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Influence of Culinary Processes on Therminal Residues of Chlorinated Pesticides and Vitamin E in Poultry Meat

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Introduction

Following our ecological studies (1, 2) we have concentrated firstly upon a study of terminal residues of benzene hexachloride (BHC) isomers and hexachlorobenzene (HCB) in meat of animals submitted to a feeding experiment (3). Similar studies published in the world literature are directed first of all to the metabolism of chlorinated pesticides in laboratory animals, mainly of DDT and γ-BHC (4—6). In the field of culinary experiments established on the basis of poultry feeding experiments, there are a few literary references which concern only DDT or γ-BHC (7—9).

Experimental part

Procedure, materials and methods

Samples of poultry meat from feeding experiments containing incorporated residues (at the rates of 1 and 50 mg/kg of the fodder) were used in a culinary model. The meat (ca 500 g) was processed by roasting in an electric oven with a thermostat at 150 °C during 120 min. By roasting was added 10 ml edible oil fortified with vitamin E. After roasting the samples were fried again twice in the same oil (with an added fresh piece of meat), for following the influence of repeated thermal processing on the residues.

Samples of raw, roasted and fried meat, and also the fat after roasting were analysed for the content of pesticides added to the feed (BHC isomers and HCB). The following supposed metabolites or degradation products: 2,4-dichlorophenol (DCP); 2,3,4-, 2,4,5- and 2,4,6-trichlorophenols (TCP); pentachlorophenol (PCP) and 1,2,4,5-tetrachlorobenzene (TeCB) were identified and also determined.

For the determination of residues GLC and TLC methods published earlier were used (10—12). For the determination and identification of the degradation products, we have worked out a GLC and TLC method using derivatization (13). The chlorophenols studied were determined by the gas chromatographic method with ECD on a column with a mixed packing of 1.0% Igepal CO 880 + 2% Apiezon L + 1.0% H_3PO_4 on Chromosorb W 80/100 mesh.

For the identity confirmation thin layer chromatography on commercial SiO_2 plates with a detection by $AgNO_3$ and an exposure to the UV-light is convenient. For the separation of the mixture of chlorophenols, the system of n-hexane + benzene + ethylacetate (6+4+1) was suitable.

For the identification of the chlorophenols, the retention times of the original substances and their methyl derivates were compared. The methyl derivates (anisoles) were prepared by methylation with diazomethane in alkaline media. The recovery of this method is 99%. HCB was identified by conversion to pentachloroanisole (PCA) using a methoxylating agent ($NaOH$ + CH_3OH + pyridine).

For the determination of α-tocopherol (vitamin E) saponification of the sample and a combined purification of the extract by column chromatography on Al_2O_3 resp. on SiO_2 plates, followed by a spectrophotometric determination at 520 nm according to *Emmerie* and *Engel* (14) was used.

Results and discussion

Prior to the culinary processing, the contents of the pesticides administered as well as their metabolites were determined in the meat (muscle) of the slaughtered birds. The analyses showed that PCP is a metabolite of HCB which also occurs in the meat samples of the poultry fed with γ-BHC whereas 2,4,6-TCP was only found after feeding with HCB. 1,2,4,5-TeCB was also found after feeding with HCB and not only in the meat of the birds fed with lindane (15). Our results on identification of pentachlorobenzene by mass spectrometry have been published (16).

The results of the determination of terminal residues of HCB and BHC isomers (the lower levels 1 mg/kg) in cooked and roasted meat in comparison with raw meat (on fat basis) demonstrate a general decline of the residues (except for β-BHC and HCB) as well as of most metabolites and degradation products after thermal processing. In the meat broth the contents of β-BHC as well as HCB increase and the contents of most metabolites decrease (17).

The dynamics of disappearance of pesticides (from experiment of the rates 50 mg/kg HCB), and metabolites by roasting the meat with vitamin E fortified edible oil, were also studied. In order to express the results as close as possible to the consumers view, the evaluation of the distribution has been based on the absolute amounts (contents in a weighed sample) and not on the concentrations (average weight 0.488 g). The distribution of HCB and its metabolites by roasting and frying resp. has been calculated this way and the results are shown in table 1.

