Effect of Commercial Processing Techniques on Lindane- and DDT-^{14}C Residues in Rapeseed Oil

J. G. Saha,[1] M. A. Nielsen,[2] and A K. Sumner[2]

The effects of simulated commercial vegetable oil processing techniques on the removal of lindane and DDT residues in rapeseed oil were studied. Alkali-refining and bleaching had little or no effect on lindane and DDT in the oil. Deodorization of the oil by heating it in the presence of water vapor at 230 to 260° C. and 6 mm. Hg for 4 hours removed 95 to 99% of the residue.

Recent studies have shown that commercial and home processing techniques considerably reduce the levels of pesticides in raw garden vegetables (Elkins *et al.*, 1968; Farrow *et al.*, 1966; Farrow *et al.*, 1968; Hemphill *et al.*, 1967; Lamp *et al.*, 1968a and 1968b; Saha and Stewart, 1967; Seidler *et al.*, 1968). While it is rather easy to remove pesticides residues from vegetables by commercial and home processing techniques, it is rather difficult to remove fat soluble pesticides from milk or butter fat by the commercial processing techniques. Ledford *et al.* (1968) reported that commercial vacuum processing of milk did not significantly reduce the heptachlor, dieldrin, and DDT content of milk but it reduced the lindane content by only about 24%. Liska (1968) observed that spray drying removed more than 80% of lindane residues in raw milk but sterilization caused little change. He also observed that most organochlorine insecticides were relatively resistant to processing techniques used in the milk and dairy industry. Mild deodorization treatments were ineffective in reducing the heptachlor epoxide and dieldrin levels in butter oil and severe treatment at 180° to 195° C. and 0.01 to 0.5 mm. Hg was required to completely remove these two pesticides (Kroger, 1968).

Edible vegetable oils are subjected to alkali-refining, bleaching, deodorization, and sometimes hydrogenation treatments before they are sold on the market. Studying the effect of each of these operations on the levels of lindane and DDT residues in one edible vegetable oil, rapeseed oil, was of interest.

EXPERIMENTAL

Lindane-^{14}C (specific activity 129 μCi/mg.) and *p,p'*-DDT-^{14}C (specific activity 12.9 μCi/mg.) were purchased from the Radiochemical Centre, Amersham, England. Both the compounds were analyzed by thin-layer and gas-liquid chromatography and were at least 99% pure. Lindane-^{14}C was diluted with cold lindane to give specific activity 13 μCi/mg.

The rapeseed oil was extracted from the seeds and processed under conditions simulating those used by a local rapeseed oil processing plant (Saskatchewan Wheat Pool). In the local plant, rapeseeds are crushed in a roller crusher and the rapeseed flakes are cooked with hexane at 60° to 105° C. for 35 minutes. The cooked flakes are then extracted with hot hexane for 30 minutes in a Soxhlet type extractor. The hexane extract is then passed into the desolventizer where it is heated to 60° to 105° C. to remove most of the hexane and the last traces are removed by heating the oil at 127° C. and 17 mm. Hg. The oil from the desolventizer is then subjected to an alkali-refining treatment by vigorous agitation in the presence of aqueous NaOH at 71° to 82° C. for 15 minutes, followed by two washings with water. The refined oil is then bleached by stirring it with 2.5 to 5.0% activated bentonite–carbon mixture at 82° to 105° C. for about 30 minutes, followed by filtration. The bleached oil is finally deodorized by vacuum steam distillation of the volatile components. For this purpose the oil is heated in batches at 232° to 260° C. and 5 to 7 mm. Hg for 3.5 to 5 hours while water vapor is passed through the oil at a rate per hour of less than 10% of the oil being processed.

Fortification of Rapeseed Flakes and Oil with Lindane- and DDT-^{14}C. Rapeseed flakes obtained from Saskatchewan Wheat Pool's oil processing plant were fortified with lindane- or *p,p'*-^{14}C in pentane solution at 4 mμCi/g. (0.3 p.p.m.) and the pentane was removed in a film evaporator. The fortified rapeseed flakes were stored in stoppered bottles for 2 weeks at room temperature. The total radioactivity in the treated material was determined by extracting a representative sample with 1:1 chloroform/methanol mixture in a Soxhlet apparatus for 8 hours. The radioactivity in the extract was determined by counting an aliquot in a scintillation counter. This method of extraction gave 100% recovery of the radioactivity present in the treated rapeseed flakes.

Crude rapeseed oil was fortified with lindane- or *p,p'*-DDT-^{14}C. at 4 mμCi/g. (0.3 p.p.m.). The total radioactivity present in the oil was determined by counting an aliquot in a scintillation counter.

Cooking of Rapeseed Flakes and Extraction of Oil. A 10-gram sample of the fortified rapeseed flakes and 75 ml. of hexane were placed in a three-neck round-bottomed flask fitted with a condenser and a stirrer. The contents of the flask were stirred and heated on a boiling water bath for 30 minutes and filtered under suction. The filtrate was made up to 100 ml. in a volumetric flask and 1-ml. aliquots were counted in a scintillation counter. The residue (rapeseed meal) was extracted in a Soxhlet apparatus with 1:1 chloroform to methanol for 8 hours. An aliquot of the Soxhlet extract was counted in a scintillation counter.

