Distribution of Chlorinated Pesticides in Soybeans, Soybean Oil, and Its By-products during Processing

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ABSTRACT

Soybean samples were collected from seven different locales in Central Illinois and subjected to analysis for chlorinated pesticides. Different parts of the beans showed varying levels of residue concentrations. It was found that pesticide residues had a tendency to accumulate, in descending order, in hypocotyls, hulls and cotyledons on the basis of ground samples. When oils extracted from the same fractions were analyzed, much higher concentrations of residues were located in hulls than hypocotyls, which had greater concentrations than cotyledons. Crude, refined, bleached and deodorized oils, soapstock, Fuller's earth sludge and deodorization condensate were analyzed for hexachlorobenzene isomers, heptachlor, heptachlor epoxide, aldrin, dieldrin, DDT, DDD and DDE. None of the processing steps except deodorization were completely effective in the removal of chlorinated pesticide residues. Oil deodorized at 250 C under 1-5 mm pressure was almost free of such residues, whereas all the residues were concentrated in deodorization condensate.

INTRODUCTION

Occurrence of chlorinated residues in soils due to intentional uses as pesticides or unintentional contamination or translocation from other environments has been reported and discussed by many workers (1-5). Bruce et al (5) have correlated the translocation of some chlorinated pesticides from the treated soils to the oil-bearing plants. Effective removal of these residues has also been carried out by various techniques, as discussed by Meemken (3), Smith et al (6), Gooding (7), Mounts et al (8), and Addison (9). However, the effectiveness of each processing step, viz, refining, bleaching and deodorization of oil, in the removal of a complex mixture of pesticide residues has not been thoroughly investigated. Chaudry et al (10) have studied the distribution of aldrin and dieldrin in soybeans, oil and by-products during processing. This report discusses the distribution of commonly occuring chlorinated pesticide residues in soybeans, their fractions, and in the oil and processing by-products, and evaluates the effectiveness of each processing step on the removal of residues.

MATERIALS AND METHODS

The sources of the samples, their preparation and method of oil extraction from them have been discussed earlier (10). Refining of oil was carried out according to AOCS method No. Ca 9b-52. (11). After decanting the oil, soapstock was transfered to a centrifuge tube and centrifuged at 2000 rpm. The supernate was decanted and added to the bulk of the oil; soapstock was weighed and saved for cleanup and residue analysis. The refined oil was bleached using official activated bleaching earth of the American Oil Chemists' Society, following the method No. Cc 8b-52 from the Official and Tentative Methods of Analysis of the American Oil Chemists' Society (11).

Deodorization was performed on bleached oil in an all glass minideodorizer. A 10 g sample was weighed into a 100 ml round bottom distillation flask, equipped with a 360 C thermometer, and placed in a heating mantle. The outlet was attached to a vacuum pump capable of producing <1 mm pressure under the conditions outlined. The outlet line was equipped with a cold water condenser, a dry ice/acetone trap and a liquid nitrogen trap to avoid escape of any volatiles into the pump. The equipment was also supplied with an internal steam generation system so that the amount of steam passing through the oil could be controlled. The oil was heated to ca. 240 C, and freshly generated steam was introduced under <1 mm pressure. The temperature of the oil was held at 250±2 C for two hours, with continuous flow of steam through the oil. The steam was passed at the rate of about 30% water to oil per hr. The condensate was collected in both the dry ice and the liquid nitrogen traps.

The samples of crude oil, refined oil, soapstock, bleached oil, bleaching earth sludge, deodorized oil and deodorization condensate were collected for pesticide residue analysis.

Processing by-products (soapstock, bleaching earth sludge and deodorization condensate) were extracted with nanograde petroleum ether (Mallinckrodt, Inc., St. Louis, Mo.). All the above extracts and oil samples were partitioned with acetonitrile, then extracted with petroleum ether and evaporated to about 10 ml, according to Official Methods of Analysis of the Association of Official Analytical Chemists, method No. 29.014 (12).

The above extracts were cleaned using a Florisil column following the procedure detailed in Official Methods of Analysis of the Association of Official Analytical Chemists, method No. 29.015 (12). The fractions obtained from cleanup were analyzed by gas liquid chromatography for thirteen most common chlorinated pesticides, namely, αBHC, lindane, βBHC, heptachlor, aldrin, heptachlor epoxide, pp′ DDE, dieldrin, op′ DDD, endrin, op′ DDT, pp′ DDD and pp′ DDT. A gas chromatography (HP5710A), equipped with electron capture detector (Ni 63) maintained at 300 C, was used. A 6 ft. glass column (3 mm ID) packed with 1.5% SP 2250:1.95% SP 2401 on 100-120 Supelcoport (Supelco Inc., Supelco Park, Bellefonte, PA 16823), at a temperature of 210 C, was employed for the analyses. Identification and quantitation was achieved by comparison of retention times and peak area measurements of appropriate standards. Peak areas were measured by triagulation of the peaks and the use of a planimeter.

