With the apparatus used in Figure 1 as many as six samples were simultaneously adsorbed on the SEP-PAKs. Although the chemicals were usually immediately eluted from the SEP-PAKs, they could be stored in this manner for long periods in the refrigerator without noticeable decomposition.

This analytical technique was developed for applicator exposure samples for which we expected to have minimal background material. However, this procedure may have more widespread application, especially for aquatic samples. This procedure provides a rapid, sensitive and inexpensive technique for the analysis of applicator exposure pads, plus multiple samples can be worked up at the same time. The use of methanol and ethanol (certified grade) for extraction eliminates the need for the more expensive pesticide grade organic solvents (halogenated hydrocarbons, acetonitrile, dioxane), which are also environmentally sensitive and require proper waste disposal along with the accompanying costs. The lower limit of detection for carbaryl is 0.5 ng and for diflubenzuron 3.0 ng. The procedure concentrates the extract (50:1), ensuring a sensitive technique, 50 ng of carbaryl or 240 ng of diflubenzuron per 103.2-cm^2 sample pad, which is necessary for applicator exposure experiments since large multiplication factors are typically used to convert pad residues to appropriate skin surface area. The procedure eliminates the need for liquid/liquid extraction or solvent evaporation steps typically found in most residue analysis procedures.

Registry No. Carbaryl, 63-25-2; diflubenzuron, 35367-38-5.

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Chlorinated Dibenzo-*p*-dioxins, Chlorinated Dibenzofurans, and Pentachlorophenol in Canadian Chicken and Pork Samples

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Analysis of 144 chicken and pork tissue samples for pentachlorophenol (PCP) showed more than 60% of fat samples contained greater than 10 parts per billion (ppb; ng/g) PCP while chicken liver had a lower (27%) incidence of positives, and all pork livers contained values over 50 ppb. With the use of new methodology capable of determining all tetra- to octachlorinated dibenzo-*p*-dioxins (CDDs) and chlorinated dibenzofurans (CDFs), the incidence of positives in selected samples of chicken fats for hexa-, hepta-, and octachlorinated CDDs was 50, 62, and 46% with averages of 27, 52, and 90 parts per trillion (ppt; pg/g), respectively. Similar levels of hexa- and heptachlorinated CDFs were also found in some of these samples but tetra- and pentachlorinated CDDs and tetra-, penta-, and octachlorinated CDFs were not detected. A comparison between the chicken tissues and PCP-treated wood with regard to specific isomers and congeners of CDDs and CDFs and their relative proportions showed a marked similarity, indicating that PCP was the source of contamination of the food samples.

INTRODUCTION

Chlorinated dibenzo-*p*-dioxins (CDDs) and chlorinated dibenzofurans (CDFs) are two classes of toxic environmental contaminants that arise from a variety of sources including chlorophenols. The most common chlorophenol, pentachlorophenol (PCP) used as a wood preservative, is known to contain a variety of CDDs and CDFs (Firestone, 1977; Associate Committee on Scientific Criteria for Environmental Quality, 1981) in the high (over 100, sometimes over 1000) parts per million (ppm; μg/g) concentration, with the higher (hexa-, hepta-, octa-) chlorinated congeners predominating. Ryan and Pilon (1982a) detected the higher CDDs in chicken tissues from an incident in which birds were raised in contact with PCP-contaminated wood shavings. This relationship was further documented by Newsome et al. (1984), who, in a controlled laboratory experiment, measured CDDs, pre-CDDs, and

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chlorinated diphenyl ethers in tissues from chickens raised on PCP-treated wood shavings. The higher CDDs have also been implicated (Ryan and Pilon, 1983) in the mortality of young pigs kept on a PCP-contaminated wooden floor. In the latter incident, levels between 1 and 5 ppb (ng/g) were found in selected tissues.

