Identification of Degradation Products of Terbutol in Environmental Water from Golf Courses

Toshinari Suzuki,*,† Kumiko Yaguchi,† Kazuo Ohnishi,† and Tetsuya Suga‡

Tama Branch Laboratory, Tokyo Metropolitan Research Laboratory of Public Health, 3-16-25 Shibazaki-cho, Tachikawa, Tokyo 190, Japan, and Department of Clinical Biochemistry, Tokyo College of Pharmacy, 1432-1 Horinouchi, Hachioji, Tokyo 192-03, Japan

Degradation products of terbutol (2,6-di-*tert*-butyl-4-methylphenyl *N*-methylcarbamate) in drainage and ground water from golf courses, on which terbutol had been applied as a herbicide, were identified by capillary GC/MS and reversed-phase HPLC. Terbutol and 4-carboxy-, *N*-demethyl-, and 4-carboxy-*N*-demethylterbutol were detected in all water samples at concentrations of parts per billion levels. In addition, 4-(hydroxymethyl)- and 4-formylterbutol, 2,6-di-*tert*-butyl-4-methylphenol (BHT), and 4-(hydroxymethyl)-, 4-formyl-, and 4-carboxy-BHT were observed in some water samples at concentrations of parts per thousand levels. These results demonstrated that terbutol applied on golf courses was mainly degraded by *N*-demethylation, oxidation of the 4-methyl group, and hydrolysis of the carbamate ester linkage.

Keywords: *Terbutol; 2,6-di-tert-butyl-4-methylphenyl N-methylcarbamate; identification; degradation*

INTRODUCTION

Water pollution by insecticides, fungicides, and herbicides, which are applied on golf courses in Japan, has become of interest in recent years. Contaminant levels of those compounds in drainage from golf courses have been reported by many researchers (Tsuji et al., 1991; Noguchi et al., 1991; Terasawa et al., 1991). Diazinon and fenitrothion (insecticides), isoprothioran and flutoluanil (fungicides), and simazine, mecoprop, and terbutol (herbicides) were frequently detected in drainage from golf courses at concentrations from parts per thousand (ppt) to parts per billion (ppb) levels.

Terbutol (2,6-di-*tert*-butyl-4-methylphenyl *N*-methylcarbamate) is a herbicide belonging to the phenylcarbamate family (Aizawa, 1989). A commercially available herbicide, Azak, containing terbutol (40%) and 2-methyl-4-chlorophenoxyacetohydrazide (30%), has been used on golf courses in Japan for controlling crab grass, goose grass, and broadleaf weeds in turf grass on the fairway and in the rough. In our laboratory, contaminant levels of insecticides, fungicides, and herbicides in ground water and drainage from golf courses in Tokyo have been investigated by GC/MS and HPLC/UV analysis of CH_2Cl_2 extracts of the waters and by HPLC/fluorescence detector (HPLC/FD) analysis after derivatization with 9-anthryldiazomethane (ADAM) of acidic CH_2Cl_2 extracts of the waters (Suzuki and Watanabe, 1992). In the case of the ground water and drainage containing terbutol, several unknown peaks were observed on the GC/MS, HPLC/UV, and HPLC/FD chromatograms. The investigation of degradation products of terbutol has been scarcely reported. Kumar et al. (1975) reported the photolysis of terbutol by UV irradiation at 265 nm in ethanol, indicating that one hydrolysis compound 2,6-di-*tert*-butyl-4-methylphenol (BHT), and two rearrangement compounds, 3,5-di-*tert*-1-methyl-4-oxo-2,5-cyclohexadiene-*N*-methylcarboxamide and 2,5-di-*tert*-butyl-3-methyl-6-hydroxy-*N*-methylbenzamide, were produced.

This paper reports the identification of new degradation products of terbutol in drainage and ground water from golf courses treated with terbutol, leading to the proposal of a possible degradation pathway.

EXPERIMENTAL PROCEDURES

Materials. 9-Anthryldiazomethane (ADAM) was provided by Funakoshi Co., Tokyo. BHT, 2,6-di-*tert*-butyl-4-(hydroxymethyl)phenol (4-hydroxymethyl-BHT), and 2,6-di-*tert*-butyl-4-formylphenol (4-formyl-BHT) were purchased from Tokyo Chemical Industry, Tokyo, Japan. 2,6-Di-*tert*-butyl-4-carboxyphenol (4-carboxy-BHT) was obtained from Aldrich Chemical Co., Milwaukee, WI. Terbutol was purchased from GL Science, Tokyo. The purity of these compounds was more than 98%, and GC/MS data are listed in Table 1.

