Behavior of DDT, Polychlorinated Biphenyls (PCBs), and Dieldrin at Various Stages of Refining of Marine Oils for Edible Use[1]

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ABSTRACT

Two 300-lb batches of Eastern Canadian herring (*Clupea harengus*) oil were subjected to pilot plant processing to margarine stock for edible use. Samples were taken at various stages during processing for analysis of residues of the insecticide DDT and its metabolites DDD and DDE, of polychlorinated biphenyls (PCBs) and of dieldrin. Residue concentrations in the oil were not affected by degumming (phosphoric acid wash), alkali refining, or bleaching with activated earth. DDT and dieldrin were readily and completely destroyed by commercial hydrogenation over Ni catalyst, and DDD was largely removed at the same time. DDE and PCBs were partially reduced during hydrogenation in the one run in which DDD was completely removed, but were unaffected in another run, in which DDD was only partially removed. Deodorization of the oil with steam and vacuum effectively removed those residues which survived hydrogenation. Analysis of the Ni catalyst before and after hydrogenation showed that removal of residues during hydrogenation was not due to their adsorption to the catalyst, but was more probably due to metal-catalyzed degradation to unidentified products. Deodorizer condensates showed only a slight enrichment in residue levels over those found in the oil.

INTRODUCTION

In a previous paper (1) we described the effective removal of residues of polychlorinated biphenyls (PCBs) and DDT-group insecticides (*p,p'*-DDT, *p,p'*-DDD, and *p,p'*-DDE) from marine oils during processing to edible use. [The following abbreviations are used: *p,p'*-DDT, 2,2-bis-(*p*-chlorophenyl)-1,1,1-trichloroethane; *p,p'*-DDD, 2,2-bis-(*p*-chlorophenyl)-1,1-dichloroethane; *p,p'*-DDE, 2,2-bis-(*p*-chlorophenyl)-1,1-dichloroethylene.] In considering the various processing steps involved (alkali refining, pre- and post-hydrogenation bleaching, hydrogenation over Ni to IV 80, and deodorization with steam under vacuum), and in reviewing the relevant literature (2-4), we concluded that the most likely steps at which residues were removed were hydrogenation and (more probably) deodorization. We were not able to assess the relative importance of either of these steps.

During the past two years, we have obtained samples of Eastern Canadian herring (*Clupea harengus*) oil from various stages during pilot plant processing similar to the manufacture of margarine stock for edible use, and have analyzed these samples for chlorinated hydrocarbon residues. In this paper, we present a more detailed picture of the fate of residues of *p,p'*-DDT and its metabolites *p,p'*-DDD and *p,p'*-DDE and of the PCBs during such processing and compare our conclusions with those from the recent literature (5-10).

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EXPERIMENTAL PROCEDURES

Herring oil was produced at Shippegan, New Brunswick, by reduction of whole herring captured in the Gulf of St. Lawrence. The reduction process consisted of grinding, cooking, and pressing the fish, with centrifugal separation of oil from stickwater followed by a centrifugal polishing and settling in storage tanks. Forty-gallon drums were filled from one tank and processed in a pilot plant as described previously (1).

Samples were taken from two lots of 300 lb processed six months apart. Run No. 1 was sampled at the following stages: crude oil, degummed oil after a phosphoric acid wash, alkali refined oil, bleached oil, and oil hydrogenated to IV 118, IV 105, IV 90, IV 79 (final IV), and as post-hydrogenation deodorized oil. Run No. 2 was sampled at similar stages: after bleaching and prior to hydrogenation, and after hydrogenation to IV 105, IV 91, and IV 80. Samples of the catalyst in oil at normal concentration, collected before use and after hydrogenation, and of deodorizer condensates, were also taken during run No. 2.

Samples of oil and deodorizer condensates were warmed until clear, thoroughly mixed, and accurately weighed subsamples of ca. 400 mg were dissolved in *n*-hexane. Oil-catalyst samples were extracted with chloroform-methanol (2:1, v/v) (11), and the chloroform phases were gently reduced in volume and taken up in *n*-hexane. Residues were cleaned up on Florisil ®, and the eluates were subjected to gas liquid chromatography on two columns of widely different polarity (Dexsil 300 and XE-60) essentially as described previously (12) before and after dehydrochlorination (13). PCBs were quantified as described previously (12).