Because of the known association of CDDs and CDFs with PCP and the possibility that food-producing animals are exposed to these compounds through treated wood, we decided to investigate the degree and scope of contamination in food samples from across Canada. Our study was aided by the advancement of analytical technology. In particular, tandem mass spectrometry (MS/MS) (Sakuma et al., 1984) obviated elaborate cleanup procedures while still retaining specificity and sensitivity for the CDDs and CDFs. In addition, the development of efficient cleanup techniques (Ryan et al., 1984a), the greater availability of pure standards of isomers, and superior gas chromatography (GC) bonded phase columns enabled isomeric analysis to be carried out for most of the tetra- to octachlorinated CDDs and CDFs particularly those with 2,3,7,8-tetrachlorine substitution. This report gives the result of a survey of 144 poultry and pork fat and liver samples for PCP of which 37 were also analyzed for CDDs and CDFs. PCP was found in most of the samples commonly in the range of 10–30 ppb. CDDs and CDFs values averaging between 25 and 100 ppt of the higher chlorinated congeners were found in about half the samples along with an isomeric pattern similar to that found in PCP.

EXPERIMENTAL SECTION

Sampling. A total of 144 samples of poultry and pork fat and liver were collected in 1980 mostly at wholesale outlets such as packers, farm sales, and co-ops and also at retail outlets such as supermarkets and local groceries. The samples originated from farms in Ontario (59 samples), Quebec (59 samples), and the Maritimes (26 samples), provinces in which wood shavings are known to be widely used in broiler production. They consisted of poultry fat (97 samples), poultry liver (26 samples), pork fat (16 samples), and pork liver (5 samples). Portions (100 g or more) were placed in 4-oz acetone–hexane-washed glass jars and sealed with aluminum foil lined screw tops.

PCP Determination. Both liver and fat samples were first homogenized in a grinder or blender. Fat samples (10 g) were then extracted with dichloromethane (150 mL) and liver samples (10 g) were first adjusted to between pH 2 and 3 with hydrochloric acid prior to extraction sequentially with 100 mL of acetone and then 150 mL of dichloromethane. After the combined organic phases were dried with sodium sulfate, an aliquot equivalent to a 2-g portion of either fat or liver extract was ethylated in diethyl ether with diazoethane. The ethylated mixture was then purified on a 5% water-deactivated Florisil (5 g) column by eluting with 300 mL of 5% dichloromethane in hexane. Detection and quantitation was carried out on a Tracor 220 GC with an electron-capture (EC) detector on a 180-cm long by 6-mm i.d. glass column packed with either 1.5% OV-17 and 1.5% SP-2401 or 10% OV-101, both on Chromosorb W (80–100 mesh). Samples were injected from a hexane solution, and quantitation was carried out by comparison to ethylated external standards. Average recoveries of PCP from fat at the 100 ppb level were over 90%. The detection limit of the method was 10 ppb for PCP and was limited mainly by PCP levels found in blanks from laboratory reagents rather than by absolute GC detection limits. The presence of PCP was confirmed in some samples by using a GC equipped with a Hall chlorine detector or by GC–MS in which case the full spectra of ethylated PCP was obtained in several instances. The method also simultaneously extracted and determined 2,3,4,5- and 2,3,5,6-tetrachlorophenol, both their methyl ethers (anisoles), and the methyl ether of PCP.

CDD and CDF Determination. Fat (2–3-g aliquots) and liver (5–10-g aliquots) were analyzed by a multistep procedure as outlined for fish (Ryan et al., 1983) and human fat (Ryan et al., 1984b), respectively. In summary, tissue samples were extracted with acetone–hexane, fat degraded and removed by partitioning with concentrated sulfuric acid, and CDDs and CDFs fractionated from PCB and other chlorinated aromatics in disposable activated Florisil columns (Ryan et al., 1984a). Screening for all tetra- to octachlorinated CDDs and CDFs (up to 136 possible isomers and congeners) was carried out using a Taga 6000 (Sciex, Inc.) GC–MS/MS as described (Sakuma et al., 1984). To maximize sample output this technique uses a short (12–15 m) DB-5 bonded phase silica column with fast temperature programming (GC cycle time between 12 and 15 min) coupled to a triple quadrupole MS/MS system. Detection limits of the method were between 2 and 4 ppt for all analytes except octachlorodibenzo-*p*-dioxin (OCDD) whose limit was between 10 and 20 ppt. In the latter case, the detection limit was governed by the level found in reagent blanks and not by absolute MS sensitivity. Particular attention was also paid to the segregation and solvent washing of laboratory glassware in order to minimize false positives.