Residues in meat (after substracting the values from the control group) demonstrated the most pronounced persistence for HCB which showed only a slight decrease in roast meat compared to raw meat; the HCB content decreased markedly only after the third thermal processing (fried). The elution of HCB into

Table 1. Distribution of HCB residues and degradation products at thermal processing of contaminated meat (mg in the samples)

Thermal processing	Terminal residues (on fat basis)				
	HCB	2, 4, 6-TCP	1, 2, 4, 5-TeCP	PCP	2, 4-DCP
Raw meat	214.1	76.7	28.8	0.6	0.3
After roasting	180.6	20.5	2.1	0.1	0.2
% related to raw meat	84.3	26.7	7.3	16.7	66.7
Raw oil	0.2	0.3	0.2	0	0
After roasting	8.7	0.2	0	0	0
% related to raw meat	4.6	0.3	0	0	0
Fried meat					
once	6.9	0.1	0	0	0
twice	2.3	0.5	0.2	0	0

the oil after roasting was proved by its 43.5 times increase in the oil used for thermal processing of the meat compared to the control. In the total balance sheet in per cent (related to the raw meat), the content of HCB in meat and oil after roasting represents 88.4% of the amount introduced by the raw meat i. e. a 11.6% decrease. The persistence (distribution) of HCB in meat was 84.3% and in oil 4.6% only.

From the metabolites under study 2,4-DCP showed a marked persistence in meat after roasting (66.7%), followed by 2,4,6-TCP, PCP and 1,2,4,5-TeCB which was the least persistent. The persistence of the metabolites was similar also after cooking (17).

Potential losses of the pesticides and/or metabolites by volatilization during the thermal processing cannot be excluded; in this connection it should be noted that chlorophenols and tetrachlorobenzenes have a higher vapour pressure than HCB (18) which is in accordance with the results shown in table 1.

Vitamin E losses were studied by roasting the meat obtained from a feeding experiment with fodder containing HCB and BHC isomers (the lower levels i. e. 1 mg/kg each, figure 1). These losses of vitamin E in sunflower oil are greater in contaminated meat than in the meat of the controls. No differences were found, however, by varying incorporated pesticides.

The effect of repeated thermal processing on vitamin E was investigated during roasting and frying of the meat from the feeding experiment with a higher level of HCB under the same conditions as indicated before. Results presented in figure 2 show the percentual losses of vitamin E in the oil after triple conse-

