Degradation of Chlorinated Hydrocarbon Pesticides in Milk and Butteroil by Ultraviolet Energy

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Abstract
High-intensity ultraviolet energy produced by a carbon arc lamp will degrade organochlorine insecticides contaminating fluid whole milk or butteroil. Rate of degradation was a function of the film thickness and depth of penetration of the rays when operating conditions were held constant. Degradation of methoxychlor in butteroil was 96% after one exposure; smaller percentages of other insecticides were degraded. The degradation products for methoxychlor were identified and are structurally similar to those reported for DDT. Removal of pesticides from milk and butteroil by ultraviolet light is still unsatisfactory. Apparently, the most satisfactory control measures involve monitoring the contaminants in the rations fed to lactating animals.

Continued demands on farmland for increased production currently necessitate the use of pesticides. As a result, inadvertent contamination of crops, misuse, and occasionally mislabeling lead to pesticides in our food supplies. With the exception of the chlorinated hydrocarbons, the dairy cow detoxifies almost all insecticides during normal metabolism. However, the organochlorine pesticides are stored in the body fat of the cow. Because of an equilibrium between the blood lipids and depot fat, pesticides are circulated through the animal, and some quantities are transported into the milk.

Several dairy researchers have investigated the possibility of removing organochlorine pesticides that might be in milk and milk products. Cardwell, Mandhare, and Smith (3) reported that milk contaminated with DDT and analogs could have approximately 50% of these residues removed by treatment with 0.06% H₂O₂ for 2 hr at 4.4 C. Hydrogen peroxide apparently causes dehydrochlorination. Langleis, Liska, and Hill (8, 9) and Stemp and Liska (10) indicated that routine dairy processing, such as pasteurization, ice cream manufacture, cheese and buttermaking, and storage of products from these processes removed little DDT, lindane, endrin, dieldrin, heptachlor epoxide, telodrin, and methoxychlor. However, condensing and drying of fluid whole milk markedly reduced the concentration of these pesticides. Kroger (6) reported that milk fat could be completely stripped of heptachlor epoxide and dieldrin by steam deodorization at 180-195 C and 0.01-0.5 mm Hg for 5 hr. Bills and Sloan (2) demonstrated that molecular distillation of milk fat at 200 C and a pressure of 5 × 10⁻¹ Torr would remove 95 to 99% of large contaminations of lindane, aldrin, heptachlor, heptachlor epoxide, and DDT and analogs.

Since many of the organophosphate and organochlorine pesticides are photosensitive, our objective was to study the destruction by ultraviolet (UV) energy of the chlorinated hydrocarbon pesticides in milk and butteroil.

Materials and Methods
Treatment of milk and butteroil. Raw whole milk and melted butteroil, 35-liter and 22.7-kg quantities, respectively, were contaminated with the appropriate pesticide dissolved in ethanol. On a fat basis, these products contained 1 ppm of pesticide. Contaminated milks were pumped with a Waukesha, variable-speed, positive pump to a 66.6-by 90.9-cm surface cooler at 1,200 ml/minute; whereas, butteroil samples were pumped at 2,500 ml/minute. To maintain the fluidity of the butteroil, tap water at approximately 57 C was circulated through the surface cooler. These flow rates gave film thicknesses of 0.16 and 0.36 cm, respectively. Product was permitted to flow only on one side of the surface cooler; therefore, an entire lot was irradiated with one exposure.

Irradiation of samples. An Eveready carbon arc lamp and Union Carbide type W electrodes were used to generate high-intensity ultraviolet energy between 2,200 and 3,300 Å. The arc source was located 45.7 cm from the surface cooler, and a 1.2-m, satin-finish, elliptical reflector was in focus and 91.4 cm from the cooler.

Analysis for pesticides. During analysis for pesticide residues, aliquots of irradiated milk

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were de-emulsified using the method proposed by Lampert (7). Three grams of liquid fat from the samples of butteroil and de-emulsified milk were taken for subsequent cleanup and extraction according to the procedures recommended by the Federal Food and Drug Administration (1). A model 810 F and M gas chromatograph equipped with an electron capture (H3) detector and a 6 mm- by 1.2 m-glass column packed with 4% SE-30 on Anakrom ABS was employed to determine quantitatively the concentration of the insecticides in the extracted fat samples.