Confirmation of selected samples that showed positive results in the screening tandem MS measurement and had acceptable recoveries of the isotopically labled internal standards (over 50% for [^{13}C]-2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) and [^{37}Cl]-2,3,7,8-tetrachlorodibenzofuran (TCDF), and over 30% for [^{13}C]-OCDD) was carried out in two ways. First, after Florisil chromatography and GC–MS/MS analysis, some samples were cleaned up further through reversed-phase high-pressure liquid chromatography (HPLC) as described (Ryan and Pilon, 1980, 1982b). According to information from the first MS run, specific collection times were chosen for certain analytes and these fractions run again on GC–MS/MS as outlined above. Second, because the GC resolution of different isomers and congeners was only moderate using the rapid temperature programming and short column of the tandem GC–MS, some sample extracts were reanalyzed a second time by high-resolution GC–MS. In this case slower temperature programming was used, resulting in longer (20–40 min) retention times on the DB-210 bonded phase polar column which was coupled to a VG Analytical ZAB-2F MS operating in the low-resolution (about 2000) electron-impact ionization mode. The exact GC conditions have been reported (Lau et al., 1984). With this combination, and an extensive library of pure analytical standards, samples could be analyzed for all tetra-, penta-, hexa-, hepta- and octachlorinated CDD and CDF congener groups. Moreover, this can be done unequivocably for those biologically important isomers having 2,3,7,8-tetrachlorine substitution except 2,3,7,8-TCDF.

RESULTS

Pentachlorophenol. PCP values in the 144 poultry and pork tissues are tabulated in histogram form in Figure 1 for fat (left) and liver (right) samples. For both poultry and pork fat, over 60% had readily detectable (>10 ppb) levels of PCP, with most of the positives lying between 20 and 30 ppb. The number of samples for liver tissues is smaller, particularly for pork, but the results indicate a lower frequency (27%) of positive (more nondetectable samples) for chicken liver than for fat with levels generally

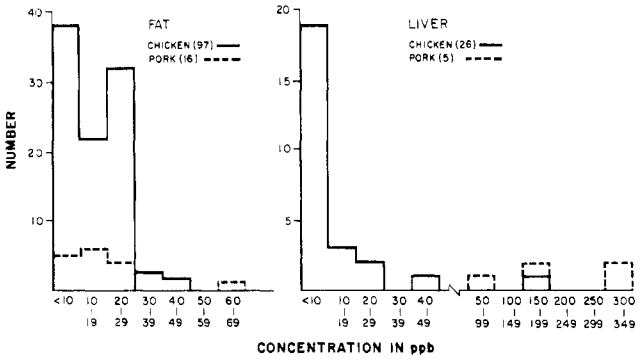

Figure 1. Histogram of PCP levels in ppb from 144 poultry and pork fat and liver samples collected in Canada in 1980. Nondetectable samples listed as less than 10 ppb.

Table I. Higher CDDs in 26 Chicken Fat Samples from Three Canadian Provinces (ppt)

sample	PCP[a]	degree of chlorination: hexa	hepta	octa
		Ontario		
1	22	67	70	181
2	48	30	37	30
3	22	33	142	238
4	29	60	93	204
5	22	ND[b] (20)	ND (20)	ND (20)
6	23	ND (20)	35	72
7	33	ND (20)	ND (20)	ND (20)
8	42	ND (20)	32	57
9	26	55	48	98
10	26	ND (10)	57	ND (20)
11	21	22	76	48
12	35	ND (10)	ND (10)	ND (10)
13	27	10	28	32
14	24	ND (10)	ND (10)	ND (10)
15	22	13	21	ND (20)
16	22	ND (10)	64	ND (20)
		Quebec		
17	ND (10)	21	ND (5)	ND (10)
18	ND (10)	9	ND (5)	17
19	ND (10)	10	16	67
20	ND (10)	12	25	23
		Maritimes		
21	ND (10)	ND (5)	ND (10)	ND (10)
22	ND (10)	8	ND (10)	ND (10)
23	22	ND (10)	ND (10)	ND (10)
24	24	ND (10)	ND (10)	ND (10)
25	26	ND (10)	54	ND (10)
26	22	ND (10)	26	ND (10)
no. pos of 26	20	13	16	12
av all pos ±S.D.		27 ± 21	52 ± 33	90 ± 76
range		8–67	16–142	17–238
av pos from Ontario		36 ± 22	59 ± 34	107 ± 80

