γ Irradiation of DDT: Radiation Products and Their Toxicity

This work was undertaken to determine the fate of DDT residues stored in the lipids of foods processed by γ radiation. The major radiation products produced by γ irradiation of DDT in simulated fat were identified. Within experimental limits, the acute oral toxicity of technical DDT in adult female rats is not increased by γ irradiation in the simulated fat medium.

The irradiation of DDT with ultraviolet and visible light under a variety of conditions has been studied by Miller and Narang (1970), Plimmer *et al.* (1970), and Mosler *et al.* (1969). The chain dechlorination of DDT in alcohol solution induced by ionizing radiation has been reported by Evans *et al.* (1970).

Products resulting from the action of γ irradiation of DDT in a simulated fat medium will also include the products formed by the action of the radiation on the fat. Aspects of the action of ionizing radiation on lipids have been studied by Chipault and Mizuno (1966), Fukada and Masuzawa (1966), Hyde and Verdin (1968), and Dubravcic and Nawar (1968).

The work described here was undertaken to study the effect of ionizing radiation on the DDT residues stored in the lipids of foods to be preserved by γ irradiation, specifically to determine what products result and to establish the toxicity of these products.

Technical DDT is composed of 85 to 90% 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane, *p,p'*-DDT, 10 to 15% 1,1,1-trichloro-2-(*o*-chlorophenyl)-2-(*p*-chlorophenyl)ethane, and traces of several other compounds, including 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethylene, *p,p'*-DDE, and 1,1-dichloro-2-(*o*-chlorophenyl)-2-(*p*-chlorophenyl)ethylene (Haller *et al.*, 1945).

EXPERIMENTAL

Irradiation of Technical DDT. A mixture of 1 part of technical DDT and 2 parts of tristearin was warmed to 70° C, where a clear solution was obtained. This hot solution was poured into an ice water mixture in a blender. The wet powder was collected on a funnel and will be referred to as "a." A 50-g emulsion of "a" mixed with 25 g of water was irradiated with 0.66 MeV γ rays from a 12,000-Ci cesium-137 source, 1.4 Mrads per hr, for 20 hr, that is, 28 Mrad. Fricke dosimetry as described by Palmer *et al.* (1961) was used. During the irradiation the material puffed up about 25% and turned yellow.

Analysis of Gaseous Radiation Products. An emulsion of 2 parts of "a" and 1 part of water was sealed under air in a glass container and was irradiated. The gaseous products were collected over water and analyzed by gas chromatography. Hydrogen was determined on alumina with argon, the carrier gas, and nitrogen was determined on molecular sieve with helium, the carrier gas.

Analysis of Solid Radiation Products. The radiation products were concentrated as follows: irradiated "a," 600 g, was dissolved in 3 l. of boiling hexane and 2.8 g of insoluble material was removed by filtration. The solution was cooled and the solid that formed was collected on a filter. The solution was concentrated and the solid collected until a total of 540 g of material (mostly *p,p'*-DDT but containing some *o,p'*-DDT) had been collected. The remaining 60 g of material was analyzed by gas chromatography on SE-30 at 250° C with nitrogen, the carrier gas, and by thin-layer chromatography, 0.25 mm of silica gel on aluminum (E. Merck, Darmstadt) with hexane being the solvent. The strips were developed with iodine vapor and with silver nitrate–bromophenol blue. The strip was sprayed with 0.5% silver nitrate in ethanol, dried 5 min at 100° C, sprayed with 0.2% bromophenol blue, 0.15% silver nitrate in ethyl acetate/ethanol, 1:1, and dried 10 min at 100° C.

Toxicity of Irradiated Material. The toxicity of the concentrated radiation products to which the hexane insoluble material had been added was compared to the toxicity of technical DDT that was processed in the same way, mixed with tristearin, and concentrated from 600 g to 60 g, excluding only the irradiation. (Gas chromatographic analysis showed that there was the same ratio of *p,p'*-DDT to *o,p'*-DDT in the two samples.)

