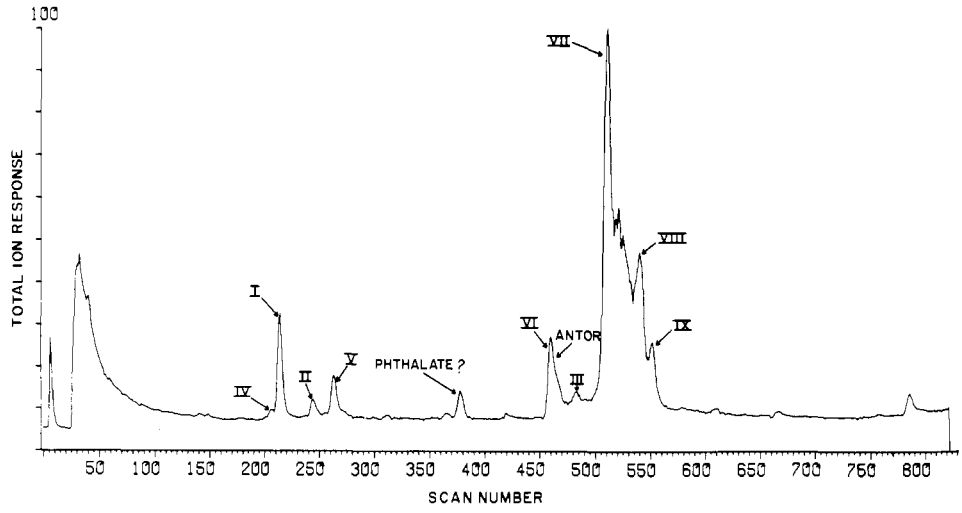

Figure 2. Gas–liquid chromatogram of the Antor herbicide products as they eluted through the GC/MS. Each peak is labeled with the number corresponding to the product (Figure 3) which was identified from the mass spectral data taken at that scan number.

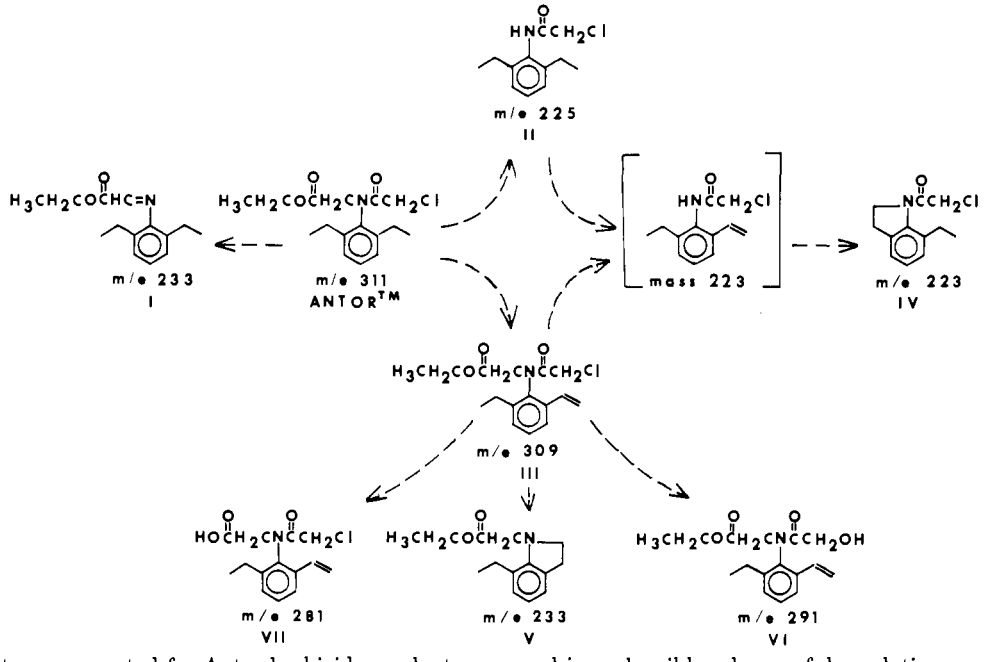

Figure 3. Structures suggested for Antor herbicide products arranged in a plausible scheme of degradation.

fication by Hercules chemists based on their GC/MS analysis of these products which we provided them and by comparison to the spectra of the imine which they had synthesized (Black, 1976). They had reported finding the imine (AI) as a photodegradation product. However, in this experiment the imine was not found as a component when Antor herbicide was incubated without cells. As all flasks were incubated in the dark, AI was not produced by light.