Preparation of Comparison Compounds. The following *N*-methylcarbamates were synthesized with the corresponding phenols, methyl isocyanate, and triethylamine in dimethylformamide for 12 h at room temperature according to the method of Douch and Smith (1971), after which time the reaction mixture was diluted with distilled water or acidified water at pH 1.5. The desired products were isolated by partitioning into ether from the water phase, evaporating the ether extract, and recrystallization from benzene. The products were as follows. 2,6-Di-*tert*-butyl-4-formylphenyl *N*-methylcarbamate (4-formylterbutol): ^{1}H NMR ($CDCl_3$) δ 1.36 (s, 18H), 2.88 and 3.05 [d, 3H, ratio of 3:1, J = 5.0 Hz, the former signal is the methyl protons *cis* to the carbamyl and the latter signal is the methyl protons *trans* to the carbamyl; Keith and Alford, 1970)], 5.12 (brs, 2H), 7.81 (s, 2H), 9.93 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 27.8, 31.1, 35.7, 128.0, 133.2, 144.8, 153.6, 155.2, 192.1; IR (KBr) 1720, 2960, 3350 cm^{-1}. 2,6-Di-*tert*-butyl-4-carboxyphenyl *N*-methylcarbamate (4-carboxyterbutol): ^{1}H NMR (acetone-d_6) δ 1.36 (s, 18H), 2.81 and 3.05 [d, 3H, ratio of 10:1, J = 5.0 Hz, refer to 4-(hydroxymethyl)-terbutol], 8.00 (s, 2H); ^{13}C NMR (acetone-d_6) δ 27.8, 31.5, 36.2, 127.7, 128.3, 144.7, 153.7, 156.4, 167.8; IR (KBr) 1700, 2960, 3350 cm^{-1}. Similar procedures were used to prepare 2,6-di-*tert*-butyl-4-(hydroxymethyl)phenyl *N*-methylcarbamate [4-(hydroxymethyl)terbutol] except that the product obtained by 4-hydroxymethyl-BHT, *tert*-butyl-dimethylsilyl chloride, and imidazole in dimethylformamide was used as a corresponding

* Author to whom correspondence should be addressed.

† Tokyo Metropolitan Research Laboratory of Public Health.

‡ Tokyo College of Pharmacy.

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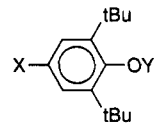
Table 1. GC/MS Data and Retention Times (t_R) of Chemically Synthesized Terbutol and Several Degradation Products[a]



peak no.	X	Y	mass, m/z (% intensity) M+	M+ − Y + 1	base peak	t_R (min)
5	$-CH_3$	−H	220 (26.7)		205 (100), 177 (14.3), 161 (5.7), 145 (14.3), 105 (10.5), 57 (28.6)	7.33
1	$-CH_3$	$-CONHCH_3$	277 (0.3)	220 (49.5)	205 (100), 177 (9.5), 161 (5.7), 145 (7.6), 105 (7.6), 57 (24.8)	10.22
9	$-CH_3$	$-CONH_2$	263 (1.1)	220 (40.0)	205 (100), 177 (11.4), 161 (6.7), 145 (10.5), 105 (8.6), 57 (25.7)	10.47
8	$-COOCH_3$	−H	264 (24.8)		249 (100), 233 (15.2), 221 (25.7), 205 (7.6), 115 (10.5), 57 (16.2)	9.90
4	$-COOCH_3$	$-CONHCH_3$	321 (0.1)	264 (28.6)	249 (100), 233 (10.5), 221 (16.2), 205 (6.7), 115 (6.7), 57 (18.1)	13.64
10	$-COOCH_3$	$-CONH_2$	307 (0.1)	264 (20.0)	249 (100), 233 (12.4), 221 (22.9), 205 (7.6), 115 (8.6), 57 (25.7)	14.02
7	−CHO	−H	234 (27.6)		219 (100), 191 (39.0), 175 (11.4), 159 (6.7), 115 (8.6), 57 (23.8)	9.42
3	−CHO	$-CONHCH_3$	ND[b]	234 (36.2)	219 (100), 191 (27.6), 175 (8.6), 159 (3.8), 115 (6.7), 57 (27.6)	12.62
6	$-CH_2OH$	−H	236 (23.8)		221 (100), 193 (14.3), 161 (9.5), 147 (12.4), 115 (6.7), 57 (26.7)	9.49
2	$-CH_2OH$	$-CONHCH_3$	293 (0.2)	236 (45.7)	221 (100), 193 (10.5), 161 (7.6), 147 (10.5), 115 (6.7), 57 (33.3)	13.24

[a] Ten nanograms of each compound was injected into GC/MS. [b] ND, less than 0.1%.

phenol. The desired product was obtained by desilylation with 1 N HCl in methanol after ether extraction and evaporation and was then recrystallized from benzene: ^1H NMR ($CDCl_3$) δ 1.32 (s, 18H), 2.04 (s, 1H), 2.84 and 2.98 (d, 3H, ratio of 3:1, J = 5.0 Hz, refer to 4-formylterbutol), 4.56 (s, 2H), 5.08 (brs, 1H), 7.24 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 27.7, 31.3, 35.5, 65.5, 125.0, 137.2, 143.2, 147.6, 156.0; IR (KBr) 1720, 2950, 3300 cm^{-1}.