Desolventization. The solvent from the hexane extract in the above experiment was removed by distillation at 100° C. for 30 minutes followed by heating the residual oil at 127° C. and 17 mm. Hg for 10 minutes. Aliquots of the resulting oil were counted in a scintillation counter.

Refining. Ten-milliliter samples of the rapeseed oil fortified with lindane- or *p,p'*-DDT-^{14}C were vigorously stirred with dilute aqueous NaOH solution at 70° to 80° C. for 15

[1] Canada Agriculture Research Station, University Campus, Saskatoon, Sask., Canada
[2] College of Home Economics, University of Saskatchewan, Saskatoon, Sask., Canada

Table I. Effect of Individual Commercial Processing Techniques on Lindane- and DDT-^{14}C in Rapeseed Flakes and Oil

Operation	% Radioactivity Retained by Processed Oil[a]	
	Lindane-^{14}C	DDT-^{14}C
Cooking of Rapeseed flakes with hexane	96.4	95.5
Desolventization	98.3	102.0
Refining	104.7	102.0
Bleaching	94.7	93.8
Deodorization	4.7	1.7

[a] Average of duplicate analysis.

minutes. The amount of alkali used was in slight excess of the free fatty acid content of the oil. The mixture was then centrifuged and washed twice with water. Aliquots of the refined oil were counted in a scintillation counter.

Bleaching. Ten-milliliter samples of the fortified rapeseed oil were vigorously stirred at 100° C. for 30 minutes with 0.5 gram of activated bentonite–charcoal adsorbent (same material as used by the Saskatchewan Wheat Pool plant). The oil was centrifuged to remove the adsorbent and aliquots of the bleached oil were counted in a scintillation counter.

Deodorization. Ten-milliliter samples of the fortified rapeseed oil were heated at 230° to 260° C. and at a pressure of 6 mm. Hg. A slow current of steam was introduced at the bottom of the flask containing the oil and this process of heating under reduced pressure in the presence of steam was continued for 4 hours. The deodorized oil was then cooled to room temperature and an aliquot counted for radioactivity in a scintillation counter.

The radioactivity present in the processed oil at the end of each operation was expressed as percentage of the radioactivity present in the original fortified rapeseed flakes or oil (Table I).

All experiments were carried out in duplicate.

Radioactivity was determined in a Beckman Model LS-100 scintillation counter using the channel ratio method. Aliquots of processed oil were counted in duplicate in 0.4% PPO in toluene solution. The statistical error in counting radioactivity was 2 to 3% and counting efficiencies were 70 to 85%.

RESULTS AND DISCUSSION

Labeled compounds were used for two reasons. First, errors involved in the determination of low levels of residues in oil by electron capture gas chromatography were expected to be higher than those in the determination of radioactivity in the oil. Second, it was not known whether any of the processing techniques would convert lindane or DDT into any other fat soluble product(s) which might escape detection by the gas chromatographic procedure. Determination of radioactivity in the processed oil would include lindane- or DDT-^{14}C and any possible degradation product(s).

The conditions of the various processing techniques (temperature, pressure, time, and adsorbent) used in this study were similar to those used in the commercial processing of edible vegetable oil. Cooking of rapeseed flakes with hexane removed from the flakes 96.4% of the lindane and 95.5% of the DDT. Therefore, only 3.6 to 4.5% of the residues were retained by the rapeseed meal which might be used as animal feed. Since the rapeseed flakes were fortified with lindane or DDT, it is questionable whether this operation would remove more than 95% of field incurred residue from rapeseed. This aspect of oil seeds processing needs further study with rapeseeds grown in pesticide-contaminated soil.

Since lindane and DDT are fat soluble, their behavior during the subsequent processing operations can be studied with oil fortified with these compounds. The results obtained with such fortified oil would be just as valid as those obtained with oil derived from field-contaminated seeds. Desolventization, alkali refining, and bleaching operations have little or no effect on the levels of lindane or DDT residues in the oil (Table I). The last step of the processing technique removed 95 to 99% of the residues. It is significant to note that simple operations like water blanching or boiling in water can considerably lower the levels of organochlorine pesticides in vegetable crops (Elkins *et al.*, 1968; Hemphill *et al.*, 1967; Lamb *et al.*, 1968a and 1968b). Severe treatment like heating in the presence of steam at high temperature (230° to 260° C.) and low pressure (6 mm. Hg) is required to remove fat soluble pesticides from vegetable oil. These results are in agreement with those reported by Gooding (1966) where he obtained complete removal of several pesticides from cottonseed oil after a three-stage processing (alkali-refining, bleaching, and deodorization) treatment in a pilot plant.

ACKNOWLEDGMENT

The authors thank S. P. Bagchi, Psychiatric Research Unit, University Hospital, Saskatoon, for the use of his scintillation counter. The authors are also indebted to the Saskatchewan Wheat Pool, Saskatoon, for supplying rapeseed flakes, oil, and the adsorbent and for the details of processing operations reported herein.

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Received for review July 22, 1969. Accepted August 25, 1969. Contribution No. 358 of the Canada Agriculture Research Station, Saskatoon, Sask., Canada