The parent peak for AII was found at m/e 225 with a P + 2 peak at m/e 227, indicating the presence of chlorine. This was confirmed by CI data. Mass spectral data were: 227 (3), 225 (9), 176 (100), 160 (5), 147 (22), 132 (12). This product was identified as 2-chloro-*N*-(2′,6′-diethylphenyl)acetamide ($C_{12}H_{16}ONCl$), which is also a major metabolite in the degradation of alachlor (Tiedje and Hagedorn, 1975), where it was termed demethoxymethylalachlor (DMM). AII had the same retention time in GLC as did the DMM derived from alachlor.

The EI data obtained for peak AIII was somewhat obscured by background, though the major fragments could be discerned. The parent mass was confirmed by CI as m/e 309; the compound contains chlorine. Mass spectral data were: 309 (3), 273 (9), 232 (7), 188 (16), 186 (16), 160 (100), 158 (45). The compound appears to be 2-chloro-*N*-(2′-ethyl-6′-vinylphenyl)-*N*-methyl(ethylcarboxylate)acetamide.

Product AIV had a parent peak at m/e 223, determined by CI and EI, and definitely contained chlorine as shown by the large P + 2 peak at m/e 225. Mass spectral data were: 225 (8), 223 (26), 210 (8), 208 (25), 174 (43), 146 (100). This fragmentation pattern is identical with that of the indoline formed by *C. globosum* during degradation of alachlor (Tiedje and Hagedorn, 1975), which was: 225 (21), 223 (66), 210 (15), 208 (45), 174 (60), 146 (100). The retention time of this compound in GLC was identical with that of the indoline from alachlor. Thus this indoline, *N*-chloroacetyl-2,3-dihydro-7-ethylindole ($C_{12}H_{14}ONCl$), is also a product of Antor herbicide.

Product AVI was formed by dechlorination and subsequent hydroxylation of the Antor herbicide molecule. The parent peak was m/e 291 by CI and EI data, and the compound does not contain chlorine. Mass spectral data were: 291 (1), 273 (11), 248 (11), 218 (14), 188 (14), 176 (34), 174 (46), 160 (100). The only suitable structure found whose mass corresponded to the parent mass and which

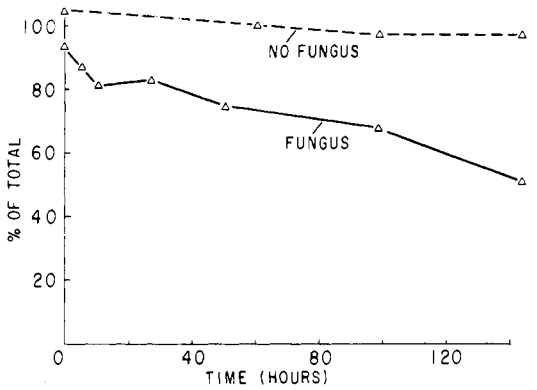

Figure 4. Degradation of metolachlor by resting cells of *C. globosum*. Metolachlor degradation was monitored by GLC analysis of the organic extract.

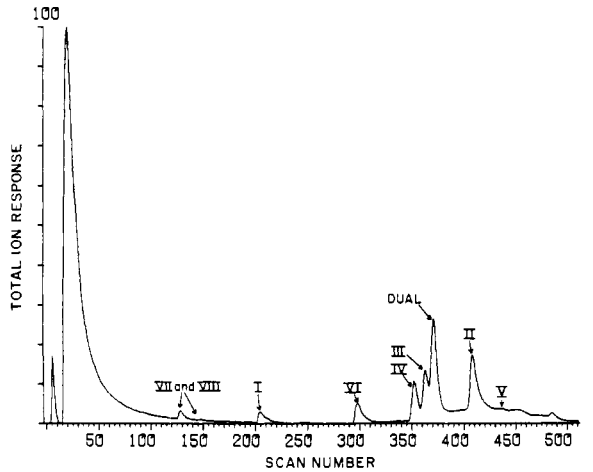

Figure 5. Gas-liquid chromatogram of the metolachlor products as they eluted through the GC/MS. Each peak is labeled with the number corresponding to the product (Figure 6) which was identified from the mass spectral data taken at that scan number.

could produce this fragmentation pattern was 2-hydroxy-*N*-(2′-ethyl-6′-vinylphenyl)-*N*-methyl(ethylcarboxylate)acetamide ($C_{16}H_{21}O_4N$). Although masses 248 and 188 do not fit possible fragmentation schemes for this compound, they could be background from the Antor herbicide peak and perhaps peak AIII, as these peaks were not well separated (Figure 2).