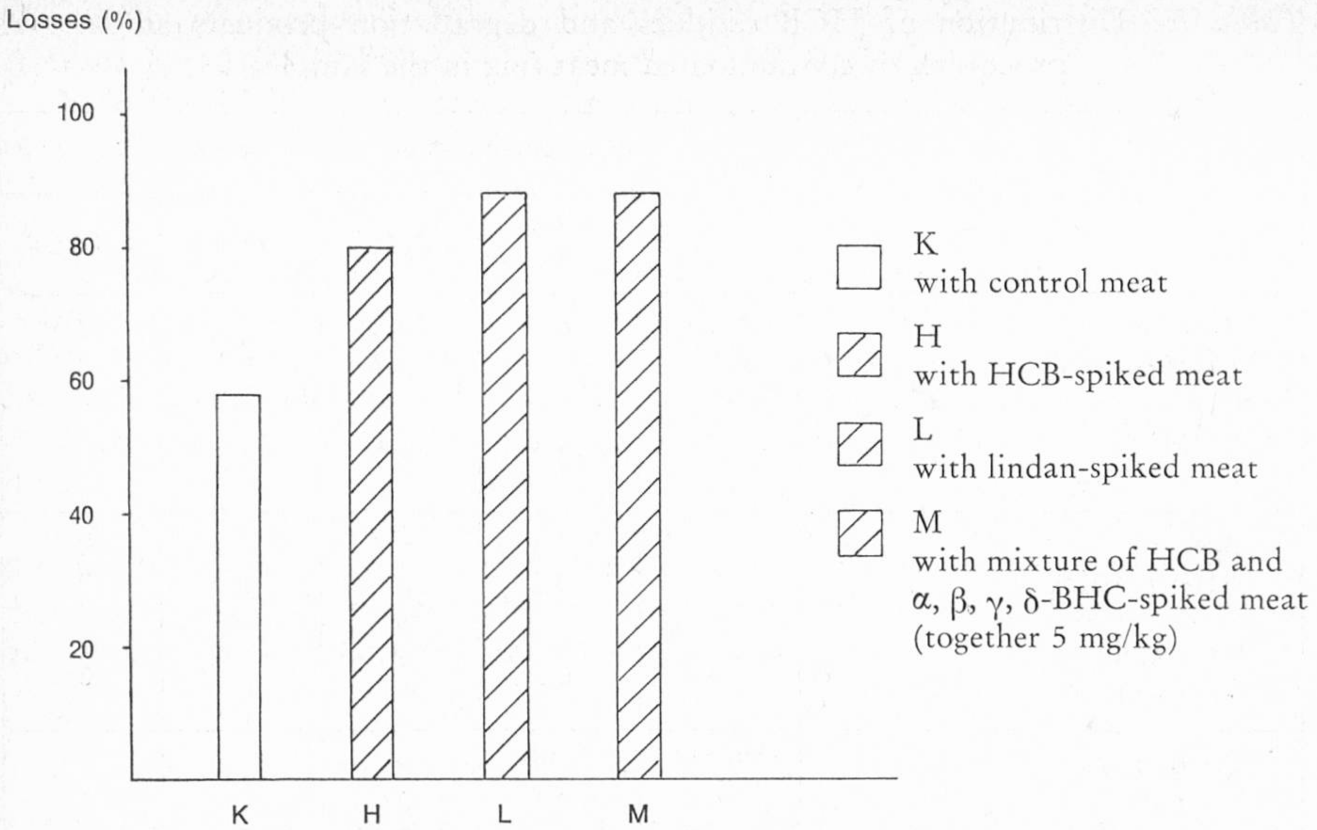

Fig. 1. Changes of the vitamin E content in oil due to roasting of meat from feeding experiment (lower levels of HCB and BHC isomers)

