Removal of Chlorinated Pesticides From Crude Vegetable Oils by Simulated Commercial Processing Procedures

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Abstract

Crude soybean and cottonseed oil were processed using simulated commercial processing procedures to determine if oil processing would remove chlorinated pesticide contaminants of either natural or spiked origin. Two crude oil lots were spiked with endrin, DDT, DDE, aldrin, dieldrin, heptachlor and heptachlor epoxide before processing. Representative samples of crude oil and products following each processing step were analyzed for pesticide contamination. Results indicated that alkali-refining or subsequent bleaching did not reduce chlorinated pesticide contamination. Hydrogenation prior to deodorization reduced endrin contamination. Deodorization, with or without hydrogenation, eliminated chlorinated pesticides. The results of this study indicate that normal commercial processing of crude vegetable oils for human consumption effectively removes any chlorinated pesticides which may be present in crude oils. It is hypothesized that chlorinated pesticide removal is achieved by volatilization during deodorization, which is supported by known volatilization characteristics, similarity of behavior in pesticides studied, and absence of the pesticide or its conversion products in the finished oils, or both.

Introduction

CHLORINATED PESTICIDES ARE USED on many farm crops and are partially responsible for the increased agricultural productivity experienced in this country during the past few years. Concern by many has focused on possible food product contamination by the chlorinated pesticides resulting from misuse of chemicals, accidental product contamination or translocation from the soil to edible portions of the plant.

The specific objectives of the present study were to confirm previous reports that chlorinated hydrocarbons are removed from vegetable oils by processing procedures, that during oil processing endrin would act similarly to other closely related chlorinated pesticides, and that endrin residues are not detectable in the edible oil.

The basis for the study was a scientific communication by Gooding (1) and some limited studies conducted by Shell Chemical Company (2). Gooding spiked a vegetable oil with the following chlorinated pesticides at the indicated levels (ppm): aldrin, 1.0; chlordane, 1.0; DDT, 21.0; dieldrin, 1.0; heptachlor, 1.0; heptachlor epoxide, 1.0; Kelthane, 1.0; lindane, 15.0 and 30.0; methoxychlor, 42.0; sesone, 18.0; Strobane, 15.0; TDE or DDD, 21.0; and toxaphene, 21.0. The oil was alkali-refined, bleached and deodorized under pilot plant conditions. Standard GLC methods employing electron-capture and microcoulometric detectors were used to analyze for residue contamination. Results showed that deodorization caused removal of the pesticide residues to levels below detectability. These results were subsequently confirmed in plant scale tests in which the crude vegetable oil was found contaminated. It was also reported that a vegetable oil containing chlordane (2.8 ppm), DDT (0.5 ppm) and DDD (0.5 ppm) was subjected to hydrogenation during processing, whereupon the pesticide residues disappeared.

A series of U. S. Food and Drug Administration reports has been published on studies of pesticide residues in total diet composite samples which would represent the relative types and amounts of food consumed by 16- to 19-year-old boys during a 14-day period (3–8). The authors reported that the lower limits of sensitivity of the analytical procedures used were 0.01 ppm (1963) and 0.001 ppm (1964–67). Endrin was not detected in the composite food samples (3–5).

Survey results directly applicable to the present study have been reported on composite samples of oils, fats, shortening and other high-lipid diet ingredients. Williams (4) first reported the high-lipid composite sample contained low levels of several chlorinated pesticides. However, endrin was not qualitatively detected at a level of 0.001 ppm. These results were later confirmed (5–7). Duggan et al., (8) reported that endrin was also present in a composite sample of oils, fats and shortenings which may be presumed to be a mixture of animal and vegetable origin. This study, however, did not state the level found or the frequency of contamination in the composite samples analyzed.

These dietary surveys would indicate that processed, edible vegetable oils and oil products should be free of endrin contamination. Even though endrin was not included in Gooding's (1) research report, it would be logical to conclude that endrin would act similarly to related chlorinated pesticides. Each of these references, either directly or indirectly, provided evidence that endrin contamination is not likely to be present in the finished edible vegetable oils.

