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Isolation of a New Organochlorine Pollutant 2,3,3,3,2′,3′,3′,3′-Octachlorodipropyl Ether From Fish

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2,3,3,3,2',3',3',3'-Octachlorodipropyl ether (bis(2,3,3,3-tetrachloropropyl) ether, OCDPE, cas#:127-90-2, commercial name S-421 in Japan) is a synergist for pyrethroid and organophosphorus pesticides widely used in commercial household insecticides. The acute toxicity of OCDPE is relatively low to rat (LD50, 3.6 g/kg) and rabbit (LD50, 2.5 g/kg) (NIOSH 1979), but it is mutagenic (Mori 1998).

Miyazaki (1982) and Uno et al. (1983) detected OCDPE residues in human breast milk in Japan and suggested that it might be due to the indoor use of commercial insecticide formulations containing OCDPE. We considered two possible routes of human exposure to OCDPE. The first was the exposure inside dwellings which they suggested and the other was a route from fish. OCDPE is stable in water (Matsunaga et al. 1981) and ubiquitous in the environment, as we have detected it in household dust (Yoshida et al. 1997), surface water, sediments and rain (Yoshida et al. 1996). OCDPE might be concentrated through the terrestrial food chain with trophic levels in the marine environment similar to other persistent organochlorine pollutants, such as HCHs, DDTs and PCBs. However, there has been no report of OCDPE detected in fish. Here we describe the isolation of OCDPE residues from fish.

MATERIALS AND METHODS

OCDPE and DDT compounds were purchased from Riedel-de Haen (Hannover, Germany). HCH isomers were from Wako Pure Chemical Industries (Osaka, Japan). Silica gel 40 (Art 10180, 70-230 mesh) for column chromatography was from Merck (Darmstadt, Germany). The reagents used for the analyses were all of special analytical grade for pesticide residues (Wako Pure Chemical Industries, Osaka, Japan).

Fish samples (three domestic, three imported) were collected from a wholesale market or retail stores in Osaka prefecture in 1996 and 1997. Samples were frozen at -30°C until they were analyzed. Analyses were done on the edible portions.

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Samples (5 g) were homogenized with 10 mL of acetone, 20 mL of hexane and 15 g of anhydrous sodium sulfate with a high-speed blender. The homogenate was centrifuged at 3,000 rpm for 5 minutes. The precipitate was further homogenized in 10 mL of acetone and 20 mL of hexane, and then centrifuged. The combined organic layer was evaporated to dryness (<40°C) under reduced pressure. The residue was dissolved in 15 mL of hexane and defatted by liquid-liquid partition with 30 mL of hexane-saturated acetonitrile three times. The combined acetonitrile layer was evaporated to dryness (<40°C) under reduced pressure. Next, the residue was dissolved in 8 mL of hexane, concentrated to 0.5 mL under a gentle stream of nitrogen, and applied to a hand-made mini column packed with 1 g of silica gel 40 (Yoshida 1994; Yoshida et al. 2000) OCDPE, HCHs and DDTs were eluted with 10 mL of diethyl ether + hexane (4 + 96, v/v), concentrated to 1 mL under a gentle stream of nitrogen, and analyzed by GC.

Quantitative analyses of OCDPE, HCHs and DDTs were performed with a Hewlett Packard (Palo Alto, CA) GC-5792 by electron-capture detection, using a capillary column and a splitless injection system. A 30 m × 0.32 mm id. DB-17 fused silica capillary column (film thickness 0.5 μm, J&W Scientific, Folsom, CA) was temperature-programmed from 100 to 280°C at 4°C/min. The detector and injector port temperatures were 330 and 200°C, respectively. The carrier gas (argon + methane = 95 + 5) velocity was 30 cm/sec and that of the make up gas (nitrogen) was 60 mL/min. The sample size injected was 2 μL. Detection limits were 0.2 ng/g for OCDPE, α-HCH and γ-HCH, 0.4 ng/g for β-HCH, p,p'-DDE, p,p'-DDD and p,p'-DDT.