[a] Pentachlorophenol (PCP) in ppb. [b] Not detected followed by detection limit in ppt in brackets.

less than 50 ppb with the occasional higher value. Pork liver is distinctive since all five samples had high (over 50 ppb) amounts of PCP with a high of 340 ppb. Low amounts (10–20 ppb) of tetrachlorophenol were occasionally found in a small portion of these samples. None of any of the corresponding three chloroanisoles were detected.

CDDs and CDFs. Thirty samples of mainly chicken fat (20 samples) but also some chicken liver and pork tissues all having PCP values above 20 ppb were selected for CDD and CDF determination as well as seven samples chosen at random with no PCP contamination. The results of these determinations for the higher (hexa-, hepta-, and octachlorinated) CDDs without specific isomeric identification are given in Tables I and II.

Table II. Higher CDDs in Three Chicken Livers, Five Pork Livers, and Three Fat Samples (ppt)

sample	PCP[a]	degree of chlorination: hexa	hepta	octa
		Chicken Liver		
1	43	ND[b] (5)	34	36
2	150	17	22	105
3	140	ND (5)	13	ND (10)
		Pork Liver		
1	315	ND (10)	ND (10)	ND (10)
2	190	ND (5)	ND (10)	54
3	340	ND (5)	ND (5)	14
4	70	ND (5)	9	12
5	170	ND (5)	ND (5)	ND (5)
		Port Fat		
1	61	5	71	428
2	22	ND (10)	17	45
3	ND (10)	ND (10)	ND (10)	16

[a] Pentachlorophenol (PCP) in ppb. [b] Not detected followed by detection limit in ppt in brackets.

Table I lists the 26 chicken fat samples by region along with corresponding PCP value, and Table II gives the three chicken liver, pork fat, and five pork liver samples. Over half the chicken fat samples had measurable amounts of the higher CDDs. The average of positives depending on chlorine content was between 27 and 90 ppt, with most positive samples originating from Ontario. No detectable amounts (limit of detection 2–4 ppt) of TCDD, or pentachlorodibenzo-*p*-dioxin (PCDD) were found in these 37 samples. However, some hexachlorodibenzofurans (HCDF) (average 37 ± 22 SD ppt) were found in six out of seven samples tested, and two out of seven samples contained heptachlorodibenzofurans (HpCDF) (average 35 ppt) with no TCDF or pentachlorodibenzofuran (PCDF) present. No octachlorodibenzofuran (OCDF) (detection limit between 10 and 20 ppt) was found in any of these samples, despite its known occurrence in PCP. It is noteworthy that the concentrations of the higher CDDs in the liver samples were generally lower than those found in fat even though liver often had much higher PCP values.

Isomeric Breakdown of Selected Samples. The data presented in Tables I and II for the CDDs are listed only in total amount for each cogener group without regard to the specific isomers within a group. With the advent of superior GC columns, and more individual pure standards, it is now possible to separate the congener groups into their individual isomers and this has been carried out for a number of samples in this study. To illustrate the isomers present and the pattern that generally arises within these tissue samples, five samples have been chosen. These are (1) a chicken fat sample from Table I (number 1), (2) a liver sample from a chicken known to have been raised in contact with PCP-contaminated wood shavings as reported by Newsome et al. (1984), (3) a pork fat from Table II (number 1), and two samples (4,5), a pork liver and wood sample from an incident in which young pigs died from contact with a PCP-treated wooden floor (Ryan and Pilon, 1983). The isomeric assignments for HCDF, HCDD, HpCDF, and HpCDD are listed in Table III for these five samples which are representative of many of the samples in Tables I and II. The chicken tissues contain more isomers of CDDs and CDFs than pork tissues. In addition, the chicken tissues are more similar to the wood sample than the pork samples in the number and relative proportion of individual isomers. The isomeric pattern pro-

