Distribution of Aldrin and Dieldrin in Soybeans, Oil, and By-Products during Processing

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ABSTRACT

Soybean samples acquired from aldrin-treated and nontreated fields were analyzed for aldrin and dieldrin content of oil from different fractions of soybeans. By simulating commercial processing techniques on a semimicro level, samples of oils and wastes collected after refining, bleaching, and deodorization were also subjected to pesticide residue analysis. In general, dieldrin levels in soybeans, or fractions thereof, had a clear positive relationship with the aldrin applications. Soybean cotyledons were found to contain lesser amounts of aldrin hypocotyles and fines than whole beans, hulls, and/or hypocotyles and fines. Deodorization of oil was noted to be the most effective in the removal of pesticides, and deodorizer distillate had high concentrations of aldrin and dieldrin, although pesticide levels in the oil decreased somewhat after each processing step. Processed oil was found to be free of aldrin and dieldrin residues up to instrumental detection limits.

INTRODUCTION

Chlorinated pesticides have long been used for increased agricultural production throughout the U.S. According to Matsumura et al. (1), the methods of introduction can vary: the majority of pesticides applied eventually reaches the soil surface, where they eventually degrade, gradually spread over, or are translocated to other environments. However, their translocation or degradation is so slow that it takes 1-6 years for aldrin and 5-25 years for dieldrin for 95% disappearance (2). Bruce et al. (3) have also demonstrated the translocation of insecticidal residues from soil reservoirs to the oil-bearing plant seeds like soybeans and peanuts. The sources of pesticides and possible means to reduce their levels during processing of oils and fats have been discussed by Meemken (4). It has been reported by Smith et al. (5) and Gooding (6) that most chlorinated pesticides are effectively removed from soybean and cottonseed oils by modern processing techniques. Mounts et al. (7) used radiochemical techniques to trace the fate of minor constituents in soybean oil and found satisfactory removal of ^{14}C-endrin by deodorization at 250 C for 2 hr at a pressure of 4.5 mm. Their findings indirectly support the hypothesis forwarded by Smith et al. (5) that chlorinated pesticide removal is achieved by volatilization during deodorization, which in turn is supported by known volatilization characteristics, similarity of behavior in pesticides studied, absence of pesticide, and/or its conversion products in the finished oil.

The objectives of this study were to determine the distribution of aldrin and dieldrin from soybean fractions, as well as oil, and to determine the levels present at each processing step in each product formed.

MATERIALS AND METHODS

Soybean Samples

Seven lots of soybeans were obtained from the 1975 crop in central Illinois areas where a record of previous pesticide treatment was available. Two records of aldrin application went back to 1959 and 1960; whereas in one other field, no aldrin, to the best of the grower's knowledge, had been applied. The record of aldrin treatment on the fields in which the previous lots of soybeans were produced is presented in Table I.

One lot of beans was sized using a 15/64 in. screen. Beans passing through the screen were labeled as "small," while beans larger than 15/64 in. were considered "large."

The following fractions were used for the purpose of oil extraction, processing of oil, and pesticide residue analysis: 1. whole soybeans (ground); 2. cotyledons (ground); 3. hulls (ground); and 4. hypocotyles and fines.

The samples were extracted with glass distilled petroleum ether and oil recovered by removal of the excess petroleum ether by distillation in vacuo.

Refining

A 100 g sample of oil was refined in a 300 ml stainless steel beaker equipped with a magnetic stirrer and placed in a constant temperature hot water bath. A reagent blank was run with each step, and the oil was refined according to AOCS Method Ca 9b-52 (8). The soapstock was centrifuged to recover as much oil as possible.

Bleaching

Bleaching was performed on the refined oils from above according to AOCS Method Cc 8b-52 (8); official activated bleaching earth was acquired from the American Oil Chemists' Society.

Deodorization

A 10 g sample of refined and bleached oil was deodorized in an all glass minideodorizer. The sample was placed in a three-mounted 100 ml round bottom flask, heated with a heating mantle, and equipped with a thermometer. The oil was heated to ca. 240 C, and freshly generated steam was introduced under $<$1 mm pressure; the oil was heated to 250 $\pm$ 2 C and pressure maintained at 4-5 mm for 2 hr. The condensate was collected in dry ice and liquid N_2 double trap, so that no volatiles escaped into the vacuum pump.

The samples were collected at all stages of the processing of oil, soapstock, bleaching sludge, and deodorization condensate for pesticidal residue analysis.

Pesticide Residue Analysis

Soapstock, sludge, and condensate were extracted with petroleum ether, nanograde (Mallinckrodt, Inc., St. Louis, MO) and partitioned with acetonitrile along with oil samples from different processing steps. These were then cleaned using a flourisil column following the procedure outlined in *Official Methods of Analysis* of the Association of Official Analytical Chemists (9).