GC/MS analysis was performed with a Shimadzu (Kyoto, Japan) GCMS-QP5050A. GC/MS conditions were as follows: column, DB-5 (J&W, CA) 30 m ×0.32 mm id. with film thickness 0.25 μm; column temperature, 80°C (1 min), 80-280°C (8°C/min); carrier gas, He (100 kPa); injection temperature, 250°C; injection mode, splitless; injection volume, 2 μL; ionization voltage, 80 eV; transfer line temperature, 280°C; chemical ionization gas, methane.

RESULTS AND DISCUSSION

The recovery of OCDPE from a sea bream sample fortified at 2 ng/g ranged from 86.0% to 98.0% (n = 5) with an average recovery of 92.6% (CV% of 5.3%). The recovery of HCHs from the sea bream sample (n = 5) fortified at 1.6 ng/g (α-HCH and γ-HCH) and 6.4 ng/g (β-HCH) averaged 95.5% (α-HCH, CV% of 4.0%), 101.0% (β-HCH, CV% of 9.5%) and 95.3% (γ-HCH, CV% of 6.1%). The recovery of DDTs from the sea bream sample (n=5) fortified at 3.2 ng/g (p,p'-DDE) and 6.4 ng/g (p,p'-DDD and p,p'-DDT) averaged 94.9% (p,p'-DDE, CV% of 20.2%), 112.3% (p,p'-DDD, CV% of 11.8%), and 106.6% (p,p'-DDT, CV% of 5.6%).

A typical capillary-column ECD-gas chromatogram for fish samples is shown in Figure 1. OCDPE appeared just after HCH isomer peaks. The mass spectra of OCDPE detected in a sea bream sample are shown in Figure 2. Data from 200 to

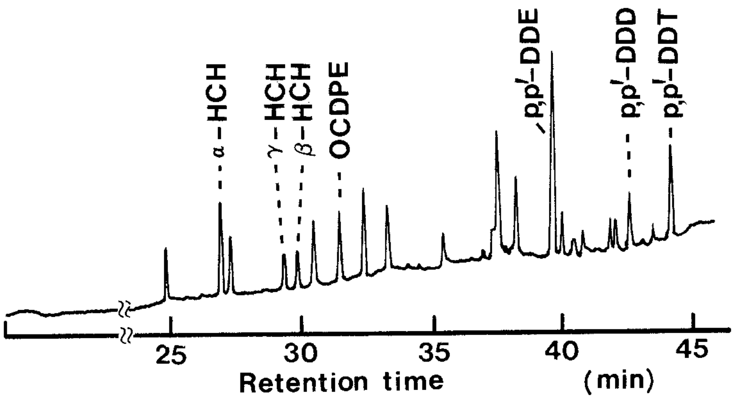

Figure 1. Typical ECD gas chromatogram from fish

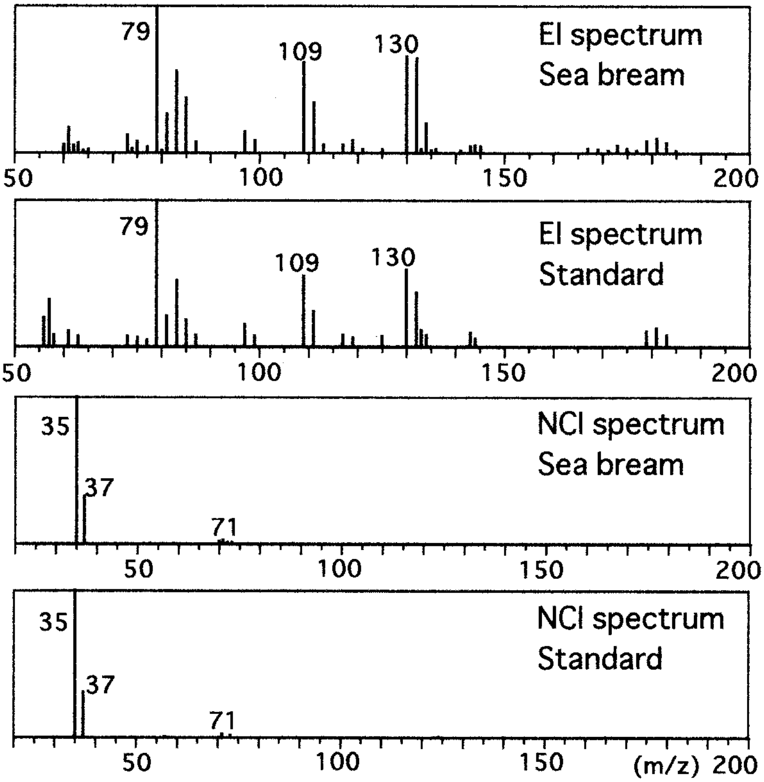

Figure 2. Mass spectra of 2,3,3,3,2',3',3',3'-octachlorodipropyl ether from sea bream