Table III. Isomeric Composition of Chlorinated Dibenzo-*p*-dioxins (D) and Chlorinated Dibenzofurans (F) in Five Samples (Two Chicken, Two Pork, One Wood) (ppt)

isomer	sample no. (descrpn)				
	1 (chicken fat)	2 (chicken liver[a])	3 (pork fat)	4 (pork liver)	5 (wood[b])
134678-F	6.2	8.3			74
124689-F	11.0	20.6			540
123678-F	2.9	6.6		26	
total HF	20.1	35.5	[c]	26	614
124679-D	4.3	25.5			105
123679-D	18.7	23.1			216
123678-D	31.9	75.3	4.5	54	197
123789-D	2.0	25.0			42
total HD	56.9	148.9	4.5	54	560
1234678-F	14.6	43.4		3020	990
1234689-F	19.6	25.0			4790
1234789-F				131	190
total HpF	34.2	68.4		3151	5970
1234679-D	21	28	8	26	1600
1234678-D	69	351	71	1370	2270
total HpD	90	379	79	1396	3870
12346789-F		20		5100	3470
12346789-D	186	447	428	10100	9070

[a] Also contained 12378-D or 12367-D at 5.0 ppt and 12468-F at 8.5 ppt. [b] Values in ppb. [c] Not detected.

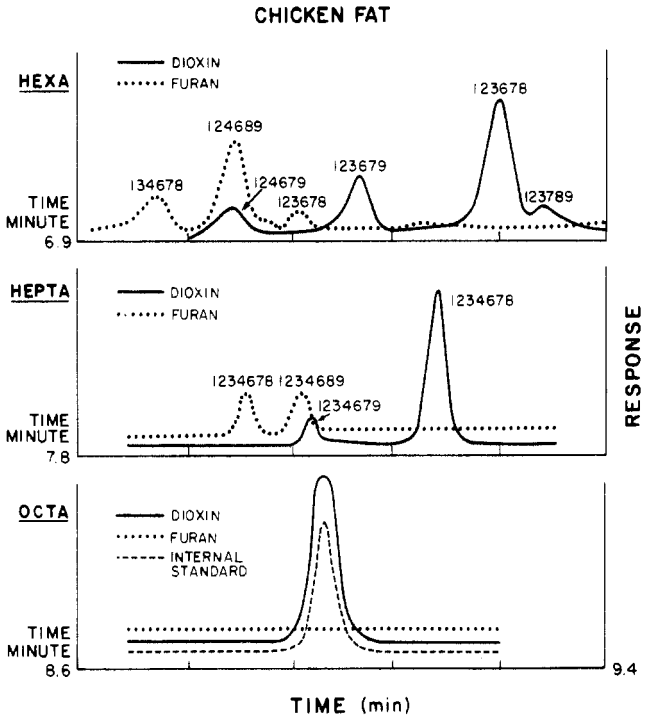

Figure 2. Schematic diagram of GC profile on DB-5 column from tandem MS measurement of CDDs (—) and CDFs (···) in chicken fat sample number 1 from Tables I and III. (– –) [^{13}C]-OCDD internal standard. MS scans: hexacongeners from 6.9 min and then switches to hepta congeners at 7.8 min and so forth. Values as noted in Table III.