Experimental Procedures

A total of 10 crude oils, 5 soybean and 5 cottonseed lots were processed in a pilot plant (Votator Division, Chemetron Corporation, Louisville, Kentucky) designed to simulate commercial oil processing procedures. Eight samples of crude oil, suspected of pesticide contamination, were processed. To insure that the processing conditions would not produce any unknown artifacts which could be interpreted as pesticide contamination, a crude soybean oil (SBO) sample and a cottonseed oil (CSO) sample analyzed free of chlorinated pesticides were included as negative controls. All lots were alkali-refined, followed by bleaching and deodorization.

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Two soybean oil samples were hydrogenated and then deodorized. Two cottonseed oil samples were fortified prior to refining with commonly used chlorinated hydrocarbons. The fortification levels for endrin, DDE, aldrin, dieldrin, heptachlor and heptachlor epoxide were 1.0 ppm and for DDT, 21.0 ppm.

Representative samples of crude oil, oil following each processing step and the by-products of processing were obtained, aliquoted and distributed to three analytical laboratories (Shell, Velsicol and Wisconsin Alumni Research Foundation) for pesticide analyses.

Pilot Plant and Oil Processing

Before processing each individual oil sample, all pilot plant equipment was thoroughly washed with hot (180 F) tap water, rinsed with commercial grade hexane followed by a 20° Be sodium hydroxide solution and finally flushed with distilled water. Extensive care was taken in each processing step to prevent external contamination of the samples.

Crude oil lots were thoroughly mixed and then emptied into a 50-gal stainless steel refining kettle. The crude oil was rapidly propeller-agitated (550 rpm) and the caustic solution was slowly added according to AOCS specifications (9). The agitation was continued for 20 min at ambient temperatures (80–90 F). Agitation was then reduced to 10–15 rpm (paddle-type-agitator) and the oil was heated (SBO, 160 F; CSO, 140 F) by circulating steam in the jacket of the refining kettle. When the desired temperature was reached, steam and agitation were turned off and the oil was allowed to settle until a clean break was observed. The soapstock was drained, weighed and sampled.

The refined oil was washed with 15 wt per cent hot water (SBO, 150 F; CSO, 140 F). Under rapid agitation, the temperature of the oil was increased (SBO, 170 F; CSO, 160 F) and held at temperature for 30 min. The oil was then allowed to settle until the break was complete. Wash water was removed and samples of wash water and refined oil were obtained.

The refined oil was transferred to the vacuum bleaching vessel and bleaching agent added (SBO, 1% acid clay; CSO, 1% neutral clay plus 0.2% activated carbon; both oils, 0.5% filter aid). Under vacuum (50 mm Hg abs), the oils were slowly heated (approx ½ hr) to temperature (SBO, 220 F; CSO, 200 F) and held at temperature for 20 min. The oil was then pumped through a horizontal-plate pressure filter to remove the adsorptive clay. The refined-bleached oil was weighed and sampled.

Two samples of soybean oil were hydrogenated. After the hydrogenation vessel was charged with oil and the residual air removed by vacuum (50 mm Hg abs), the oil temperature was increased (230–250 F) to dehydrate the oil. The vacuum was broken with hydrogen. Nickel was used to catalyze the reaction (0.05%). During hydrogenation, the hydrogen pressure was maintained at 40 psig and the temperature at 275 F. After the desired iodine number was obtained (70–80), the oil was cooled under vacuum (50 mm Hg abs to approx 175–185 F). Vacuum was then broken with nitrogen and the hydrogenated oil was filtered through a horizontal-plate pressure filter to remove the used catalyst. The hydrogenated oil was weighed and sampled.

During deodorization, the refined-bleached oils or refined-bleached-hydrogenated oils were heated to temperature (SBO, 485 F; CSO, 460 F) under vacuum (6 mm Hg abs) and held for 1 hr. While the oil was being taken to temperature, 3 lb. (1½ wt per cent) stripping steam was added to agitate the oil. When the oil was at temperature, a total of 6 lb. (3 wt per cent) stripping steam was passed through the vessel to accomplish deodorization. Component weights were recorded and samples were obtained for chemical analysis.

