Removal of Organochlorine Pesticides and Polychlorinated Biphenyls from Marine Oils during Refining and Hydrogenation for Edible Use

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ABSTRACT

Raw marine oils containing from 2-8 ppm DDT group pesticides, 0.00-0.03 ppm dieldrin, and 3-13 ppm polychlorinated biphenyls (as Aroclor 1254) were subjected to pilot plant refining, hydrogenation, and deodorization for margarine stock production. Residues of all 3 groups were reduced to below detectable limits (0.06 ppm, 0.01 ppm, and 0.5 ppm for ΣDDT, dieldrin, and polychlorinated biphenyls [determined as decachlorobiphenyl], respectively) as a result of processing.

INTRODUCTION

Residues of organochlorine pesticides, and related compounds of industrial importance, now are encountered almost routinely in raw oils and fats of animal or plant origin. Several studies (1-4) have dealt with the fate of organochlorine pesticides during normal processing of oils for edible use. To our knowledge, there have been no reports of the fate of polychlorinated biphenyl (PCB) residues during edible oil processing. Since these materials are now widely distributed in marine oils from various sources (5), we have examined the levels of these, and of some organochlorine pesticide residues, in a series of marine oils before and after processing to margarine stock.

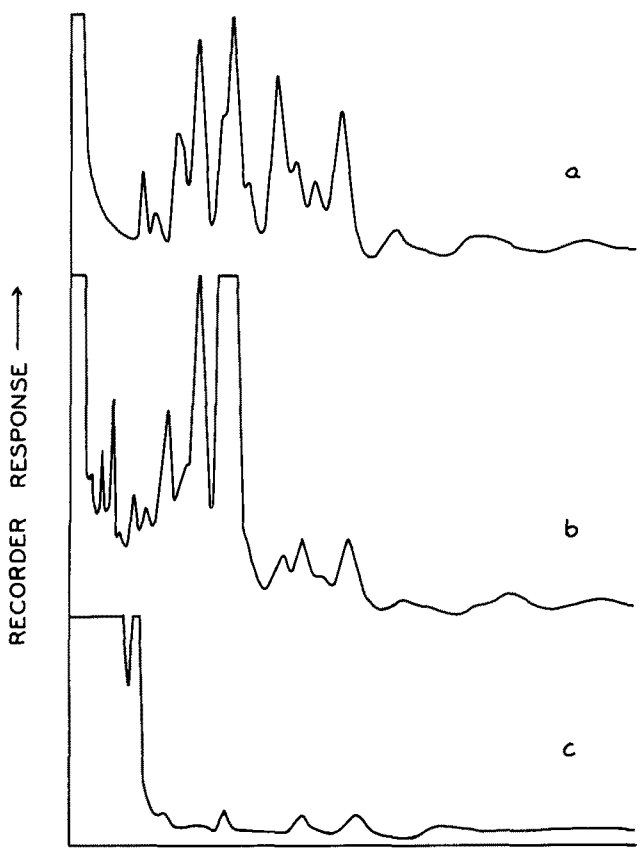

FIG. 1. Electron capture detector chromatograms of (a) Aroclor 1254, (b) 1966 East Coast raw herring oil, cleaned up and dehydrochlorinated as described in text; (c) 1966 East Coast herring oil refined, hydrogenated and deodorized and cleaned up and dehydrochlorinated as described in text.

EXPERIMENTAL PROCEDURES

Samples of normal production runs of several marine oils from reduction of fish scrap, whole fish, or seal blubber (Table I) were obtained from commercial producers; and 300 lb batches were processed in a pilot plant to produce margarine stock. The oils (free fatty acid [FFA] content 0.3-3.5%) were alkali-refined by stirring with 11.5% (w/w) NaOH solution at 65-70 C for 10 min and allowed to settle for 1-2 hr. Foots were drawn off and the oils washed to a final soap concentration of less than 50 ppm. The refined oils (FFA content < 0.2%) were bleached with 1% activated clay at 104 C for 30 min and filtered. After preheating to 177 C under vacuum, hydrogenation was carried out at 20-25 psig over a 25% Ni Rufert catalyst at temperatures of 188-214 C for 0.5-3 hr. Final iodine values were 78-80. Posthydrogenation bleaching was carried out as described above. Deodorization was carried out by heating to ca. 250 C for 2.5 hr and cooling to 50 C over a further 0.5 hr; steam was added at 1.5% wt oil/hr under an absolute pressure of 7-10 mm Hg.