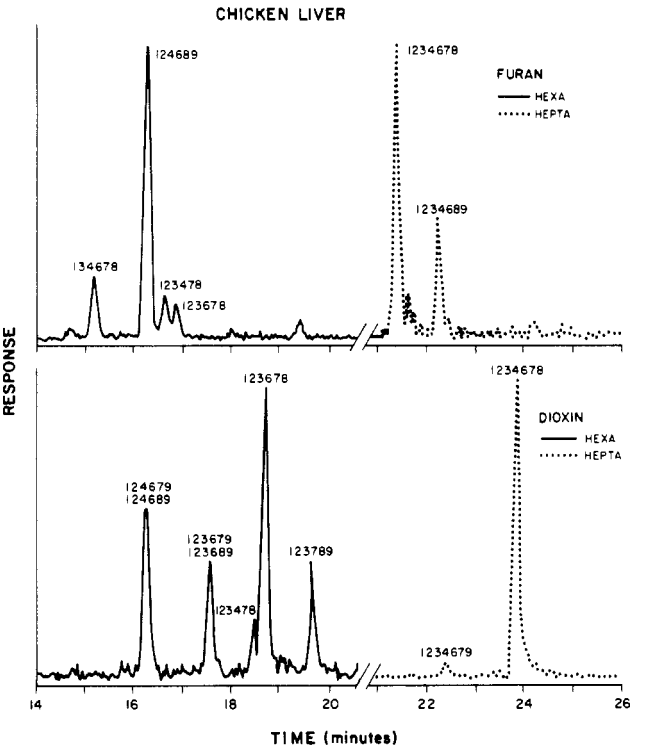

Figure 3. Schematic diagram of GC profile on DB-210 column from magnetic MS measurement of hexa- (—) and hepta-chlorinated (···) CDFs (top) and CDDs (bottom) in chicken liver sample from birds kept on PCP-contaminated wood shavings. Diagonal bar at about 21 min representative of switching of ions being monitored. Values as noted in Table III.

duced by GC is illustrated graphically in Figure 2 (chicken fat, sample 1 from Tables I and III) and Figure 3 (chicken liver, sample 2 from Table III). The fat profile is taken from the tandem MS output using fast temperature GC programming with moderate resolution on a DB-5 column, and the liver profile originates from the magnetic MS output with slower temperature programming and higher GC resolution on a DB-210 column. In both cases, the separation of the individual dioxins and furans is evident within their congeneric group and a pattern can be recognized; in particular, the individual number and relative proportion of each isomer within a group is more or less constant for these two poultry samples, which in turn are representative of many of the other poultry samples.

DISCUSSION

Even though most values are only slightly above the background level of about 10 ppb, the presence of PCP in these food samples is probably not surprising in light of its extensive use in forestry as a wood preservative and the use of wood products in agricultural production and food processing. Indeed, in the U.S. PCP is believed to be virtually ubiquitous in the environment (Kuehl and Dougherty, 1980) and meat supply (Food Chemical News 25 (May 23, 1983), pp 8–9). The frequency of positives above 10 ppb in these samples is similar to that reported by Neidert et al. (1984) in chicken liver samples from across Canada (about one-fourth positive in both studies)

but higher in chicken fat samples (60% here and only 8% in their study). The reason for the higher incidence of PCP in our chicken fat sample may be related to the difference in dates of collection of the samples (1980 in this study and 1980–1983 in their study) or, since the levels are near the detection limit of both methods, to methodology variations. The pork liver samples show PCP values 1 order of magnitude higher than chicken tissues with a higher frequency. This result is similar to 1983 U.S. data showing PCP levels greater than 500 ppb in 12% of samples. The finding of high PCP in pork livers deserves additional attention such as further analysis, examination of production practices, and toxicological evaluation.

The results in Tables I and II for the higher CDDs and CDFs are the first to document the presence of these chemicals in poultry and pork samples taken from the general food supply. However, the sampling has been biased toward those samples already containing measurable levels of PCP, only about 50% have detectable levels, and the levels are low (ppt). In addition the more toxic tetra- and pentachlorinated CDDs and CDFs were not detected. The values of the higher CDDs and CDFs are lower in levels but higher in incidence to those values reported briefly without details (Food Chemical News (May 14, 1979), p 40) from the analysis of 358 dairy cattle fat samples collected in 1977 from 30 U.S. states. Nine of the American samples (~2%) showed positive values (above the limit of "reliable" measurement of 190 ppt) for the higher chlorinated dioxins with a range between 210 and 860 ppt. Previous incidents in Canada (Ryan and Pilon, 1982a, 1983) had originated from cases in which animal production problems had been occurring, and the tissue levels measured were often higher (300–1500 ppt) than the average values (25–100 ppt) reported here. The latter, however, are closer to those values reported by Newsome et al. (1984) in tissues from chickens raised on PCP-contaminated bedding. In light of the historical knowledge of the presence of CDDs and CDFs in commercial chlorophenols (Firestone et al., 1972) and selected chicken feeds (Firestone, 1973) and their continued presence at high levels in commercial chlorophenols (Associate Committee on Scientific Criteria for Environmental Quality, 1981), these findings in the food supply are not unexpected.