RESULTS

The crude herring oil used in run No. 1 contained residues of *p,p'*-DDE, *p,p'*-DDD, *p,p'*-DDT, PCBs, and dieldrin in concentrations of 0.67, 0.41, 0.36, 2, and 0.15 ppm, respectively. Table I summarizes the distribution of residues during processing. None of the residues was detectably affected by the processing stages up to hydrogenation, but at an early stage during hydrogenation, *p,p'*-DDT and dieldrin concentrations dropped to undetectable levels. *p,p'*-DDD and *p,p'*-DDE concentrations also dropped during hydrogenation to (respectively) 16% and 37% of their initial concentrations. The PCBs, together with the traces of *p,p'*-DDD and *p,p'*-DDE which survived hydrogenation, were effectively removed during deodorization, reaching undetectable levels. Minimum detectable levels of residues during this suite of analyses were: *p,p'*-DDE, 0.01 ppm; *p,p'*-DDD, 0.03 ppm; *p,p'*-DDT, 0.02 ppm; PCB, 0.2 ppm; and dieldrin, 0.01 ppm.

Refined oil prior to hydrogenation in run No. 2 contained residues of *p,p'*-DDE, *p,p'*-DDD, *p,p'*-DDT, PCBs, and dieldrin at concentrations of 0.59, 0.44, 0.60, 3.3, and 0.13 ppm, respectively. During hydrogenation from IV 120

TABLE I

Survival of Residues of *p,p'*-DDE, *p,p'*-DDD, *p,p'*-DDT, PCBs, and Dieldrin during Pilot Plant Processing of Herring Oils (Run No. 1 and No. 2)[a]

Stage of processing	Residue				
	p,p'-DDE	*p,p'*-DDD	*p,p'*-DDT	PCB	Dieldrin
Run No. 1					
Crude oil	[100]	[100]	[100]	[100]	[100]
Phosphoric acid wash	101	105	100	100	93
Alkali refined	94	98	97	100	88
Bleached (IV 128)	107	95	94	100	113
Hydrogenated to IV 118	105	37	ND	100	ND
Hydrogenated to IV 105	87	29	ND	100	ND
Hydrogenated to IV 90	81	27	ND	100	ND
Hydrogenated to IV 79	37	16	ND	100	ND
Deodorized	ND	ND	ND	ND	ND
Run No. 2					
Bleached oil (IV 120)	[100]	[100]	[100]	[100]	[100]
Hydrogenated to IV 105	81	ND	ND	73	ND
Hydrogenated to IV 91	71	ND	ND	73	ND
Hydrogenated to IV 80	31	ND	ND	58	ND

[a]Data expressed as percentage of initial concentrations in crude oils (listed in text). ND = not detected.

to IV 80, these concentrations dropped in a fashion generally similar to those run in No. 1. Thus, *p,p'*-DDT and dieldrin were removed at an early stage during hydrogenation, and *p,p'*-DDE was partially removed during hydrogenation. *p,p'*-DDD was removed more rapidly than in run No. 1 (where 16% of it survived hydrogenation); in run No. 2, it was completely removed at an early stage of hydrogenation. PCBs were reduced by hydrogenation to about 60% of their initial concentration during run No. 2, whereas they were apparently unaffected by hydrogenation in run No. 1.

Only residues of *p,p'*-DDE and PCBs were found in the sample of used catalyst in oil, and in the deodorizer condensates (Table II). No organochlorine compounds could be detected in fresh catalyst. Concentrations (on a lipid weight basis) in used catalyst in oil (after hydrogenation) were slightly higher than those in the oil hydrogenated to IV 80. Residue concentrations of *p,p'*-DDE and of PCBs in the deodorizer condensates were about 1.5-2.0 times as high as those in the oil at IV 80, i.e., just prior to deodorization.

DISCUSSION

The residues of organochlorine compounds in the herring oils studied in this report were fairly typical of those of Eastern Canadian marine oils (12), and since they were acquired adventitously rather than by deliberately spiking uncontaminated oils, conclusions about their fate are especially valuable to studies of commercial processing. The data presented here support our previous conclusions that conventional processing of marine oils for edible use effectively removes their organochlorine burden. Our new data also allow us to identify the processing stage at which residues are removed and to suggest possible mechanisms.