The following carbamates were synthesized with the corresponding phenols and sodium isocyanate in dimethylformamide by adding trifluoroacetic acid dropwise according to the method of Loev and Kormendy (1973). The reaction mixture was diluted with distilled water or acidified water at pH 1.5. The desired product was obtained by partitioning into ether from the water phase and evaporating the ether extract. For 2,6-di-*tert*-butyl-4-methylphenyl carbamate (*N*-demethylterbutol), further purification was performed by silica gel column chromatography (10 mm i.d. × 10 cm), first with 200 mL of *n*-hexane−benzene (90:10 v/v) to remove BHT, second with 100 mL of ethyl acetate to elute the objective compound, and by recrystallization from benzene. ^1H NMR ($CDCl_3$) δ 1.36 (s, 18H), 2.30 (s, 3H), 7.09 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 21.5, 31.4, 35.4, 127.0, 134.5, 142.6, 145.8, 156.5; IR (KBr) 1740, 2950, 3350 cm^{-1}. For 2,6-di-*tert*-butyl-4-carboxyphenyl carbamate (4-carboxy-*N*-demethylterbutol), the ether extract was applied on reversed-phase HPLC [Lichrosorb RP-18, Merck, 7 μm, 10 mm i.d. × 25 cm; solvent, CH_3CN−0.02% H_3PO_4 (25:75 v/v), 4 mL/min; UV 240 nm]. The desired compound was extracted with ether from the eluent at a retention time of 3.5−4.5 min. ^1H NMR (acetone-d_6) δ 1.39 (s, 18H), 8.00 (s, 2H); ^{13}C NMR (acetone-d_6) δ 31.5, 36.2, 127.6, 128.4, 144.7, 156.1, 160.3, 167.7; IR (KBr) 1720, 2960, 3400 cm^{-1}.

GC/MS data of the chemically synthesized compounds mentioned above are listed in Table 1.

Sampling of Drainage and Ground Water. The drainages from five golf courses (A−E) in Tokyo and one ground water sample from golf course E, at a depth of about 10 m beside a pond into which drainage flowed, were collected (Table 2). Azak, containing 40% terbutol and 30% 2-methyl-4-chlorophenoxyacetohydrazide, had been applied last on the fairway and rough of the five gold courses in 1991. The total amount of Azak used was from 2 to 120 kg per treatment, and its concentration was about 0.8 g/m^2 (Table 2).

Preparation of Sample. *Dichloromethane (CH_2Cl_2) Extract.* A 1000 mL water sample with 50 g of sodium chloride added was extracted twice with 100 mL of CH_2Cl_2 by vigorously shaking the sample for 5 min. The CH_2Cl_2 was dehydrated with Na_2SO_4 and concentrated to about 10 mL with a rotary evaporator at 40 °C. *n*-Hexane was added to the CH_2Cl_2 extract and reconcentrated to 1 mL with a rotary evaporator and a stream of nitrogen gas (N_2). The resulting solution was analyzed by GC/MS and HPLC/UV.

Acidic CH_2Cl_2 Extract and Derivatization. A 1000 mL water sample acidified with hydrochloric acid to pH 2 was extracted twice with 100 mL of CH_2Cl_2 by vigorously shaking the sample for 5 min. The CH_2Cl_2 was dehydrated with Na_2SO_4 and concentrated to 5 mL with a rotary evaporator at 40 °C. For GC/MS analysis, a 2.5 mL portion of the acidic CH_2Cl_2 solution was evaporated to dryness under a stream of N_2 and reacted with 1 mL of 0.1 N HCl in methanol at 50 °C for 12 h. The methylated compounds were extracted with 1 mL of *n*-hexane. The *n*-hexane solution was concentrated to 0.25 mL. For HPLC/fluorescence detector (HPLC/FD) analysis, a 0.5 mL sample of the acidic CH_2Cl_2 solution was evaporated to dryness under a stream of N_2 and reacted with 0.25 mL of 0.05% ADAM in acetone according to the previous method (Suzuki and Watanabe, 1992).

Table 2. Sample Collection and Treatment with Azak at Golf Course

golf course	sample	collection time	treatment with Azak time	amt (kg)	area (m^2)
A	drainage	Jan 1993	May 1991	16	19 500
			Oct 1991	16	19 500
B	drainage	Jan 1993	Nov 1991	36	55 000
C	drainage	Jan 1993	May 1991	89	89 000
D	drainage	Jan 1993	April 1991	26	33 000
			Sept 1991	4	5 500
E	drainage ground water	May 1992	May 1991	120	150 000

Apparatus and Conditions. GC/MS analysis was performed with an HP5890 Series II gas chromatograph (Hewlett-Packard) and a TRIO-1000 mass spectrometer (VG MassLab) at an ionization potential of 70 eV, an ionization current of 150 μA, and ion source temperature of 200 °C. The temperatures of the GC injector and transfer line were 220 and 250 °C, respectively. The column head pressure was 40 kPa, and the carrier gas was helium. The injection volume was 1 μL with splitless injection. The GC oven temperature was programed as follows: held at 50 °C for 1 min, increased from 50 to 180 °C at 20 °C/min and from 180 to 270 °C at 4 °C/min. The analytical column used was a DB-5 capillary column, 0.25 mm i.d. × 15 m, film thickness 0.25 μm (J&W Scientific).

HPLC analysis was performed with an LC800 system (Jasco, Tokyo) equipped with a C-R4A integrator (Shimadzu, Kyoto). For the analysis of the CH_2Cl_2 extract, a UV detector was set at 260 nm and an analytical column, an Ultrasphare ODS, 0.46 mm i.d. × 25 cm (Beckman) was used. The mobile phase was acetonitrile−water (75:25 v/v), and its flow rate was 1 mL/min. The injection volume was 25 μL. For the analysis of the ADAM derivatives of the acidic CH_2Cl_2 extract, the fluorescence detector was set at an excitation of 365 nm and an emission of 412 nm, and the column over temperature was set at 40 °C. The analytical column was a TSKgel ODS 120T, 0.46 mm i.d. × 25 cm (Tosoh, Tokyo). The mobile phase was acetonitrile−water (70:30 v/v), and its flow rate was 1 mL/min. The injection volume was 25 μL.