The results for CDDs and CDFs in chicken and pork also shed some light on their origin. No TCDD or TCDF has been found in any of these tissues and no PCDF (except 1,2,4,6,8-PCDF in one liver sample) or PCDD. Hence, the tissue contaminants reported here could not have arisen from the herbicides 2,4-D and 2,4,5-T or from incineration processes. Tetrachlorinated and lower chlorinated congeners of the CDDs are expected as contaminants from the two pesticides named. Fly ash from incineration contains mono- to octachlorinated CDDs and CDFs, with levels among the congener groups being similar, and it would be expected that all such groups would be represented, at least partially, if they were translocated to food tissues and this is not the case. The number and types of isomers listed in Table III show a marked similarity between the chicken tissues and wood samples. Inspection of the patterns shows an almost complete overlap, e.g. PCP contains four HCDDs and two to three HCDFs, and the same isomers (and no others) are found in chicken fat and liver. The similarity is not as great for pork tissue, but in this instance, the question of source could be confounded by bioaccumulation and/or slow metabolism of those isomers having 2,3,7,8-tetrachlorine substitution. In particular the relative amount of 2,3,7,8-tetrachlorine-substituted isomers is higher for pork than for chicken tissues, with the latter showing other isomers (also common to PCP). In this regard a difference in the metabolism or pharmacokinetics of isomers of the related chlorinated aromatic hydrocarbon PCB in chickens and pigs has been noted recently by Hansen et al. (1983). It would be informative to test this proposed difference for CDDs and CDFs between classes of animals in a controlled experiment. From the above information, it is believed that the source of CDDs and CDFs in the chicken and pork samples is PCP. These could arise from PCP-treated wood shavings or, less likely, from beef and sheep tanning operations where PCP and dioxin-contaminated fleshings are used as animal feed (Food Chemical News (May 9, 1983) p 31). This conclusion is also supported by recent work of Neidert et al. (1984) who showed that all chicken liver samples having PCP levels above 100 ppb had originated from flocks raised on PCP-contaminated litter.

The toxicological significance of levels of PCP, CDDs, and CDFs in animal foods is being addressed. In January 1981, after these samples had been obtained, both the farm and home use of PCP in Canada was restricted. It would now be informative to see if these changes have had any effect on the levels of the CDDs and CDFs in poultry and pork products. Nevertheless, it is prudent to reduce the levels of these higher CDDs and CDFs in foods, and the simplest approach would be to decrease their levels in commercial PCP.

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Synthesis and Insecticidal Activities of Pyrethroids Derived from Bicyclo[*n*.1.0]alkenecarboxylic Acids

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Seventeen pyrethroid esters derived from 13 bicyclo[*n*.1.0]alkenecarboxylic acids were synthesized by a newly developed synthetic method. Thus, the cycloaddition products of dichloroketene and substituted cyclopentadienes, dialkylfulvenes, indene, and dialkylbenzofulvenes are used as precursors for the subsequent monodechlorination and Favorskii-type ring contraction to yield the pyrethroid acids. The acids were esterified with a variety of known pyrethroid alcohols. None of the esters showed insecticidal activity in the absence of synergists and very weak synergized insecticidal activity.