Analytical Procedures

The three participating laboratories employed analytical methods for determination of the chlorinated hydrocarbons which were essentially equivalent to those described in the FDA Pesticide Analytical Manual (10). Small variations in procedures used by the respective laboratories are considered of no significance in this collaborative effort.

In general, the oil material was extracted with hexane, partitioned into acetonitrile and exchanged back into hexane. After washing and drying the hexane solution with sodium sulfate solution, aliquots were cleaned by liquid-solid chromatography through an activated Florisil column. Three separate elutions were collected and subjected to gas chromatographic analysis for chlorinated hydrocarbons.

The utilization of standard GLC methods employing electron-capture and microcoulometric detection systems permitted extreme sensitivity to the chlorinated hydrocarbons. Based on the equipment capability, normal background noise, and the interfering

TABLE I

Results Obtained in Processing the Vegetable Oils Under Pilot Plant Conditions[a]

Process	SBO-1	SBO-2	SBO-3	SBO-4	SBO-5	CSO-1	CSO-2	CSO-3	CSO-4	CSO-5
Refining										
Quantity of oil refined, lb.	222	226	210	222	295	225	212	221	203	295
Free fatty acids in oil, wt. %	0.71	0.72	1.17	0.30	0.30	2.70	2.75	2.60	2.20	0.49
Caustic used, lb.	12.6	19.2	20.4	16.9	22.5	21.6	20.8	21.0	17.9	23.2
Refined oil recovered, lb.	209	204	182	187	260	191	178	182	178	241
Refining loss, wt. %	5.9	9.7	13.3	15.8	11.9	15.1	16.0	18.4	12.3	18.3
Bleaching										
Quantity of oil bleached, lb.	206	201	179	184	255	188	175	179	175	236
Bleached oil recovered, lb.	197	200	176	175	245	187	168	176	162	225
Hydrogenation										
Quantity of oil hydrogenated, lb.		197		172						
Hydrogenated oil recovered, lb.		147		86						
Deodorization										
Quantity of oil deodorized, lb.	194	147	173	200[b]	200	184	165	173	159	200
Deodorized oil recovered, lb.	189	136	170	198	190	172	156	166	144	186
Condensate recovered, lb.	0	0.25	0.25	4.0	4.0	3.75	0.5	0.25	0.25	0.25

[a] SBO = Soybean oil.
CSO = Cottonseed oil.
[b] Composed of 86 lb. hydrogenated SBO-4 and 114 lb. deodorized SBO-2.

TABLE II

Level of Endrin Detected in the Various Crude Vegetable Oil Lots

Oil sample	Location produced	Level endrin found (ppm)[a]			
		Lab 1	Lab 2	Lab 3	Average[b]
SBO-1	Area suspected of contamination	0.61	0.78	0.48	0.62
SBO-2	Area suspected of contamination	0.77	0.54	0.14	0.48
SBO-3	Area suspected of contamination	0.41	0.43	0.36	0.40
SBO-4	Area suspected of contamination	0.35	0.24	0.07	0.22
SBO-5	Area not suspected of contamination	BDL	BDL	0.03	0.01
CSO-1	Area suspected of contamination	BDL	0.03	BDL	0.01
CSO-2	Area suspected of contamination	BDL	0.19	BDL	0.06
CSO-3	Area suspected of contamination	BDL	BDL	0.03	0.01
CSO-4	Area suspected of contamination	I	BDL	BDL	BDL
CSO-5	Area not suspected of contamination	BDL	0.05	BDL	0.02

[a] SBO = Soybean oil.
CSO = Cottonseed oil.
BDL = Below detectable limits of analysis.
I = Interference in sample analysis.
[b] Calculated by taking average of values reported by the three laboratories.

substance contained in the biological samples analyzed, it was believed that the lower limit of confident analysis was approximately 0.03 ppm. Based on extensive recovery data, values below 0.03 ppm were not considered analytically significant in this study.