An interesting product, AVII, was apparently formed by the cleavage of the ethyl moiety at the ester linkage, forming an acid, and dehydrogenation of the 6′-ethyl group. This compound has a mass of 281, determined by CI and EI, and has chlorine. Mass spectral data were: 283 (1), 281 (4), 232 (3), 204 (5), 202 (12), 188 (26), 186 (19), 160 (100). The structure derived from this data was *N*-(2-chloroacetyl)-*N*-(2′-ethyl-6′-vinylphenyl)glycine ($C_{15}H_{20}O_2NCl$). This was the most abundant product detected from Antor herbicide.

There appear to be two unresolved peaks eluting after AVII which could not be interpreted. Peak AVIII may have a parent ion of *m/e* 309, while peak AIX may have a parent ion of *m/e* 325. Both peaks contain chlorine. Chemical ionization data for both peaks also contained *m/e* 282 which was probably due to tailing from peak AVII.

Chemical ionization data and coinjection of Antor herbicide with the product peaks showed that Antor herbicide eluted approximately at scan number 467 (Figure 2), but was not resolved from peak AVI.

Metabolism of Metolachlor. As shown in Figure 4, GLC analysis showed disappearance of metolachlor when incubated with resting cells but no loss from the control which contained no mycelia. After 144 h incubation with cells, only 55% of the metolachlor remained. Gas–liquid chromatographic analysis of the concentrated extract from the resting cell experiment showed that at least eight extractable products were resolved (Figure 5). The proposed structures for these products are shown in Figure 6.

Metolachlor product MI had a parent mass of 211, and a strong P + 2 peak, indicating that chlorine was present. Mass spectral data were: 213 (3), 211 (8), 162 (100), 147 (9), 134 (20), 120 (25). This compound was identified as 2-chloro-*N*-(2′-ethyl-6′-methylphenyl)acetamide and corresponds to the demethoxymethylalachlor formed from both alachlor and Antor.

MII had a parent mass at *m/e* 269 (present by CI only) and contained chlorine. Mass spectral data were: 240 (9), 238 (25), 211 (2), 162 (100). The only structure derived from metolachlor which could fit these data is 2-chloro-*N*-(2′-ethyl-6′-methylphenyl)-*N*-(2-hydroxy-1-methylethyl)acetamide.

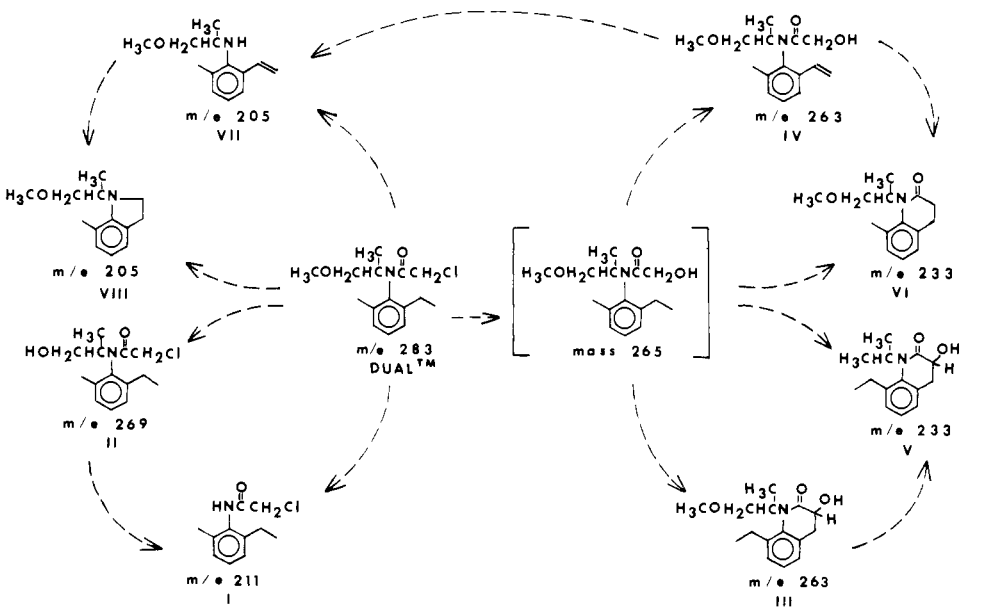

Figure 6. Structures suggested for metolachlor products arranged in a plausible scheme of degradation.