It is clear that residue concentrations were not affected by processing treatments up to the hydrogenation step (Table I). This was to be expected, since such treatments are relatively mild: e.g., degumming involves stirring the oil with about 1% by weight of phosphoric acid, at temperatures below about 70 C (14). Since most chlorinated hydrocarbon residues are stable to fuming sulfuric acid (which may be used to remove unwanted interferences in their analysis: 15), degumming seems unlikely to degrade them. Alkali refining, which involves stirring the oil with NaOH solution, could conceivably convert *p,p'*-DDT and *p,p'*-DDD to their dehydrochlorination products (13), but since relatively small amounts of base are used (less than twice the amount required to neutralize the free fatty acids) at low temperatures for short periods (14), dehydrochlorination to any significant extent seemed unlikely. Neither we, nor other workers (e.g., 5), have been able to detect degradation of residues at this stage.

Bleaching involves stirring the oil with activated earth, or activated carbon, or both. Although we were unable to find any change in residue concentration as a result of this step, conflicting conclusions abound in the literature. Thus, Kanematsu et al. (5) reported a 50% reduction in dieldrin from various edible oils bleached with activated earth and activated carbon, whereas Vioque et al. (8) reported no reduction in dieldrin, but a complete removal of endrin. A third report (3) describes no such removal of endrin. The most probable explanation for these mutually contradictory results is differences in adsorptive capacity of the bleaching agents, which could arise either from the nature of the adsorbent, or from its saturation by other adsorbates. For example, some Canadian bleaching earths are treated (activated) with concentrated sulfuric acid.

Our data (Table I) show that at an early stage in hydrogenation, *p,p'*-DDT and dieldrin disappeared completely (to below detectable limits) from the oils. Kanematsu et al. (6) reached similar conclusions from studies on hydrogenation of soybean oil. The efficiency of removal (always over 90%) of dieldrin in their studies depended to some extent on the nature of the catalyst, Cu-Cr being more effective than Ni. The partial removal of *p,p'*-DDE observed during our hydrogenation runs closely parallels that observed in their work (6).

The slight variation in the behavior of *p,p'*-DDD and of PCBs during the two processing runs described here (Table I) can probably be explained in terms of differences in the activity of the Ni catalyst. Run No. 1 appeared to have been slightly milder than run No. 2, since *p,p'*-DDD survived longer through the hydrogenation process, and since PCBs were unaffected; thus this catalyst had possibly had prior use. In this context, it is interesting that Cu-Cr was reported to cause a slight reduction in PCB content of spiked soybean oils, whereas hydrogenation over Ni caused no change (6). It appears that no data comparable to ours exist for the fate of *p,p'*-DDD during hydrogenation.

It has been suggested that the mechanism by which residues are removed from oils during hydrogenation is via adsorption to the catalyst (2,4). A cursory inspection of the residues surviving hydrogenation would support this view, since the surviving structures are those which are least "polar" as indicated by TLC behavior (16) or by distribution between polar and nonpolar solvents (17), and so

TABLE II

Residue Concentrations (ppm lipid)[a] in Hydrogenated Oil, Catalyst, and Deodorizer Condensates from Run No. 2

Sample	Residue				
	p,p'-DDE	*p,p'*-DDD	*p,p'*-DDT	PCB	Dieldrin
Hydrogenated oil (IV 80)	0.18	ND	ND	1.9	ND
Catalyst (before hydrogenation)	ND	ND	ND	ND	ND
Catalyst (after hydrogenation)	0.28	ND	ND	2.0	ND
Deodorizer condensates	0.36	ND	ND	2.6	ND

[a]ND: not detected.

would be least likely to be readily adsorbed to catalysts or other adsorbents. However, Table II shows that none of the residues expected to be adsorbed (*p,p'*-DDT, *p,p'*-DDD, or dieldrin) was extractable in detectable amounts with $CHCl_3$-MeOH from the catalyst. Indeed, the only residues present in the catalyst were *p,p'*-DDE and PCBs, and since the catalyst was collected as a suspension in the partially hydrogenated oil, it was not surprising that the concentrations of these residues in the "catalyst" (expressed on a lipid weight basis) were roughly similar to those in the hydrogenated oil.