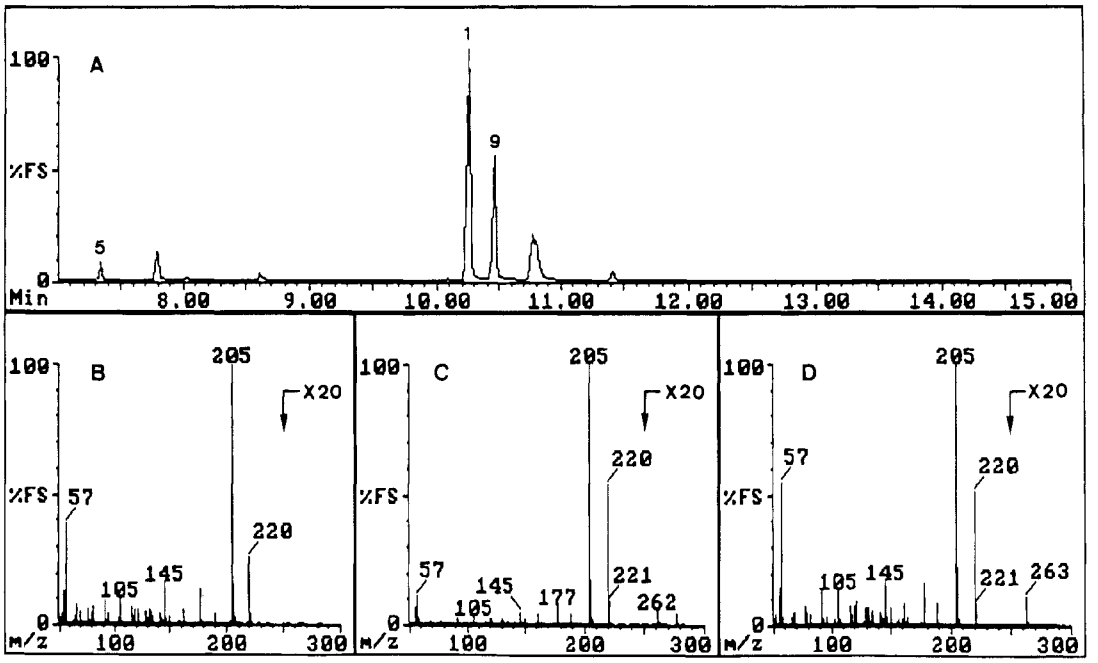


Figure 1. (A) GC/MS chromatogram of the CH_2Cl_2 extract of a ground water sample. GC/MS spectra: (B) Peak 5; (C) peak 1; (D) peak 9.

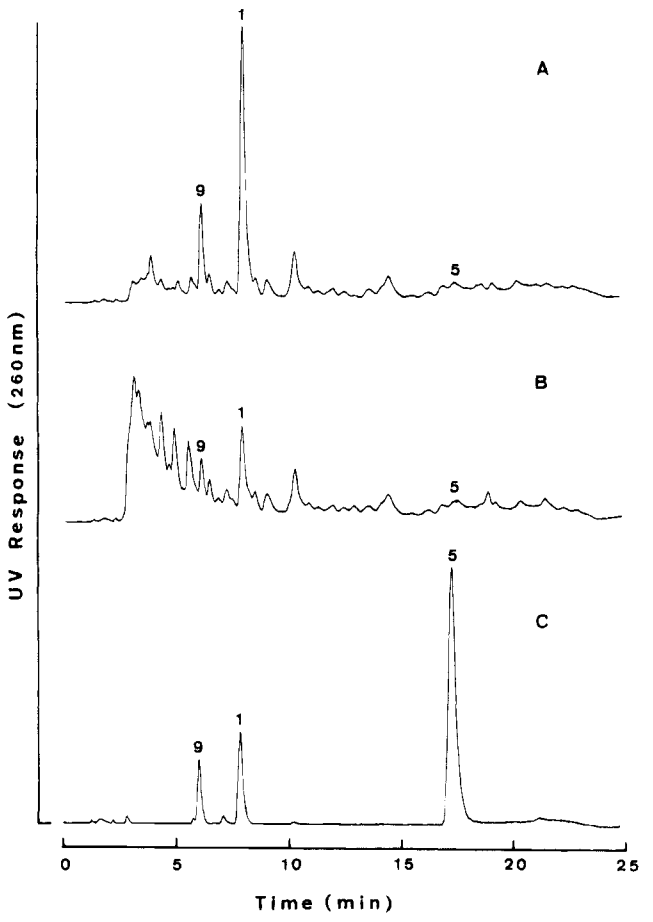


Figure 2. HPLC/UV chromatograms of the CH_2Cl_2 extracts: (A) ground water; (B) drainage; (C) chemically synthesized standards.

Infrared spectra were measured on an IR-810 spectrometer (Jasco) with a KBr pellet. ^1H and ^{13}C NMR spectra were obtained by a JNM-A500 FT NMR system (JEOL, Tokyo) at 500 MHz for ^1H NMR and at 125 MHz for ^{13}C NMR. The spectra of $CDCl_3$ or acetone-d_6 solutions were obtained in 5 mm o.d. NMR tubes with tetramethylsilane as the internal standard.