Results and Discussion

A plot of the percentages of pesticides lost with each repeated exposure to ultraviolet energy is shown in Fig. 1. These are the results of duplicate analyses on separate trials involving the use of one pesticide per trial. The pesticide most susceptible to destruction by UV energy is methoxychlor, whereas heptachlor epoxide is the least susceptible.

The Federal Food and Drug Administration has established a maximum of 400 units of vitamin D per quart of whole milk. The data in Table 1 are the results of vitamin D assays along with the results of vitamin A and β-carotene analyses. The maximum amount of vitamin D was produced during one exposure to UV energy, and subsequent exposures served only to decrease the concentration. The presence of a strong sunlight flavor or an aroma resembling burned chicken feathers, first reported by Weckel et al. (11), made this irradiated milk unpalatable. Vacuum treatment of hot milk reduced the flavor somewhat, but it was not considered acceptable.

The obstacles of lack of penetration of ultraviolet light into the product and undesirable flavor were overcome by using butteroil as an experimental medium. The butteroil was maintained fluid at 49 C by circulating hot water in the tubes of the surface cooler. A plot of the pesticide loss in these trials is shown in Fig. 2. The rate of destruction was increased markedly over that observed when milk was used as the carrier. Approximately 96% of the methoxychlor added to the butteroil was destroyed during one exposure, whereas much smaller percentages of the other pesticides were destroyed. No objectionable off flavors were developed in the butteroil even after three exposures to the ultraviolet energy. During irradiation, the following amounts of vitamin D were produced; control (no irradiation), 40.8 units/kilogram; samples that were exposed one, two, and three times had in excess of 1,360.8 units/kilogram.

Upon degradation, some pesticides, especially the organophosphates, produce compounds with toxicities greater than that of the parent compound. Since methoxychlor was the only pesticide significantly destroyed by ultraviolet energy, we tried to identify the products of ultraviolet-induced degradation of this insecticide. Several techniques were used to prepare, collect, and identify these degradation products, including preparative-scale and conventional thin-layer chromatography, organic synthesis (5), and gas chromatography using hydrogen flame and electron capture detectors. The peaks on the gas chromatograms repre-

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Table 1. Effect of ultraviolet energy on the vitamin D, vitamin A, and β-carotene content of raw whole milk.

<table>
<thead>
<tr>
<th>Exposures (no.)</th>
<th>Vitamin D (units/liter)</th>
<th>Vitamin A (units/liter)</th>
<th>β-carotene/liter (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>705</td>
<td>0.078</td>
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<td>451</td>
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<td>376</td>
<td>216</td>
<td>0.029</td>
</tr>
<tr>
<td>4</td>
<td>188</td>
<td>141</td>
<td>&lt;0.029</td>
</tr>
</tbody>
</table>

Fig. 1. Destructive effect of ultraviolet energy on six chlorinated hydrocarbon insecticides in raw whole milk.

J. DAIRY SCIENCE VOL. 52, No. 1
DEGRADATION OF PESTICIDES

Fig. 2. Destructive effect of ultraviolet energy on five chlorinated hydrocarbon insecticides in butteroil.

Fig. 3. Degradation products of methoxychlor.

senting the materials extracted from the fat of irradiated samples containing methoxychlor showed several peaks not in the extractions from samples not irradiated. The chemical compounds shown in Fig. 3 are the decomposition products of methoxychlor that were identified. The direct cleavage products are methyl anisole and methoxyphenol. Another route of degradation was through the progressive dechlorination of the trichloro structure. The loss of one chlorine atom results in formation of methoxychlor-DDE, and subsequent dechlorination causes formation of condensation products. The duration of existence of these strained compounds is a function of the electronegativity of the constituent group at the p and p' positions of the benzene rings (4). In methoxychlor, the charge is plus; therefore, the condensation products are less strained and will exist much longer than for DDT, which has a highly negative chlorine group in the p and p' positions. The final end product is dimethoxybenzophenone. This evidence and that reported by Fleck (5), respectively, indicate that the closely related compounds, methoxychlor and DDT, decompose in the same manner and that the rate of decomposition is regulated partially by the group attached at the p and p' positions on the benzene rings. The toxicity of these compounds is insignificant compared to that of the parent compound.

This evidence and that reported previously in the literature indicate that complete removal of all chlorinated hydrocarbon insecticides from milk and milk products is difficult. Apparently, the most satisfactory method to prevent contamination in milk and milk products is to control the pesticide contamination by monitoring the animal rations.

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