It seems unlikely, therefore, that simple adsorption on the catalyst would explain the disappearance of *p,p'*-DDT, *p,p'*-DDD, and dieldrin (together with some *p,p'*-DDE and PCBs) during hydrogenation. A conclusion more consistent with the disappearance of residues completely is that they are decomposed to unidentified products. In this context, we note that the residues which even partially survive hydrogenation are those which are generally considered the least reactive. Although this statement is difficult to quantify, *p,p'*-DDT and *p,p'*-DDD are both susceptible to various reactions at the side chain, including dehydrochlorinations, dechlorinations, and oxidations (13,18,19) whereas *p,p'*-DDE is very unreactive at the side chain (the electrons of the: CCl_2 group are fully delocalized with the aromatic rings and that bond cannot be catalytically hydrogenated: R.F. Addison, unpublished data). *p,p'*-DDE can only be oxidized to the ketone (with difficulty) (20). Reactions at the aromatic rings on either the DDT group or the PCBs can require quite severe conditions (21). Although we cannot propose any specific decomposition process for these residues during hydrogenation, we conclude that degradation is the most likely mechanism for their disappearance. The partial disappearance of even the more inert compounds, which increases with more chemically reactive catalysts (6), suggests that if nothing else, degradation in the presence of hydrogen is probably metal catalyzed.

Our observations that the final traces of *p,p'*-DDE and PCBs (and, in run No. 1, *p,p'*-DDD) were removed during deodorization, are consistent with varous other observations (3,5), and we have discussed previously (1) the expected behavior of some residues under the physical conditions prevailing during deodorization. Following commercial practice, the input of steam, choice of temperature, and application of vaccum (14) during the pilot plant process studied here were balanced to prevent a loss of more than 1%, or at most 2% of the oil charge (cf. Ref. 3). A good deal of the oil component of the condensate mixture is reported (G. Helmel, private communication) to be triglyceride carried over mechanically as oil droplets, with the balance consisting of free fatty acids, sterols, tocopherol, and in the case of marine oils, natural hydrocargons such as pristane (24). The deodorizer condensate oil or lipid contained (Table II) *p,p'*-DDE and PCBs at 1.5-2.0 times the concentration of the deodorizer charge of partially hydrogenated marine oil. This represents a recovery of, at most, about 4% of the possible yield. The hydrocarbon pristane (2,6,10,14-tetramethylhexadecane) was determined in the partially hydrogenated herring oil of IV 80, and in the deodorizer condensate from deodorization of that oil. Respective concentrations of pristane were 0.01 and 0.02% of the oils, supporting the thesis that chlorinated hydrocarbons were mostly transferred to the condenser with oil and only condensed to a small extent from vapor.

Comparable data on recovery of residues during deodorization are limited. Since it is difficult to recover deodorizer condensates quantitatively (3), no mass balance for residues during deodorization can be constructed. However, Vioque et al. (8) found that deodorizer condensates trapped in dry ice-acetone contained lower residue concentrations than those in the starting olive oil, whereas Chaudry et al. (9) found some enrichment of residues in deodorizer condensate in a lab scale deodorization of soybean oil. Smith et al. (3) did not report residue concentrations in deodorization condensates during pilot plant processing of soybean oil. In general, it seems that commercial practice with deodorizers may result in almost total disappearance of these materials, presumably as pure vapor entrained and carried away to the vacuum pump by water vapor. However, specialized equipment can give substantial, if incomplete, recovery of chlorinated hydrocarbon under certain conditions.

The conclusion that deodorizer condensates may contain moderate amounts of chlorinated hydrocarbon residues could have important consequences. Firstly, if the deodorizer condenser oil or fat material is highly enriched, it should be restricted to industrial use; otherwise it might be used in animal feed formulations. Secondly, if not condensed, the chlorinated hydrocarbons could determine the way in which plant aqueous effluents may be separated or mixed to meet environmental standards.

Limits (which range from 0.1 ppm for aldrin and dieldrin to 1 ppm for DDT plus metabolites, or 0.2 ppm PCBs in the fat of dairy products [as of April 1, 1977]) are set in Canada for chlorinated materials in certain high fat foods, but there are effectively no standards for chlorinated hydrocarbons in vegetable oils subject to normal processing and refining, including partial hydrogenation and/or deodorization before edible use. The very low levels found in refined and partially hydrogenated marine oils indicate that these oils in the form of margarine or shortenings are equally acceptable from the chlorinated hydrocarbon residue point of view for normal human diets.

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