RESULTS AND DISCUSSION

Pesticide residue concentrations in various soybean fractions are reported in Table I. Residues found in the corresponding extracted crude oils from these fractions are summarized in Table II. All the soybean fractions and oils extracted therefrom contained varying concentrations of the residues except for pp′ DDE and op′ DDD. Among the latter residues only op′ DDD was found in small concentrations in the hulls fractions. Generally, all other residues were found in cotyledons, whole soybeans, hulls and hypocotyls and fines, in ascending order. Total polychlorinated pesticides were found to be 80.9, 108.4, 144.2 and 326.2

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TABLE I

Pesticide Residues in Various Fractions of Soybeans[a]

Pesticide	Whole Beans[b]	Cotyledons	Hulls	Hypocotyls and Fines
αBHC	9.1(9.4)	3.8(2.6)	5.6(2.5)	18.7(16.6)
Lindane	4.0(5.1)	1.7(1.3)	4.9(4.3)	11.0(6.8)
βBHC	3.3(3.1)	1.8(0.9)	8.3(3.9)	17.7(12.2)
Heptachlor	1.8(2.5)	1.8(1.3)	6.9(6.1)	17.6(14.5)
Aldrin	6.9(8.9)	2.2(4.3)	6.6(4.4)	25.0(26.5)
Heptachlor-epoxide	10.1(8.2)	8.4(7.2)	14.0(13.7)	46.4(27.0)
pp' DDE	---	---	---	---
Dieldrin	46.8(39.6)	46.4(28.1)	69.3(65.5)	117.3(91.6)
op' DDD	---	---	1.1(0.3)	---
Endrin	10.0(8.9)	5.9(6.2)	12.6(9.1)	25.5(19.5)
op' DDT	6.3(5.6)	3.2(4.3)	6.9(6.8)	10.3(8.3)
pp' DDD	1.8(1.9)	1.8(2.1)	2.3(3.5)	6.9(8.1)
pp' DDT	8.3(6.4)	3.9(2.8)	5.7(5.2)	29.8(28.8)
Total Residues	108.4	80.9	144.2	326.2

[a]Mean parts per billion from 8 samples, with standard deviations in the parentheses.
[b]Whole beans composed of 90.18% cotyledons, 7.35% hulls and 2.47% hypocotyls and fines.

TABLE II

Pesticide Residues in Extracted Crude Oil[a]

Pesticide	Whole Beans	Cotyledons	Hulls	Hypocotyls and Fines
αBHC	44.6(45.9)	18.0(12.6)	166.3(74.8)	76.2(67.7)
Lindane	19.7(24.9)	8.0(6.2)	145.2(128.8)	45.0(27.8)
βBHC	16.0(15.4)	8.5(4.5)	247.3(115.5)	72.1(49.7)
Heptachlor	8.6(12.3)	8.8(6.1)	204.9(180.9)	71.7(59.1)
Aldrin	33.8(43.6)	10.4(20.4)	196.9(131.1)	102.0(108.2)
Heptachlor-epoxide	49.6(40.3)	40.4(34.6)	415.6(405.9)	189.2(110.3)
pp' DDE	---	---	---	---
Dieldrin	229.5(194.2)	222.6(134.7)	2056.7(1944.6)	478.7(374.0)
op' DDD	---	---	33.6(10.1)	---
Endrin	48.9(43.4)	28.3(29.7)	375.0(270.6)	104.0(79.6)
op' DDT	30.7(27.3)	15.4(20.6)	204.7(200.5)	42.1(33.7)
pp' DDD	8.7(9.1)	8.5(10.2)	68.0(105.0)	28.3(32.9)
pp' DDT	40.5(31.5)	18.8(13.5)	170.5(153.3)	121.6(117.5)
Total Residues	530.6	387.7	4284.7	1330.9

[a]Mean parts per billion in oils extracted from 8 different samples of each soybean fraction, with standard deviations in the parentheses.

parts per billion in cotyledons, whole beans, hulls and hypocotyls and fines, respectively. When the concentrations of the residues were calculated in the extracted crude oil (Table II) rather than in ground bean fractions, it was found that the residues were more concentrated in hull oil followed by oil extracted from hypocotyls and fines, whole beans and cotyledons, respectively. The total concentrations of chlorinated residues were 387.7, 530.6, 1330.9 and 4284.7 parts per billion in the oils extracted from cotyledons, whole beans, hypocotyls and fines, and hulls, respectively.