INTRODUCTION

The natural pyrethrins have been widely used as effective insecticides due to their high insect toxicity and low mammalian toxicity (Elliott and Janes, 1978). However, a major disadvantage of the natural pyrethrins, especially for use against agricultural pests, lies in the lack of stability in the presence of air and sunlight. The synthesis of new pyrethroid acids and structure–activity studies have received much attention in the literature in recent years (Plummer and Stewart, 1984; Ayad and Wheeler, 1984). A variety of new synthetic pyrethroid esters have been synthesized and reported as effective insecticides with a higher activity and stability than the natural pyrethrins.

We have recently reported a simple yet versatile synthesis of pyrethroid acids (Brady et al., 1983) from conjugated dienes that we believe offers an attractive alternative to existing pyrethroid acid syntheses. This paper describes the synthesis of bicyclo[*n*.1.0]alkenecarboxylic acids, esterification with known pyrethroid alcohols, and the insecticidal activity of the resultant pyrethroid esters.

EXPERIMENTAL SECTION

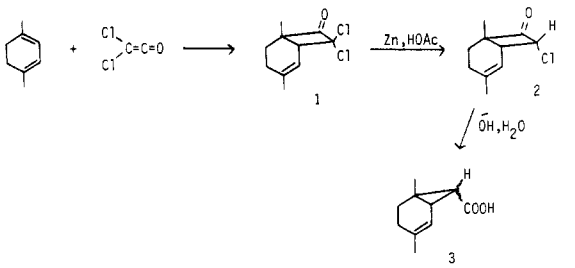
Synthetic Methods. The bicyclo[*n*.1.0]alkenecarboxylic acids were synthesized in three steps as previously described (Scheme I) (Brady et al., 1983).

^{1}H NMR spectra were recorded on a Perkin-Elmer R-248 nuclear magnetic resonance spectrometer, employing deuteriochloroform as the solvent with tetramethylsilane as the internal standard. ^{13}C NMR spectra were recorded on a JEOL FX-90Q FT nuclear magnetic resonance spectrometer.

Ether, hexane, triethylamine, and benzene were dried and purified by distillation from sodium–potassium alloy prior to use.

8,8-Dichloro-3,6-dimethylbicyclo[4.2.0]oct-2-en-7-one (1). (This procedure is typical of the in situ cycloaddition of dichloroketene with a diene to yield the α,α-dichlorocyclobutanone.) To a mixture of 5 g (0.046 mol) of 1,4-dimethyl-1,3-cyclohexadiene and 3.5 g of activated zinc in 250 mL of anhydrous ether was added over a 6-h period a solution of freshly distilled 5.2 mL (0.046 mol) of trichloroacetyl chloride and 4.3 mL (0.046 mol) of phosphoryl chloride in 250 mL of anhydrous ether at ambient temperature. After the addition was complete, the mixture was stirred for an additional 2 h. The excess zinc was removed by filtration and the solution concentrated to about 50 mL and then mixed with 150 mL of hexane. The solution was decanted from the zinc chloride etherate and washed with a solution of sodium bicarbonate and water until neutral. The solvent was removed under reduced pressure and the residue vacuum distilled: bp 69–72 °C (0.10 mm); 6 g (59%); ^{1}H NMR ($CDCl_3$) δ 1.0–3.0 (m, 11 H), 5.25 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 193 (s), 139.4 (s), 124.4 (d), 84.2 (s), 65.1 (d), 20–40 (m).

Scheme I



8-Chloro-3,6-dimethylbicyclo[4.2.0]oct-2-en-7-one (2). (This procedure is typical of the selective reductive removal of only one chlorine atom from the α,α-dichlorocyclobutanones.) To a solution of 4 g (0.0182 mol) of 1 in 100 mL of acetic acid was added 1.15 g (0.0176 mol) of zinc dust in portions over a 1-h period. The mixture was then stirred at ambient temperature for 24 h. A 200-mL portion of ether was added to the reaction mixture, and then it was washed with water until neutral. The ether solution was then dried over anhydrous magnesium sulfate and the solvent removed under reduced pressure: yield 3.1 g (93%) of **2**; IR (film) 1785 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.0–2.5 (m, 10 H), 2.7 (m, 1 H), 4.5 (m, 1 H), 5.3 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 199.0 (s), 139.4 (s), 124.4 (d), 68.8 (d), 20–40 (m).

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