Results and Discussion

Pilot Plant Processing of Oil

Data obtained in the pilot plant processing of the vegetable oils are shown in Table I. The weight of soapstock can be calculated by determining the differences between the crude oil refined and refined oil recovered. The weight of soapstock is dependent upon content of the free fatty acids, phosphatides, etc., in the crude oil and the amount of neutral oil occluded with the soapstock. In the batch refining procedure used in this pilot plant study, more than usual occluded neutral oil occurred in the soapstock because of difficulties in obtaining a clean-cut soapstock-neutral oil separation. Samples of soapstock analyzed for neutral oil showed that approximately 30–35% of the weight of soapstock was neutral oil. Therefore, the refining loss was high when compared to commercial refining where the normal range is 15–22% occluded neutral oil in soapstock.

During deodorization, approximately 9 lb. of stripping steam was passed through the oil. The stripping steam and the vaporized materials were pulled from the closed vessel and were partially condensed in a water condensate trap. The amounts of condensate recovered per batch varied from none to 4 lb. Freezing out more condensate was attempted and found impractical.

Analytical Laboratory Results

Table II shows data on endrin contamination of the four test soybean and four test cottonseed oils that were randomly sampled from two crude oil mills in the area suspected of producing crude oils with pesticide residue contamination. One crude soybean oil and one crude cottonseed oil were chosen from an area which uses little or no endrin; the oils were analyzed and found free of pesticide contamination prior to processing. This table shows that the negative control soybean and cottonseed oils were at or below the sensitivity of the analytical methods for endrin. Chlorinated pesticide contamination of the crude cottonseed oils used in this study was doubtful.

Table III illustrates a comparison of endrin analytical values for four soybean oils in stages of processing. Considerable variation was observed between the endrin content of the oil lots. Within the precision of this experiment, endrin levels were equivalent in the crude, refined and bleached oils; none was detected at the sensitivity level of the analytical method in deodorized oil.

The average analytical values obtained when two fortified cottonseed oils were processed and analyzed by three laboratories are presented in Table IV. Processing had a similar effect on all chlorinated pesticides studied: the refined and bleached oils had similar amounts of pesticides present, while pesticide contamination could not be established in the deodorized oils. Trace levels of DDT and endrin were reported by one laboratory; however, the other two laboratories could not confirm the presence of detectable levels of chlorinated residues.

Table V gives calculated amounts of endrin in each of the processing fractions. Since essentially all the endrin can be accounted for during refining and bleaching, it would appear that these processes would be of minimal importance in reducing the pesticide level of contaminated oils.

Vacuum deodorization removed endrin and other chlorinated pesticides studied. This was not surprising considering the similarity in the physical and chemical properties of the related chlorinated pesticides and the previous research reports on the removal of certain pesticides from oil by deodorization (1,2,11). These reports should eliminate possible concern over edible oils being produced from crude oils containing significant amounts of pesticides since all edible vegetable oils are deodorized in processing.

Two soybean oils were hydrogenated prior to deodorization and the level of endrin was reduced to near or below the lower detectable limits for the analytical method. These results confirm observations by Gooding (1) and Shell (2).

Since it has been established that hydrogenation or deodorization, or both, will eliminate endrin from the resulting edible oil, the question arises as to the fate of these pesticides during these processes.

TABLE III

Effect of Processing on Endrin Residue Levels in Four Soybean Oils Initially Suspected of Pesticide Contamination[a]

Oil sample	Crude oil	Refined oil	Bleached oil	Deodorized oil
		ppm		
SBO-1	0.62	0.59	0.51	BDL[b]
SBO-2	0.48	0.30	0.35	BDL
SBO-3	0.40	0.64	0.48	BDL
SBO-4	0.22	0.30	0.29	BDL
Mean	0.43	0.46	0.41	BDL

[a] Individual crude, bleached and deodorized oil values represent mean analyses of the three laboratories. Two analyses compose the refined oil values.
[b] BDL = Below detectable limits of analysis.