400 m/z were omitted because they were very low intensity. The mass spectrum in the EI (electron ionization) mode showed the specific fragment ions. OCDPE afforded the base peak at m/z 79 of C_2H_4OCl (Miyazaki et al. 1981). The NCI (negative chemical ionization) mode used here is reported to be sensitive and selective for the identification of residual organochlorine compounds (Obana et al. 1994). In the NCI mode, the mass spectra of OCDPE did not show a specific ion around its molecular mass (377.7), whereas characteristic ions were observed at m/z 35 and 37. These were considered to be chlorine ions released from OCDPE. The ratio of the ion intensity of m/z 35 to 37 was almost 10:3, which is the mass ratio of the naturally occurring chlorine atom.

Table 1 shows the concentrations of OCDPE, HCHs and DDTs detected in the fish samples analyzed. OCDPE was detected in all samples analyzed at 0.2 to 1.5 μg/g. The levels of OCDPE detected here were lower than those of DDTs and almost the same as those of HCHs. The results suggested widespread environmental pollution of OCDPE by bioaccumulation in the terrestrial food chain. Thus, the intake of fish can be considered to be a probable route of OCDPE pollution of human milk, the highest trophic level.

OCDPE was first produced in Germany and have been used worldwide (S-421 by BASF Aktiengesellschaft, CP-16226 by Monsant, Herc9437 by Hercules). In Japan, OCDPE has been produced at approximately 200 tons a year from 1972 to the present. The acute toxicity of OCDPE is low, but it is ubiquitous and mutagenic. Other reported toxicities of OCDPE are subacute hepatotoxicity (Sekita et al. 1988), cytotoxicity (Ikarasi et al. 1997) and contact allergenicity (Yamano et al. 1995). The chronic effects and carcinogenicity of OCDPE on humans have not been studied well. In a previous work (Yoshida et al. 1997), we detected OCDPE in all samples of household dust analyzed in Osaka, Japan, and

Table 1. Concentrations of 2,3,3,3,2',3',3',3'-Octachlorodipropyl Ether, HCH Isomers and DDT Compounds in Fish

Sample	Country	Concentration (ng/g)						
			HCHs			p,p'-	p,p'-	p,p'-
		OCDPE	α-	β-	γ-	DDE	DDD	DDT
Sea bream	Japan	1.5	ND	ND	0.3	1.2	ND	ND
Yellowtail	Japan	0.9	1.1	0.9	ND	29.4	13.1	17.1
Sweetfish	Japan	0.3	ND	ND	ND	1.0	0.6	0.8
Salmon	Chile	0.2	ND	ND	0.2	0.5	ND	ND
Prawn	India	0.3	0.6	1.1	ND	0.4	ND	ND
Trout	Norway	0.2	0.4	ND	0.4	1.8	0.6	0.6

ND: below detection limit

OCDPE: 2,3,3,3,2',3',3',3'-Octachlorodipropyl ether reported that the application of insecticides for termite control of a house, the mothproofing of household items and spraying aerosol pesticides for domestic use might have elevated the OCDPE pollution level in a house. OCDPE finally accumulates in sea water through rain or underground water.

More attention should be paid to the behavior of OCDPE in the environment as well as other persistent organochlorine pesticides, such as HCHs, DDTs and chlordane, which have long half-lives in the environment. Their chemical stability can result in considerable health risks for humans and other nontarget life forms as widespread pollutants can remain for a long time in the environment. If OCDPE continues to be used, its global pollution level will surely rise further. We are now studying the OCDPE levels in many domestic and imported fish and shellfish in Osaka.

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