The cleaned samples were analyzed by gas liquid chromatography on a 6 foot glass column with 3 mm inside diameter, packed with 1.5% SP 2250/1.95% SP 2401 on 100-120 Supelcoport, mounted in an HP 5710A gas chromatograph, set at 210 C, equipped with electron capture (Ni 63) detector at 300 C. The results of the analysis are reported in Tables I and II.

RESULTS AND DISCUSSION

A history of aldrin application to various fields from which the soybean samples were obtained, and aldrin and

TABLE I

Pesticide REsidues in Various Fractions of Soybeans[a]

Source[b]	Pesticide	Cotyledons (ppm)	Whole beans (ppm)	Hulls (ppm)	Hypocotyles and fines (ppm)
A	Aldrin	.006	.011	.013	.071
A	Dieldrin	.055	.037	.030	.284
B	Aldrin	.011	.028	.011	.062
B	Dieldrin	.065	.048	.052	.122
C	Aldrin	–	.006	.005	.010
C	Dieldrin	.073	.123	.141	.178
D	Aldrin	–	–	.003	.006
D	Dieldrin	.064	.060	.099	.146
E	Aldrin	–	.003	.004	.001
E	Dieldrin	.014	.021	.009	.014
F	Aldrin	–	.003	.008	.013
F	Dieldrin	.074	.074	.144	.139
G	Aldrin	–	–	.002	.014
G	Dieldrin	.009	.011	.013	.039
H	Aldrin	–	.005	.002	.023
H	Dieldrin	.017	.001	.006	.019

[a]Calculated on the basis of ground samples.

[b]A-Rantoul beans (small soybeans) from a field in the vicinity of Rantoul, IL; the beans were grown to be used for seed, and aldrin was applied during current season.

B-Rantoul beans (large soybeans); as above.

C-Montgomery County, IL (No. 1 soybeans); continuous corn with aldrin from 1960 through 1971. Corn with aldrin in 1973; soybeans in 1972 and 1974.

D-Montgomery County (No. 2 soybeans); continuous corn with aldrin from 1968-1973. Soybeans in 1974.

E-Montgomery County (No. 3 soybeans); corn in 1970 and 1971 with aldrin only in 1970. Since then soybeans. Earlier this field was in diverted acres and wasteland.

F-Montgomery County (No. 4 soybeans); yearly corn-soybean rotation since 1959. Aldrin applied to corn in 1959, 1961, 1963, 1965, 1967, 1969, 1971, and 1973.

G-Montgomery County (No. 5 soybeans); aldrin applied to corn in 1963, 1965, 1967, 1969, 1971, and 1973.

H-Montgomery County (No. 6 soybeans); no aldrin was ever used in the field.

TABLE II

Pesticide Residues (ppm) in Oil Samples from Different Stages of Processing

Source[a]	Pesticide	Crude oil	Refined oil	Soapstock[b]	Bleached oil	Bleaching sludge[c]	Deodorized oil	Deodorized condensate[d]
A								
Cotyledons	Aldrin	.0298	–	.0021	–	.0205	–	.4906
Cotyledons	Dieldrin	.2573	.1070	.0392	.0938	.0700	–	5.9902
B								
Cotyledons	Aldrin	.0537	.0095	–	–	–	–	.8307
Cotyledons	Dieldrin	.3126	.1726	.0320	.0951	.0586	–	9.3569
C								
Cotyledons	Aldrin	–	.0200	.0064	.0063	.0303	–	.8960
Cotyledons	Dieldrin	.3512	.3472	.0989	.3142	.1666	–	15.7686
D								
Cotyledons	Aldrin	–	–	–	–	.0123	–	.0251
Cotyledons	Dieldrin	.3039	.2781	.0560	.2548	.1191	–	6.1846
E								
Cotyledons	Aldrin	–	.0024	.0019	.0060	.0809	–	2.2494
Cotyledons	Dieldrin	.0666	.1158	.0168	.0399	.1561	–	9.7705
F								
Cotyledons	Aldrin	–	–	.0089	–	–	–	1.3190
Cotyledons	Dieldrin	.3560	.2725	.0534	.2816	.1051	–	13.8575
G								
Cotyledons	Aldrin	–	–	–	–	.0539	–	.6361
Cotyledons	Dieldrin	.0431	.0364	.0157	.0616	.0831	–	–
H								
Cotyledons	Aldrin	–	.0289	–	.0261	–	.0069	.6237
Cotyledons	Dieldrin	.0838	.1043	.0185	.0003	.0089	–	3.1750

[a]Source references as per Table I.