TABLE IV

Pesticide Residues Found in Fortified Cottonseed Oils at Various Stages of Processing[a]

	Refined oil	Bleached oil	Deodorized oil
	ppm		
Endrin	0.42	0.65	[b]
DDT	11.1	12.5	[c]
DDE	0.92	0.83	BDL[d]
Aldrin	0.55	0.65	BDL
Dieldrin	0.72	0.64	BDL
Heptachlor	0.58	0.69	BDL
Heptachlor epoxide	0.77	0.86	BDL

[a] Average pesticide value of two oils with three independent laboratory analytical values per oil.
[b] Values (CSO-1, 0.07; CSO-2, 0.08) were reported by one laboratory and the other two laboratories could not confirm the presence of a detectable level of residue.
[c] A value of 0.06 ppm was reported for CSO-2 by one laboratory and not confirmed by other laboratory analyses.
[d] BDL = Below detectable limits of analysis.

Endrin may be eliminated from the bleached oil during hydrogenation by adsorption onto the activated carbon contained in the catalyst, by reductive dehalogenation of the chlorinated hydrocarbon endrin molecule (12), or by volatilization of the molecule under the pressure-temperature conditions of hydrogenation. It would be unlikely that complete isomerization would occur at the hydrogenation temperature (275 F), since Phillips et al. (13) showed that isomerization occurred but at much higher temperatures (450+F). The analytical laboratories were unable to detect endrin rearrangement products or unknown chlorinated breakdown products in the hydrogenated oil.

The data indicate that the chlorinated hydrocarbons are removed from the neutral oil during deodorization by forced volatilization. Endrin or its isomerization products, or both, appeared to act in a similar manner.

Evans (14) reported a preliminary study to assess the fate of endrin using radioactive carbon-labeled endrin. Laboratory deodorization showed that at low levels (under 3.5 ppm) 96% of the radioactivity was removed from the oil. Seventy-five per cent of the original activity was recovered in the condensate. It was stressed that these results were of preliminary nature.

Ott and Gunther (15) used forced volatilization of chlorinated pesticides (lindane, aldrin, dieldrin, DDD, DDE and heptachlor epoxide) for quantitative isolation from butterfat. The equipment described in their paper is essentially a small scale deodorizer; the temperature of the liquid material is essentially the same in both systems (530 F vs. 475 F for the pilot plant deodorizer). The only difference between systems is that one bubbles nitrogen and the other dry steam. The volatility of chlorinated pesticides was stressed as a possible source of error in pesticide measurements (16).

The foregoing references emphasize the volatility of chlorinated pesticides. It would appear that one could be completely justified in considering that chlorinated pesticides and their rearrangement or breakdown products behave in a similar fashion.

TABLE V

Average Endrin Content in Various Oil Fractions Obtained in Processing the Four Soybean Oils[a]

	Total endrin content
	mg
Crude oil	43.1
Soapstock oil loss	4.8
Refined oil	40.9
Bleached oil	36.5
Deodorized oil	BDL[b]

[a] Values are calculated from mean endrin analyses and oil fraction weights of the four soybean oils.
[b] BDL = Below detectable limits of analysis.

Therefore, if endrin does rearrange (13,17) at the temperature experienced in deodorization, it would not be of great concern since the conversion product would be volatilized.

A material balance for the pesticides was not established because of incomplete recovery of the deodorizer condensate. Rapid distillation of the chlorinated hydrocarbons and the lack of sophisticated collection equipment are two factors which probably prevented the complete recovery of the pesticide contaminants.

The overwhelming preponderance of evidence obtained in this study appears to justify fully the conclusion that vegetable oils processed for human consumption are free of chlorinated pesticide residues, including endrin. The data strongly support the hypothesis that if contamination of crude vegetable oils should occur from the use of pesticides during the growth period of the oilseeds, or artificially in handling of the seed or extracted oil, such pesticides will be removed through the pathway of volatilization during hydrogenation or deodorization, or both.

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