MIII and MIV had identical parent peaks determined by CI only as m/e 263; neither compound had a chlorine moiety. Mass spectral data for MIII were: 218 (20), 191 (22), 160 (100). The structure which best fits these data is 8-ethyl-3-hydroxy-*N*-(2-methoxy-1-methylethyl)-2-oxo-1,2,3,4-tetrahydroquinoline ($C_{15}H_{21}O_3N$). Mass spectral data for MIV were: 218 (19), 191 (11), 174 (10), 160 (100). The structure which best fits these data is 2-hydroxy-*N*-(2′-methyl-6′-vinylphenyl)-*N*-(2-methoxy-1-methylethyl)acetamide ($C_{15}H_{21}O_3N$). These two structures can be concluded from the data but it is less certain as to which of the two peaks each structure corresponds.

MVI shows a parent peak at m/e 233, with no indication of a chlorine moiety. This was confirmed by CI data. Mass spectral data were: 233 (42), 218 (11), 204 (12), 188 (38), 161 (95), 160 (60), 146 (100). The peak for MV also has a parent ion at m/e 233, but there was no confirming CI data. Mass spectral data for MV were: 233 (4), 218 (18), 191 (17), 160 (100). A structure whose fragmentation and mass correspond to the data for MVI is 8-methyl-*N*-(2-methoxy-1-methylethyl)-2-oxo-1,2,3,4-tetrahydroquinoline ($C_{14}H_{19}O_2N$), while the structure which best fits the data for MV is 8-ethyl-3-hydroxy-*N*-isopropyl-2-oxo-1,2,3,4-tetrahydroquinoline.

Peaks MVII and MVIII both had parent peaks of m/e 205. Mass spectral data for MVII were: 205 (10), 175 (5), 160 (100), 145 (28), 144 (12), 132 (11), 130 (6); for MVIII they were: 205 (5), 160 (100), 145 (36), 144 (28), 132 (27), 130 (18). Of several possible structures, two compounds appear to be likely choices: *N*-(2-methoxy-1-methylethyl)-*N*-(2′-methyl-6′-vinyl)aniline ($C_{13}H_{19}ON$) and *N*-(2-methoxy-1-methylethyl)-7-methyl-2,3-dihydroindole ($C_{13}H_{19}ON$). A third possibility is 8-methyl-*N*-(1-hydroxyethyl)-2-oxo-1,2,3,4-tetrahydroquinoline ($C_{12}H_{15}O_2N$), although the expected fragmentation for this compound would not yield a m/e 145 component, a fragment which was found in both scans. The quinoline could be formed from further breakdown of MVI.

Metolachlor was eluted at scan number 372. The parent peak for metolachlor was visible only by CI. Mass spectral data were: 240 (9), 238 (28), 213 (1), 211 (5), 162 (100).

DISCUSSION

The structures of Antor herbicide and metolachlor products were derived from GC/MS data only. Although the structures can only be confirmed by comparison of our data with that of actual compounds or by further spectral analysis of purified products, we believe that these data are adequate for identification. Though the products identified probably are metabolites formed by fungal metabolism, we can not rule out nonbiological alterations of intermediates which could occur in solution or during extraction and analysis. However, if such reactive intermediates do exist they could be expected to react with other organic compounds in nature.

We believe the Antor herbicide products having masses 225 (AII), 309 (AIII), 291 (AVI), and 281 (AVIII) are firmly identified. Considering that the compounds had to be derived from Antor herbicide, there were, in these cases, no other possible structures which could fit the fragmentation data. The structure of AIV is presumed to be the indoline because comparison of this product with the breakdown product of alachlor showed identical retention times and fragmentation patterns. Additional evidence for the biological formation of the indoline was recently obtained by Chou (1977). He showed that the indoline peak collected from the GLC effluent had the same R_f values on TLC as did the uninjected material. Thus GLC conditions did not cause ring closure.

Antor herbicide products I and V are a bit more tentatively identified as the imine and the indoline on the basis of these data alone, although Black (1976) concluded that the identity of AI and AV as shown in Figure 5 is correct. In this case the imine, discovered by Hercules chemists as a product of photodegradation, may also be a biodegradation product.

We consider metolachlor products having masses 211 (MI), 269 (MII), and 263 (MIII and MIV) to be firmly identified. The structures corresponding to the products having mass 233 (MV and MVI, Figure 6) were selected because their expected fragmentation pattern fit the data exactly. Also, MV and MVI appear to be logically derived from compounds III and IV, respectively. The alternatives would be *N*-(2-methoxy-1-methylethyl)-6-ethyl-2-oxindole and 8-methyl-*N*-(2-methoxy-1-methylethyl)-2-methyl-1,2,3,4-tetrahydroquinoline. The former compound (oxindole) is similar to MVIII, except that it has a ketone group on the two position, beside the nitrogen. Its fragmentation may fit the data, but it seems more likely to expect a m/e 147 rather than m/e 146, which was found, if this compound were fragmented. In the degradation scheme (Figure 6), this oxindole would have to be derived from the compound labeled mass 265 by removal of the hydroxymethyl and coupling to the methyl on the ring. This also seems rather unlikely as most RNC(O)R bonds (i.e., peptides) are broken or formed between the nitrogen and carbonyl moieties, not between the carbonyl and the "R" group.