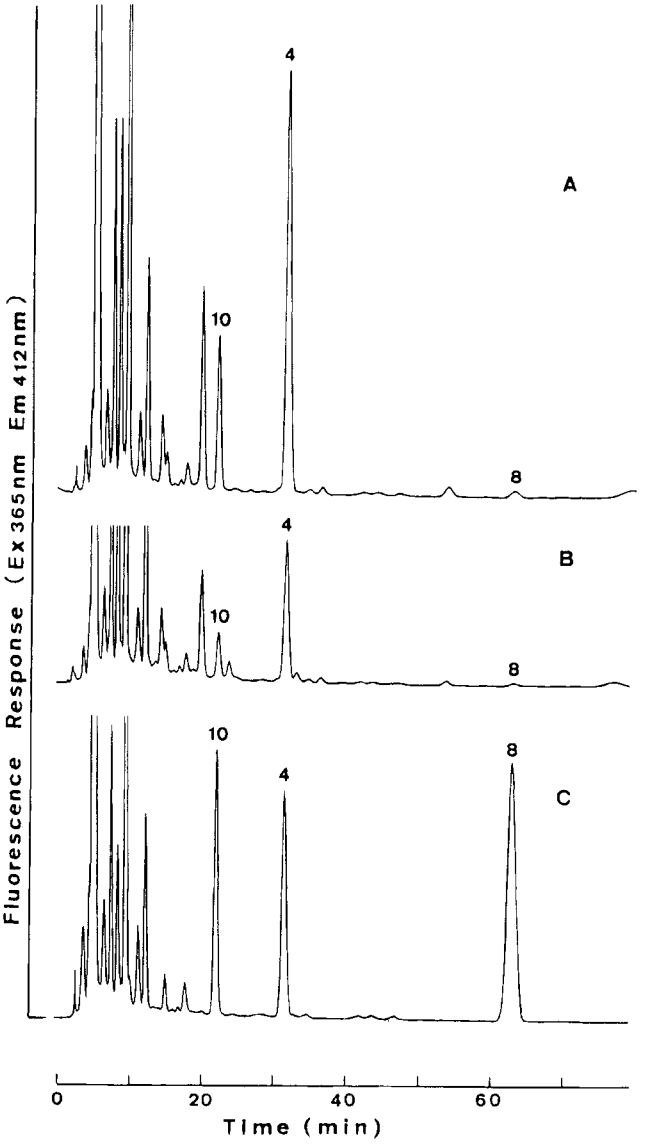


Figure 3. HPLC/FD chromatograms of the ADAM derivatized CH_2Cl_2 extracts: (A) ground water; (B) drainage; (C) chemically synthesized standards.

Table 3. Terbutol and Several Degradation Products in Drainage and Ground Water at Golf Courses A–E

	concentration of compounds (ppb)									
drainage	peak 5[a] (0.1)[b]	peak 1[a] (0.1)	peak 9[a] (0.1)	peak 8[a] (0.1)	peak 4[a] (0.1)	peak 10[a] (0.1)	peak 7[a] (0.01)	peak 3[a] (0.02)	peak 6[a] (0.05)	peak 2[a] (0.1)
A-1	0.1	2.7	0.3	0.1	4.4	1.0	0.01	0.03	ND	ND
A-2	ND[c]	0.7	0.3	0.3	1.4	0.5	ND	ND	ND	ND
B	0.1	1.8	0.6	ND	1.9	0.6	0.01	0.03	ND	ND
C	ND	1.8	0.3	0.1	4.7	1.1	0.06	0.03	ND	ND
D-1	ND	3.1	1.0	0.1	7.9	1.8	ND	ND	ND	ND
D-2	ND	3.2	0.5	0.1	6.5	1.6	0.01	0.11	ND	0.4
E-1	0.1	11.5	6.8	0.4	15.3	3.8	0.01	0.07	0.05	0.3
E-2[d]	0.3	35.8	14.3	0.6	38.2	12.6	0.05	0.13	0.05	0.1

[a] Numbers refer to Figure 6. [b] Detection limits shown in parentheses. [c] ND, lower than detection limits. [d] Ground water.