Samples of the raw and refined oils were analyzed for organochlorine residues, substantially as described previously (5,6). The presence of *p,p'*-DDT[1] in the oils was confirmed by dehydrochlorination to *p,p'*-DDE (7) and that of *p,p'*-DDE by subsequent oxidation to *p,p'*-dichlorobenzophenone (8). Peaks resistant to both these procedures, and corresponding to those present in PCB mixtures (Aroclors: Monsanto, St. Louis, Mo.), were estimated as Aroclor 1254 by comparing average peak heights in samples to those in standards (6). In selected cases (raw redfish plus flatfish oil, raw flatfish oil, and all processed oils), the sample was rechromatographed on Florisil at this point; and the 5% diethyl ether/hexane eluate, containing PCBs if originally present in the sample, freed of *p,p'*-dichlorobenzophenone by adsorption on Florisil, was taken to dryness and perchlorinated with $SbCl_5$ (9). In these cases, PCB concentrations in the oils were expressed in terms of the decachlorobiphenyl product after correction for the efficiency of the reaction as determined with standard Aroclor 1254.

RESULTS

The residue concentrations found in the oils are summarized in Table I. All the raw oils contained residues of the DDT group; *p,p'*-DDE and *p,p'*-DDT were always present and *p,p'*-DDD sometimes present, but relative proportions of the three components varied considerably. Total DDT group (ΣDDT = DDD + DDE + DDT) in the oils were ca. 2-8 ppm. Dieldrin, the expected metabolite of some

[1] Abbreviations used throughout are: *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.

TABLE I

Organochlorine Residues in Raw and Partially Hydrogenated Marine Oils (ppm)[a]

Oil		DDE	DDD	DDT	ΣDDT	Dieldrin	PCB as Aroclor 1254	PCB as decachlorobiphenyl
Redfish and flatfish, mixed, East Coast (Louisburg), spring, 1973	Raw	0.8	ND	1.0	1.8	0.03	12	8
Redfish and flatfish, mixed, East Coast (Louisburg),spring, 1973	Part. hyd.	ND	ND	ND	ND	ND	ND	ND
Flatfish oil, East Coast (Louisburg), spring, 1973	Raw	1.0	ND	1.3	2.3	0.03	8	3
Flatfish oil, East Coast (Louisburg), spring, 1973	Part. hyd.	ND	ND	ND	ND	ND	ND	ND
Herring oil, East Coast (Isle aux Morts), winter, 1972-73	Raw	1.2	0.4	0.6	2.2	0.02	3	NA
Herring oil, East Coast (Isle aux Morts), winter, 1972-73	Part. hyd.	ND	ND	ND	ND	ND	ND	ND
Redfish oil, East Coast (Louisburg), spring, 1973	Raw	0.9	ND	1.9	2.8	0.01	11	NA
Redfish oil, East Coast (Louisburg), spring, 1973	Part. hyd.	ND	ND	ND	ND	ND	ND	ND
Herring oil, East Coast (Pubnico), summer, 1966	Raw	3.8	1.0	2.8	7.6	ND	8	NA
Herring oil, East Coast (Pubnico), summer, 1966	Part. hyd.	ND	ND	ND	ND	ND	ND	ND
Seal oil, East Coast (Blandford) summer, 1973	Raw	1.7	0.5	0.2	2.4	ND	4	NA
Seal oil, East Coast (Blandford) summer, 1973	Part. hyd.	ND	ND	ND	ND	ND	ND	ND
Mackerel oil, East Coast (Shippegan) summer, 1973	Raw	0.7	0.5	0.7	1.9	ND	5	NA
Mackerel oil, East Coast (Shippegan) summer, 1973	Part. hyd.	ND	ND	ND	ND	ND	ND	ND
Redfish oil, East Coast (Shippegan), summer, 1973	Raw	1.0	0.5	1.9	3.4	ND	4	NA
Redfish oil, East Coast (Shippegan), summer, 1973	Part. hyd.	ND	ND	ND	ND	ND	ND	ND
Dogfish oil, West Coast, (Vancouver) spring, 1973[b]	Raw	1.4	0.5	1.3	3.2	ND	13	NA
Dogfish oil, West Coast, (Vancouver) spring, 1973[b]	Part. hyd.	ND	ND	ND	ND	ND	ND	ND
Herring oil, West Coast, (Vancouver) summer, 1973	Raw	1.3	0.4	0.3	2.0	ND	3	NA
Herring oil, West Coast, (Vancouver) summer, 1973	Part. hyd.	ND	ND	ND	ND	ND	ND	ND

[a]PCB = polychlorinated biphenyl, Part. hyd. = partially hydrogenated, ND = not detected, and NA = not analyzed.

[b]Not normally processed as an edible oil.

cyclodiene insecticides, was found in some of the raw oils at concentrations around 0.02 ppm.

No residues of the DDT group or dieldrin were found in any of the processed oils. Minimum detectable levels were ca. 0.02 ppm each of *p,p'*-DDE, *p,p'*-DDD, and *p,p'*-DDT, and ca. 0.01 ppm dieldrin.