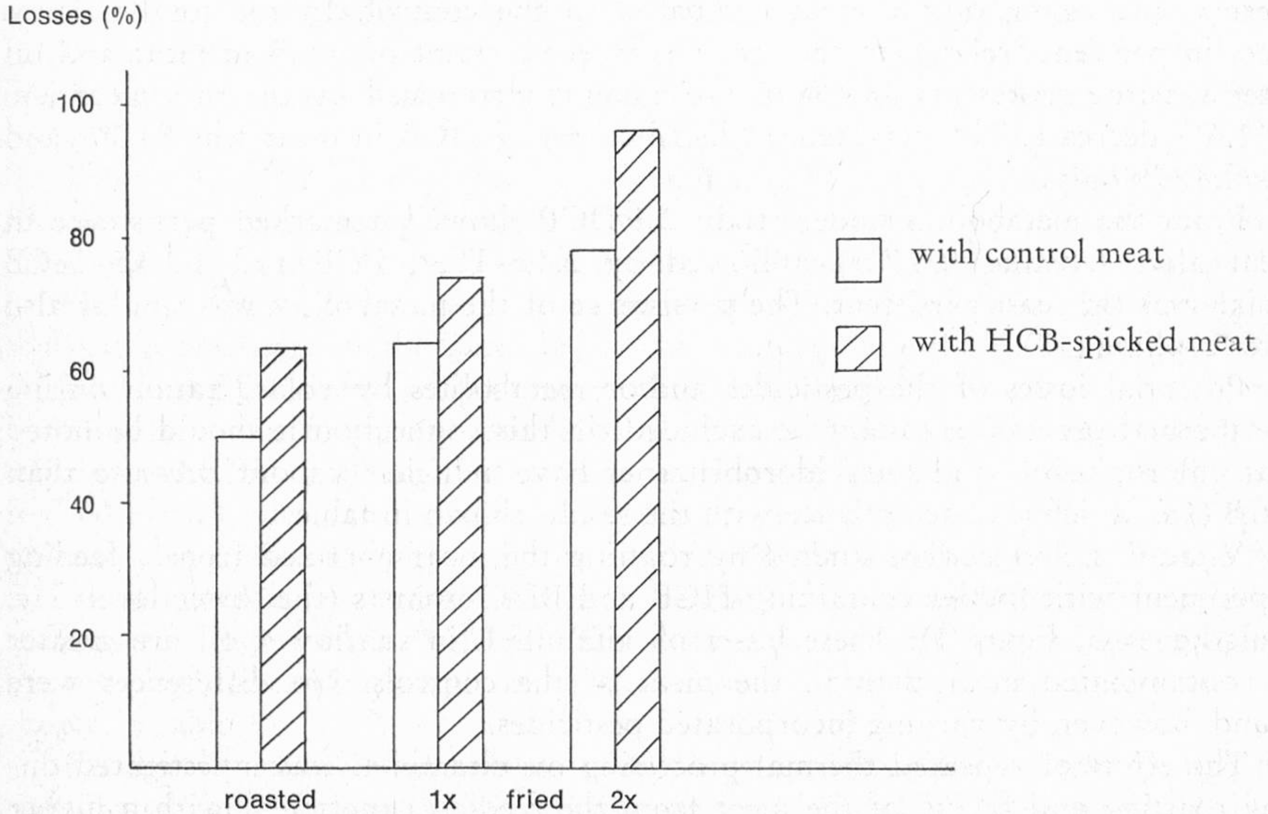

Fig. 2. Changes of the vitamin E content in oil according to different types of thermal processing of meat from feeding experiment

cutive thermal processing compared to the starting level (in oil the average level was 7.3 mg/kg). The study was carried out on the experimental group (with HCB-spiked meat) and meat from control groups (each containing 10 birds from the HCB feeding experiment 50 mg/kg in the fodder). The comparison of the experimental and control groups from the feeding experiment showed again a difference between them. However, this experiment with a high level of incorporated HCB and different types of thermal processing showed a decrease of the α-tocopherol content in the oil against the control, and a decrease in which HCB does not depend on the pesticide concentration (fig. 1 and 2).

Summary

Samples of poultry meat containing pesticide residues from a feeding experiment (hexachlorobenzene and mixture of benzenehexachloride isomers at the rates of 1 and 50 mg/kg of the fodder) were used for a culinary model. The dynamics of disappearance, degradation products or metabolites (chlorophenols and chlorobenzenes) during roasting and frying of meat samples with edible oil fortified with vitamin E were followed. The results demonstrated a 11.6% decrease of HCB residues in meat and oil together in comparison with the raw meat. However, in roasting oil a 43.5 times increase of HCB residues in comparison with control was observed.

A decrease of vitamin E content in the presence of HCB in the sunflower oil was found. This decrease was not dependent on concentration of the pesticide.

Zusammenfassung

Aus Fütterungsversuchen mit Hexachlorbenzol (HCB) und Hexachlorcyclohexan-Isomeren (HCH) (1 und 50 mg/kg Futter) stammende Geflügelfleischproben wurden küchenmäßig zubereitet. Das Verhalten der Rückstände, Abbauprodukte bzw. Metaboliten (Chlorphenole, Chlorbenzole) beim Braten im Ofen und in der Pfanne in Gegenwart von mit Vitamin E angereichertem Oel wurde untersucht. Gegenüber dem rohen Fleisch ergibt sich eine Reduktion des HCB-Gehaltes von 11,6% in Fleisch und Oel zusammen. Der HCB-Gehalt im Bratöl erhöhte sich um einen Faktor 43,5.

Der Vitamin-E-Gehalt des Oeles wurde dabei in Gegenwart von HCB vermindert. Es konnte jedoch kein Einfluß der HCB-Konzentration festgestellt werden.

Résumé

Des échantillons de viande de volaille contenant des résidus d'hexachlorobenzène (HCB) et d'un mélange d'isomères d'hexachlorocyclohexane ajoutés à la dose de 1 et de 50 mg/kg au fourrage, ont été rôtis. Les résidus et les produits de dégradation ou métabolites (chlorophénols et chlorobenzènes) ont été dosés avant et après le rôtissage des échantillons de viande dans de l'huile comestible enrichie en vitamine E. Les résultats ont montré une diminution de 11,6% de résidus d'HCB dans la viande et l'huile exa-

minées ensemble. Dans l'huile de rôtissage on a constaté une augmentation des résidus de HCB de 43,5 fois.

On a trouvé une diminution de la teneur en vitamine E de l'huile de tournesol en présence de HCB, mais la diminution ne dépendait pas de la concentration en HCB.

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