The acute oral LD_{50} values were determined for irradiated and nonirradiated technical DDT in 100 4-month-old female rats weighing 225 to 315 g. The rats were equally distributed according to a table of random numbers into ten groups. The irradiated tristearin–technical DDT formulation was dissolved in peanut oil by warming so as to give technical DDT concentrations of 3, 4, 5, 6, and 8%, respectively. These solutions were given by stomach tube to five groups of rats at the rate of 5 ml per kg of body weight to give technical DDT dosage levels of 150, 200, 250, 300, and 400 mg/kg, respectively. In a similar manner, the nonirradiated technical DDT in tristearin was dissolved in peanut oil and given to the other five groups of rats. Mortality among the rats was recorded for 1 week following dosing. The LD_{50} values were calculated according to the method of Litchfield and Wilcoxon (1949).

RESULTS

The results of the analysis of radiation products of the technical DDT–tristearin–water mixture are summarized in Table I.

Although the sample analyzed for gaseous products was sealed under air, there was no oxygen present after irradiation. (The molecular sieve does separate oxygen and nitrogen.) It is assumed that the oxygen combines with the hydrogen produced to form water. The *G* value for hydrogen given in Table I includes the hydrogen which reacted with this oxygen present originally.

In the thin-layer chromatographic analysis of the solid radiation products the iodine showed the tristearin which did not move from the origin under the conditions and did not show the DDT. Hence, polymeric tristearin would not be detected. The iodine on the strip would evaporate overnight and the same strip could be developed with silver nitrate–bromophenol blue, which visualized only chlorine-containing compounds. The irradiated material contained a chlorine-containing spot, R_f 0.25, which was not in the mixture before irradiation and was not visualized with iodine as was

Table I. Radiation Products of 1:2 Mixture of Technical DDT and Tristearin in Water

Product	G Value	Method of analysis
Hydrogen	5.7 including that which reacted with the O_2 present	Gas chromatography on alumina with argon carrier gas
p,p'-DDE[a]	0.04	Gas chromatography on SE-30 nitrogen carrier gas
o,p'-DDE[b]	0.004	Gas chromatography on SE-30 nitrogen carrier gas
DDT dimer[c]	0.001	Thin-layer chromatography
DDT-tristearin[c] addition product, hexane soluble	0.001	Thin-layer chromatography
DDT-tristearin hexane insoluble	0.2	

[a] The *G* value for the formation of this material was obtained from irradiation of pure *p,p'*-DDT–tristearin which contained no *p,p'*-DDE before irradiation. [b] The *G* value for the formation of this material was obtained from irradiation of pure *o,p'*-DDT–tristearin which contained no *o,p'*-DDE before irradiation. [c] The *G* value was estimated from the size and intensity of the silver nitrate–bromophenol blue spot compared to spots of known concentration of DDT.

tristearin, and which was therefore assumed to be dimeric or polymeric DDT. There was chlorine-containing material at the origin of irradiated material which was assumed to be DDT attached to tristearin.

The acute oral LD_{50} values in female rats were 320 mg/kg (95% confidence limits of 271 to 378 mg/kg) for the irradiated DDT and 305 mg/kg (95% confidence limits of 263 to 354 mg/kg) for the nonirradiated DDT.

CONCLUSIONS

The irradiation products found were what would be expected. The DDT is fairly resistant to ionizing irradiation. The only product formed in appreciable quantity was hydrogen, which presumably arose primarily from the action of the radiation on the alkyl tails of the tristearin. The *G* value obtained for hydrogen, 5.7, is in the same region as that for the γ-irradiation of alkanes, 5.55 (Dyne and Stone, 1961) and 5.85 (Forrestal and Hamill, 1961). This figure cannot be compared to the *G* value of 1.01 for hydrogen production in the irradiation of methyl oleate reported by Hyde and Verdin (1968), because the olefinic linkage in methyl oleate which is particularly susceptible to reaction on irradiation is not present in the tristearin used here.

The LD_{50} values of the irradiated DDT, 271–378 mg/kg, and of the nonirradiated DDT, 263–354 mg/kg, are the same within experimental error. Hence it may be concluded that the irradiation of technical DDT had no effect upon its acute oral toxicity in adult female rats.

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