Peaks with retention times similar to those in Aroclor 1254, but differing from them in relative peak intensity, and resistant to dehydrochlorination and oxidation, were found in all the raw oils (Fig. 1a,b). They were estimated as Aroclor 1254. Perchlorination of these supposed PCB residues to decachlorobiphenyl (in raw redfish plus flatfish, raw flatfish oils, and in all processed oils) confirmed their presence or absence. The reaction presented some problems; the first batch of $SbCl_5$ used (Allied Chemical, Morristown, N.J., catalog no. 109-1365; lot no. E347) contained a large blank peak coinciding with that of decachlorobiphenyl under the conditions used for routine gas liquid chromatography (GLC), and generally exceeding that expected from the decachlorobiphenyl yielded by perchlorination. Fortunately, a second batch of $SbCl_5$ (Baker and Adamson, New York, N.Y., lot no. unavailable), purchased in 1952 and closed with the original sealing plaster, was free of this interfering peak. However, the perchlorination reaction did not go to completion in our hands, and a correction was made to the oil analyses for the 50% reduction in yield as estimated from perchlorination of Aroclor 1254. The yield of decachlorobiphenyl from perchlorination of the two raw oils was less than half that expected from the original estimate of these peaks as Aroclor 1254 by peak height comparisons. Considering the scope for errors in both quantitation procedures, this might be considered reasonable agreement. We prefer to interpret the perchlorination data as confirming qualitatively, or perhaps semiquantitatively, the presence of PCBs in the raw oils.

Peaks corresponding to those in Aroclor 1254 were absent from the processed oils (Fig. 1c). Minimum detectable levels, as Aroclor 1254, were ca. 1 ppm of oil. Perchlorination of the processed oils did not yield any detectable decachlorobiphenyl. The limit of detection of this material was ca. 0.5 ppm in oil, after correction for incomplete perchlorination, which corresponds approximately to 0.3 ppm Aroclor 1254. It is clear that PCB levels originally present in the raw oils were reduced significantly by complete processing.

DISCUSSION

The residue concentrations found in the raw oils were generally similar to those we reported previously (5) in another series of marine oils. Since the levels are also similar to those reported by other authors for various marine organisms (10, 11) (calculated on a lipid basis), we conclude that these concentrations are fairly typical of Canadian commercial marine oils.

The disappearance of residues of the DDT group and dieldrin during refining agrees with the conclusions of other authors (1-4). In the light of published data, it seems likely that they were removed during either hydrogenation (2, 4) or, more likely, deodorization (1-4). Gooding (4) found that residues of the DDT group and of chlordane in cottonseed oil were removed during hydrogenation possibly through adsorption on the catalyst. Smith, et al., (2) postulated a similar process for removal of endrin during hydrogenation of soybean oils. Vacuum deodorization certainly removes significant amounts of residues, the efficiency of removal probably depending upon the severity of the process conditions. Thus, the conditions used in the present work, which were similar to those used by Smith, et al. (2), reduced residues of the DDT group from the 2-8 ppm range observed in our raw oils to below detectable limits (< 0.06 ppm). Parsons (1), however, found only 20% removal of DDT at 190 C (4 mm Hg) and 70% removal at 250 C (4 mm Hg), but his report does not mention the use of steam or the length of exposure to these conditions, either of which factors may affect residue removal.

The disappearance of PCB residues from oils under similar conditions has not been reported, to our knowledge, but was not unexpected. The vapor pressures of PCB mixtures, such as Aroclor 1254 and 1260, are higher than that of *p,p'*-DDT, at least at lower temperatures; at 100 C for Aroclor 1254, Aroclor 1260, and *p,p'*-DDT, respectively, they are ca. 2.3×10^{-1}, 1.8×10^{-1}, and 3.4×10^{-3} mm Hg (12, 13). Conditions which remove *p,p'*-DDT would, therefore, be expected to remove these PCB mixtures from oils. At 250 C, the temperature used for deodorization, Aroclors 1254 and 1260 have vapor pressures of ca. 55 mm Hg and 30 mm Hg, respectively (12). However, since the Aroclors are mixtures, these appreciable vapor pressures are probably due to their more volatile components. For example, biphenyl and the monochlorobiphenyls, all of which are major components of the lower Aroclors (14) and minor components of the higher ones (15), boil at 255-290 C at 760 mm Hg (16). The absence of later eluting PCB peaks from our chromatograms of processed oils is, therefore, of special interest. These compounds are probably considerably less volatile than members of the DDT group, at least as indicated by their longer retention times on nonpolar GLC columns (17); but, being more highly chlorinated, they have enhanced electron capture detector responses. Our failure to detect such compounds indicates that they too are removed during the processing conditions outlined above. It might be noted, however, that comparable deodorization conditions (230 C at 4 mm Hg for 60-90 min) were insufficient to remove a PCB heat transfer agent similar to Aroclor 1254 which was leaked accidentally into a rice bran oil during the deodorization process (18).

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