Formation of the latter compound, another quinoline, would also require an unlikely metabolic reaction. The structure resembles MVI (Figure 6) except that the ketone is replaced by a methyl and a hydrogen. The fungus would have to remove the entire chloracetyl group and add an ethyl or remove the methyl chloride and the ketone oxygen and add a methyl; neither possibility seems plausible biochemically.

Scan numbers (SN) 129 and 148 (peaks MVII and MVIII, Figure 5) are very similar except that SN 148 has more background; it is unclear as to whether m/e 91 (tropilium ion) is real or is background. Both scans have a parent peak at m/e 205. This is important in that an alternative structure having mass 205, *N*-(2-methoxy-1-methylethyl)-2-oxindole, seems incapable of producing the tropilium, considering the expected fragmentation pattern. This compound would be an extremely unusual product for the fungus to produce as it lacks the 6′-methyl on the phenyl. Considering the known products which were extracted from the medium, the fungus had apparently not removed any group from the ring, although it dehydrogenated the ethyl moiety to form a vinyl on both the metolachlor and Antor rings. This dehydrogenation is also a proposed reaction in the pathway of alachlor to indoline. This particular oxindole, then, is considered to be a very unlikely metolachlor product. It does not easily fit into the degradation scheme without several manipulative reactions. The last alternative structure having m/e 205 which could produce the appropriate fragmentation is *N*-(2′-ethyl-6′-methylphenyl)-*N*-(2-methoxy-1-methylethyl)imine, similar in structure to Antor herbicide product AI (Figure 3). This seems unlikely as a biologically formed product and apparently is not formed via photodegradation as there were no peaks in metolachlor control flasks incubated without mycelium.

The Antor herbicide and metolachlor products are arranged in plausible schemes of degradation (Figures 3 and 6). The arrows between the compounds indicate

possible routes of degradation. Hypothetical intermediates which were not recovered are in brackets. A general pattern of metabolism of these two new herbicides and alachlor by *C. globosum* has emerged. The general transformations which occur are: (1) Dehalogenation with hydroxylation: MIV, AVI; postulated but not observed for alachlor. (2) Dehydrogenation of the 6′-ethyl: MIV, MVII, AIII, AVI, AVII; also postulated but not observed for alachlor. (3) Dealkylation: (a) from the nitrogen, MI, MVII, AI, AII; AII is also formed from alachlor (demethoxymethylalachlor), as well as formation of 2′,6′-diethylaniline; (b) demethoxylation, leaving hydroxyl, MII; (c) deethoxylation, leaving hydroxyl (acid), AVII. (4) Dealkylation and ring formation: (a) indoline formation, MVIII, AIV, AV; AIV is also formed from alachlor; (b) oxoquinoline formation, MIII, MV, MVI.

With respect to known products, Antor herbicide is unique from alachlor and metolachlor in the formation of AVII where the ethoxy moiety is removed and an acid is formed. Similarly, formation of the three quinolines, MII, MV, and MVI, from metolachlor is a reaction unique to this herbicide. MIII is formed from the coupling of the hydroxyacetyl group with the 6′-methyl on the ring to form the oxoquinoline. Further paring of the 2-methoxy-1-methylethyl group forms the isopropyl moiety, thus MV. MVI could be formed from MIV by removal of the hydroxyl and subsequent ring formation.

Formation of an imidazole has also been observed in the degradation of isopropalin (2,6-dinitro-*N*,*N*-dipropylcumidine) in field soil (Golab and Althaus, 1975). This imidazole is structurally similar to the indoline but contains two nitrogens in the one and three positions. To our knowledge formation of the oxoquinoline is a previously undiscovered transformation.

Since approximately 50% of the Antor herbicide and alachlor products and probably some of the metolachlor products remain in the aqueous fraction after extraction, it would be of interest to determine what further types of transformations occur to cause these compounds to become water soluble. This is especially important since water-soluble products would more likely leach through soil. Recently Chou (1977) has shown several polar products from both alachlor and Antor herbicide in pyrophosphate extracts of soil. He has also reported evidence for binding of intermediates of these herbicides to soil organic matter. Some of these bound intermediates could be derivatives of the products reported in this paper.

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Supplementary Material Available: Mass spectral data used to determine the structures of Antor herbicide and metolachlor (Dual) (4 pages). Ordering information is given on any current masthead page.

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