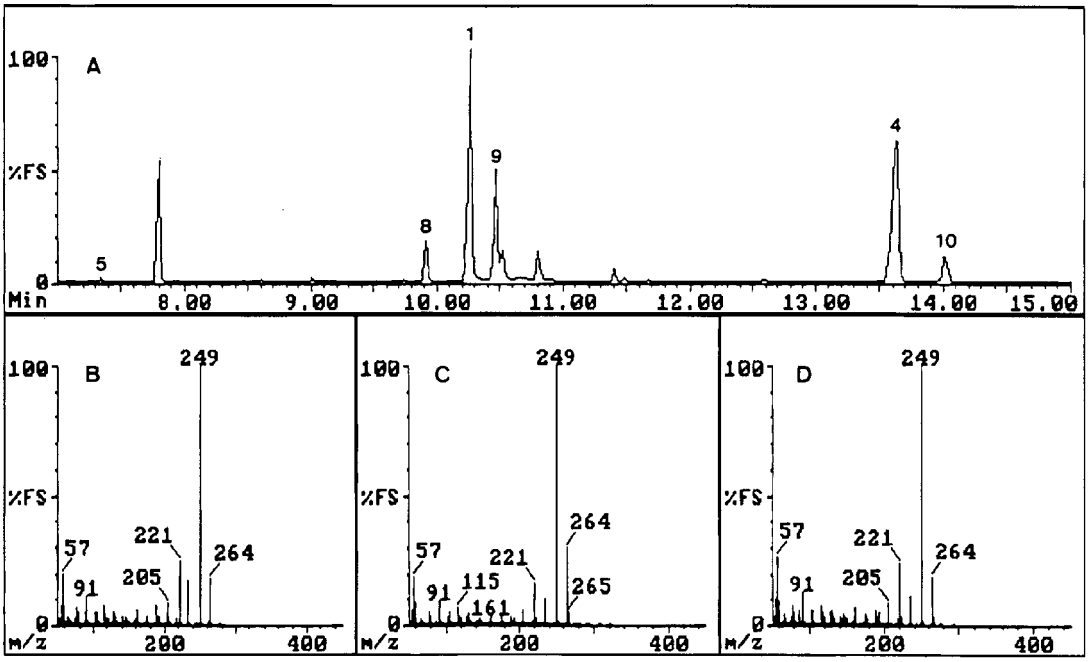


Figure 4. (A) GC/MS chromatogram of the methylated CH_2Cl_2 extract of a ground water sample. GC/MS spectra: (B) peak 8; (C) peak 4; (D) peak 10.

RESULTS

Major Metabolities of Terbutol in CH_2Cl_2 Extract. The CH_2Cl_2 extract of the ground water beside a pond, into which the drainage of a golf course flowed, was analyzed by GC/MS at scanning range from *m/z* 50 to 450 for 0.5 s. As shown in Figure 1A, terbutol (peak 1) and peaks 5 and 9 were detected. Major fragment ions of peak 5 were obtained at *m/z* 220, 205, 177, 145, 105, and 57, and a molecular ion (M^+) was observed at *m/z* 220 (Figure 1B). For peak 9, major fragment ions were obtained at *m/z* 220, 205, 177, 145, 105, and 57, and M^+ was observed at *m/z* 263 (Figure 1D). The fragmentations of the two compounds were similar to terbutol, of which the molecular ion was *m/z* 277 (Figure 1C). These results suggested that peaks 5 and 9 were BHT and *N*-demethylterbutol, respectively. The retention times and fragmentations of peaks 5 and 9 were similar to those of chemically synthesized BHT and *N*-demethylterbutol, respectively, as shown in Table 1. In addition, terbutol, BHT, and *N*-demethylterbutol were detected in the sample when the CH_2Cl_2 extract was analyzed by reversed-phase HPLC/UV as shown in Figure 2A,C. The concentrations of BHT and *N*-demethylterbutol in the ground water calculated by HPLC/UV were identical with those by GC/MS (Table 3).

Two rearrangement products of terbutol reported by Kumar et al. (1975), 3,5-di-*tert*-butyl-1-methyl-4-oxo-2,5-cyclohexadiene-*N*-methylcarboxamide and 2,5-di-*tert*-butyl-3-methyl-6-hydroxy-*N*-methylbenzamide, showed M^+ at *m/z* 277 and were identified by the GC/flame ionization detector. These compounds were not detected in the CH_2Cl_2 extract of the ground water.

Major Metabolites of Terbutol in Acidic CH_2Cl_2 Extract. The acidic CH_2Cl_2 extract of the ground water, in which terbutol, BHT, and *N*-demethylterbutol were detected, was analyzed by reversed-phase HPLC/FD after derivatization with ADAM. Peaks 4, 8, and 10 were detected on the chromatogram as shown in Figure 3A. These compounds contain a carboxyl group in the molecular structure because ADAM reacts with a carboxyl group, and those three peaks did not appear on the HPLC/FD chromatogram when the acidic CH_2Cl_2 extract of the ground water was injected. The screening method for the nine phenoxy acid herbicides (2,4-D, 2,4-DP, 2,4,5-DB, MCPA, MCPP, MCPB, 2,4,5-T, 2,4,5-TP, and 2,4,5-TB) was previously reported (Suzuki and Watanabe, 1992). Peaks 4, 8, and 10 were not the nine acid herbicides and the fatty acids (*n*-butyric, *n*-caproic, and *n*-caprylic acid). As shown in Figure 3A,C, the retention times of peaks 4, 8, and 10 were in good agreement with those of the chemically synthesized compounds 4-carboxyterbutol, 4-carboxy-BHT, and *N*-demethyl-4-carboxyterbutol, respectively.

The acidic CH_2Cl_2 extract was subjected to methylation with 0.1 N HCl in methanol and then analyzed by GC/MS at scanning range from *m/z* 50 to 450 for 0.5 s. Terbutol (peak 1), BHT (peak 5), and *N*-demethylterbutol (peak 9) were detected, and additionally peaks 4,