[b]On the basis of total soap stock.

[c]On the basis of total sludge comprising oil and earth.

[d]On the basis of oil loss, not accounting for steam condensate.

dieldrin content is reported in Table I. Consideration of Table I seems to show that dieldrin levels in the soybeans, or fractions thereof, have a weak but clear relationship with the aldrin application to the fields, which is supported by the fact that aldrin under field conditions quickly oxidizes to dieldrin and other breakdown products.

Contrary to our results, no pesticide residue should have been found in Montgomery County No. 6 sample, since no aldrin or other pesticide was ever applied to those fields to the best knowledge of the farmer. But these findings agree with those of Petty et al. (10) who found dieldrin residues in soybeans grown on untreated soils. The findings are also supported by the hypothesis of translocation of pesticides forwarded by Matsumura et al. (1).

The results of this study generally follow those found in previous works by Petty et al. (10) and Bruce and Decker (11). They showed dieldrin residues in whole soybeans that generally cover the range of pesticides found in this work.

When the pesticide residues were analyzed in various fractions of soybeans, it was noted that cotyledons, in general, had lower amounts of aldrin than whole beans, though the differences were not drastic; wherease there were higher amounts of pesticide residues in corresponding fractions of hulls and hypocotyles and fines. However, dieldrin exhibited a dissimilar trend.

Table II shows data obtained from different fractions during processing, on aldrin and dieldrin, in oil extracted from samples of cotyledons. All the samples were found to contain dieldrin residues, and two samples also contained aldrin. It is interesting to note that pesticide levels decreased with each processing step in the oil viz. refining, bleaching, and deodorization. The deodorized oil did not show any aldrin or dieldrin under the detection limits used. However, the residues were not found to be concentrated much in soapstock or bleaching sludge. In either, the levels found were usually lower than those found in the crude oil. It does not seem likely that residue levels would be lower in refined and bleached oils as well as soapstock and bleaching earth, as compared to crude oil. Most likely reasons would be that soapstock and bleaching sludge were analyzed on a total weight basis and not on the basis of their oil content only. Almost all the samples showed a high level of aldrin and dieldrin concentrations in the deodorization condensate and almost none in the deodorized oil. The findings are very strongly supported by those previous reports (4-7) that chlorinated pesticides are removed through volatilization during deodorization of the oil under the parameters of temperature and pressure used here. However with the soapstock, bleaching sludge, and deodorization condensate, the concentration of the pesticide residues cannot be compared directly with the dieldrin concentration found in crude, refined, bleached, or deodorized oil.

In conclusion, this work shows a relationship between aldrin application to the fields with residues found in the various fractions of the bean and processing by-products. Soapstock may contain high levels of residue and should not be used for animal feed unless monitored. Bleaching sludge and deodorization condensate should be disposed of properly so as not to contaminate the environment.

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REFERENCES

1. Matsumura, F., G.M. Boush, and T. Misato Editors, "Environmental Toxicology of Pesticides" Academic Press, New York, NY, 1972, p. 38.
2. Edwards, C.A., Residue Rev. 13:83 (1966).
3. Bruce, W.N., G.C. Decker, and J.G. Wilson, J. Econ. Entomol. 59:179 (1966).
4. Meemken, H-A., Sonderdruck aus fette seifen anstrichmittel, Industrieverlag von Hernhaussen KG, Hamburg 11, 77:290 (1975).
5. Smith, K.H., P.B. Polen, D.M. DeVries, and F.B. Coon, JAOCS 45:866 (1968).
6. Gooding, C.M.B., Chem. Ind. (London) 344 (1966).
7. Mounts, T.L., C.D. Evans, H.J. Dutton, and J.C. Cowan, JAOCS 46:482 (1969).
8. "Official and Tentative Methods of the American Oil Chemists' Society," Vol. 1, Third edition, AOCS, Champaign, IL, 1966, Methods Ca 9B-52 and Cc 8b-52.
9. "Official Methods of Analysis of the Association of Official Analytical Chemists," Edited by W. Horwitz, Twelfth edition, Washington, D.C., 1975, Methods 29.014 and 29.015.
10. Petty, H.B., W.N. Bruce, R. Randell, D.E. Kuhlman, and S. Moore, "III Dieldrin Residues in Soybeans in Illinois 1965-7 and 1971," Illinois Agricultural Extension Service, Illinois Agricultural Experiment Station and Illinois Natural History Survey, Urbana, IL, 1971.
11. Bruce, W.N. and G.C. Decker, J. Agric. Food Chem. 14:395 (1966).

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