Other workers (1,2) have reported similar levels of dieldrin and other residues as found in this study for whole soybeans. However, multiresidue concentrations in different fractions of beans have not been previously compared.

A tabulation of pesticide residues in oils and processing by-products from oil extracted from cotyledons is given in Table III. The values have been calculated in parts per billion and are averages of 8 different samples on the basis of total soapstock and total sludge comprising oil and earth. For deodorization condensate the basis for calculation was total oil loss during deodorization, which does not account for steam condensation. It is evident from the table that residue levels in the oil decreased as expected with refining, bleaching and deodorization, but deodorization was by far the most effective in their removal. Soapstock and Fuller's earth sludge did contain certain amounts of residues. In general, soapstock contained lower concentrations of residues than refined oil, but sludge had higher concentrations than bleached oil except for heptachlor epoxide and dieldrin. This suggests that some of the residues might be eliminated from the oil bound to the Fuller's earth particles. Almost all the compounds studied were concentrated in deodorization condensate except for op'DDD and endrin. op'DDD was not present in the oil to start with, and the endrin concentration was also very low. Deodorized oil contained only very small levels of BHC, aldrin and heptachlor epoxide, which could have been removed completely if the oil was deodorized for a longer period of time. It is apparent that chlorinated pesticide residues are removed through volatilization during deodorization of the oil, as has been suggested by previous reports (3, 6-9).

The present study has shown that the chlorinated pesticide residues were distributed among all parts of the soybean itself, more in hulls and hypocotyls and fines, and less in cotyledons. Furthermore, deodorization of the oils most effectively removes these compounds. It must be emphasized that the seemingly high levels of residues in the oil extracted from the hull, hypocotyl and fines (Table II) results from a concentration factor, since the oil content of these fractions is very small. When calculated as content of the bean fraction, these values (Table I) are not unreasonable. The relatively large standard deviations are due to the somewhat larger spread of residues in eight different samples, because of differences in the origin of the samples from different fields. However, the distribution of the residues in different fractions of the beans was as would be

TABLE III

Pesticide Residues in Samples of Cotyledonous Oil at Different Stages of Processing[a]

Pesticide	Refined oil	Soapstock[b]	Bleached oil[c]	Fuller's earth sludge	Deodorized Oil	Deodorization[d] condensate
αBHC	18.6(9.0)	3.3(2.2)	10.7(5.2)	17. 7(15.9)	1.2(3.2)	1459.0(1729.1)
Lindane	9.1(7.8)	8.5(6.1)	7.4(7.1)	29. 3(32.6)	---	178.8(130.8)
βBHC	7.9(13.2)	2.9(3.1)	2.3(4.8)	47. 8(58.2)	1.7(1.6)	173.8(271.7)
Heptachlor	14.5(23.0)	2.7(2.4)	3.2(9.1)	17. 2(31.7)	---	426.2(286.1)
Aldrin	7.6(11.1)	2.4(3.4)	4.8(9.0)	24.7 (29.4)	0.9(2.4)	883.8(663.1)
Heptachlor-epoxide	59.7(30.4)	14.5(8.6)	66.5(32.5)	29. 6(26.6)	1.6(4.6)	3648.4(1355.0)
pp' DDE	8.4(23.8)	0.8(2.2)	7.6(21.6)	27. 5(77.8)	---	930.7(2632.5)
Dieldrin	179.2(108.2)	41.3(28.2)	142.7(121.5)	95. 9(52.1)	---	8012.9(5267.9)
op' DDD	---	---	---	---	---	---
Endrin	3.2(9.1)	2.6(4.8)	---	---	---	---
op' DDT	29.6(26.5)	3.5(4.4)	1.8(3.7)	18. 0(21.8)	---	822.7(463.5)
pp' DDD	3.2(9.7)	---	---	---	---	12.4(35.0)
pp' DDT	20.8(25.7)	3.1(3.4)	12.5(19.8)	15. 2(21.8)	---	768.2(424.1)

[a]Mean parts per billion for eight samples, with standard deviations in the parentheses.
[b]On the basis of total soapstock.
[c]On the basis of total sludge comprising oil and earth.
[d]On the basis of oil loss, not accounting for the steam condensate.

expected. For example, a typical recovery of βBHC in all three fractions combined was 94.33% of the residue found in whole beans, out of which 63.6% was distributed in cotyledons, 20.8% in hulls and 15.6% in hypocotyls and fines.

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