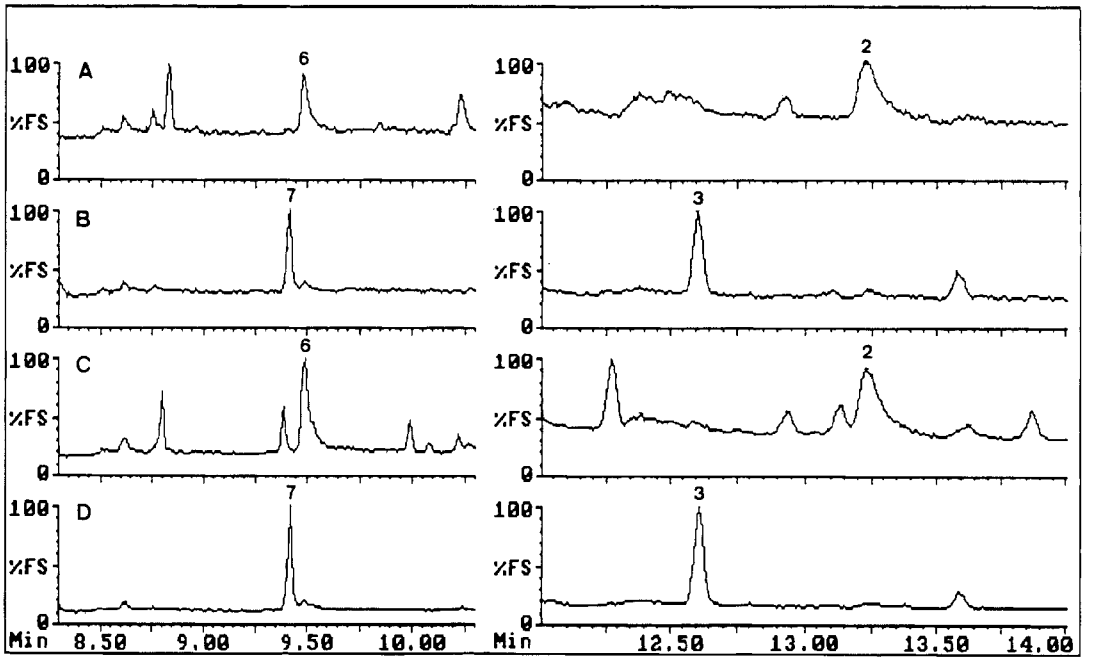


Figure 5. GC/MS/SIM chromatograms of the CH_2Cl_2 extract of a ground water sample: (A) *m/z* 236; (B) *m/z* 234; (C) *m/z* 221; (D) *m/z* 219.

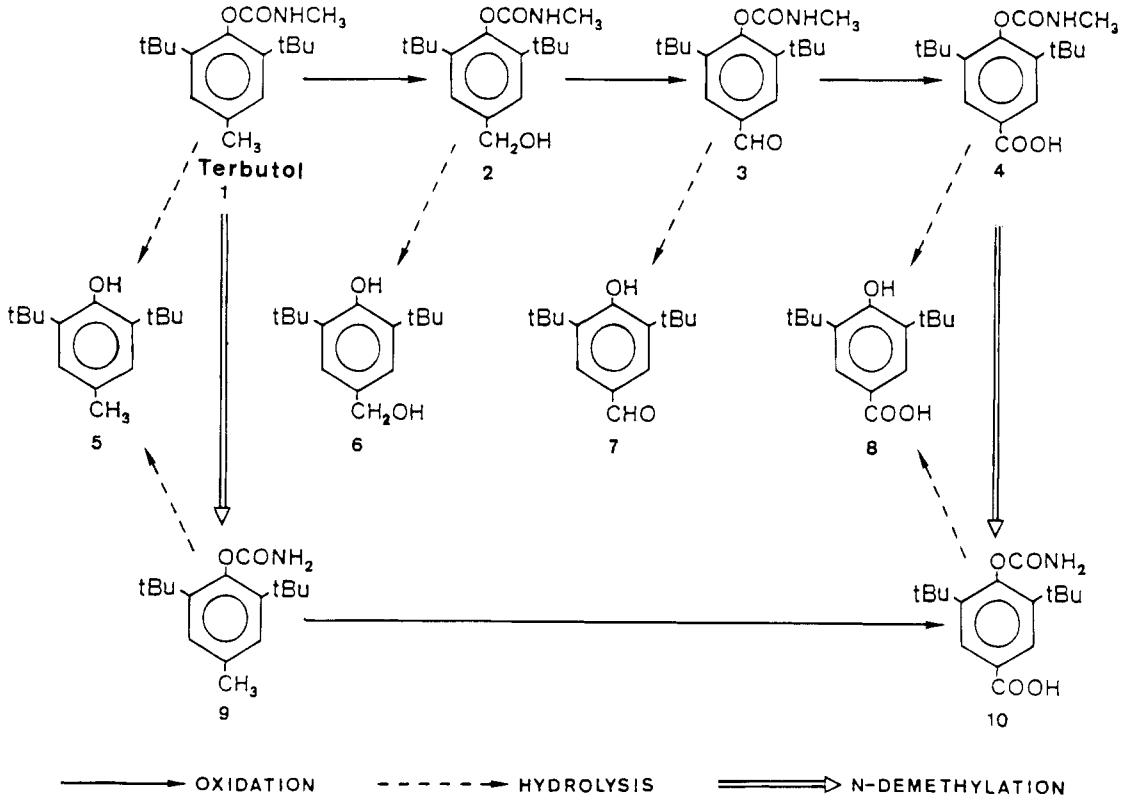


Figure 6. Proposed degradation pathway of terbutol at golf course.

8, and 10 appeared on the GC/MS chromatogram as shown in Figure 4A. Major fragment ions of peaks 4, 8, and 10 were observed at *m/z* 57, 205, 221, 249, and 264, indicating that the structures of the three compounds were similar (Figure 4C,B,D). The retention times and mass fragmentations of peaks 4, 8, and 10 were in good agreement with those of the chemically synthesized compounds 4-carboxyterbutol, 4-carboxy-BHT, and *N*-demethyl-4-carboxyterbutol, respectively, as shown in Table 1. The concentrations of the three compounds in the ground water calculated by GC/MS were identical with those by HPLC/FD (Table 3). *N*-Hydroxymethyl derivatives of *N*-methylcarbamate decomposed to the corresponding carbamates under acidic conditions (Ogawa et al., 1977). Some of the 4-carboxy-*N*-demethylterbutol detected in the acidic CH_2Cl_2 may be 4-carboxy-*N*-(hydroxymethyl)terbutol.

Oxidative Intermediates of Terbutol and Their Hydrolysis Products. The intermediates in the oxidation process, 4-(hydroxymethyl)- and 4-formylterbutol, and their hydrolysis compounds, 4-hydroxymethyl- and 4-formyl-BHT, were examined. These compounds were not detected on the chromatogram of the CH_2Cl_2 extract of the ground water by GC/MS in the scan mode and HPLC/UV. Therefore, single ion monitoring (SIM) was applied to the detection of the objective compounds.

Chemically synthesized 4-(hydroxymethyl)terbutol and 4-hydroxymethyl-BHT appeared as the fragment ions of 45.7 and 23.8% at *m/z* 236, respectively, and the base peak was at *m/z* 221 as shown in Table 1. Chemically synthesized 4-formylterbutol and 4-formyl-BHT appeared as the fragment ions of 36.2 and 27.6% at *m/z* 234, respectively, and the base peak was at *m/z* 219 as shown in Table 1. The monitor ions for these compounds were set at 219, 221, 234, and 236. The GC/MS/SIM chromatogram of the CH_2Cl_2 extract of the ground water is shown in Figure 5. Peaks 3 and 7 appeared on the chromatograms of *m/z* 219 and 234, and those retention times were the same as those of chemically synthesized 4-formylterbutol and 4-formyl-BHT. In addition, the ratios of the peak intensity of *m/z* 234 to that of *m/z* 219 were 33.2% for peak 3 and 24.9% for peak 7. Peaks 2 and 6 also appeared on the chromatograms of *m/z* 221 and 236, and those retention times were the same as those of chemically synthesized 4-(hydroxymethyl)terbutol and 4-hydroxymethyl-BHT, respectively. The ratios of the peak intensity of *m/z* 236 to that of *m/z* 219 were 44.6% for peak 2 and 20.0% for peak 6. From these results, peaks 2, 3, 6, and 7 were identified as 4-(hydroxymethyl)terbutol, 4-formylterbutol, 4-formyl-BHT, and 4-hydroxymethyl-BHT, respectively.

Concentrations of Terbutol and Its Metabolites in Drainage from Golf Courses. Terbutol and its degradation products in drainage from the five gold courses were investigated. Figures 1B and 3B show the chromatograms of the extract of the drainage. The concentrations of those compounds in the drainage are listed in Table 3. Terbutol, *N*-demethyl-, 4-carboxy-, and *N*-demethyl-4-carboxyterbutol were detected at concentrations of ppb levels in all drainage samples. In addition, the concentrations of 4-carboxyterbutol were higher than that of terbutol in any drainage. On the other hand, the oxidative intermediates, 4-(hydroxymethyl)- and 4-formylterbutol, appeared in some drainage samples at concentrations of ppt levels. The hydrolysis products of terbutol and its oxidative products were also found in some drainage samples at concentrations of ppt levels.

DISCUSSION

Several alkylphenyl *N*-methylcarbamates are used as insecticides, fungicides, and herbicides. The transformation of those pesticides by soil, plants, insects, soil fungi, and mammals (Cheng and Casida, 1973; Douch and Smith, 1971; Ogawa et al., 1976, 1977; Ohkawa et al., 1974; Suzuki and Takeda, 1976) includes modification as follows: (1) oxidation of the alkyl substituent to form alcohol, aldehyde, and carboxylic acid derivatives; (2) hydrolysis of the carbamate ester linkage to form the corresponding phenols; and (3) *N*-demethylation of the *N*-methyl group to form the corresponding carbamates via *N*-hydroxymethyl derivatives. The results obtained in this study show that terbutol applied on the golf course was degraded in a manner similar to that of the alkylphenyl *N*-methylcarbamates already investigated. Tentative degradation pathways for terbutol are given in Figure 6.

Terbutol and 4-carboxy-, *N*-demethyl-, and 4-carboxy-*N*-demethylterbutol were detected at concentrations of ppb levels in the drainage and ground water even after 1 or 2 years when terbutol was applied. On the other hand, the residual data obtained in our laboratory for pesticides such as diazinon, isoprothiofrsn, flutoluanil, and mecoprop show that these pesticides were frequently detected in the drainage at concentrations of ppb levels after the pesticide treatment but disappeared from the drainage within 1 or 2 months, and in addition, these pesticides did not contaminate the ground water. Further investigations of the degradation of terbutol in soil or by grass and permeation of terbutol and its degradation products in drainage and ground water from the soil at golf courses are necessary to explain the characteristic behavior of terbutol.

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