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DDT, DDT Metabolites, and Other Organochlorines as Affected by Thermal Processing in Three Commercial Cuts of Lamb

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The chlorinated pesticides played an important role in the history of chemical crop protection as well as human hygiene. These compounds combine high insecticidal effectiveness with low mammalian toxicity, and provide long-lasting protection against a broad spectrum of insects due to their chemical stability. The recent development of trace analysis resulted in the knowledge of their persistence in all sections of our environment. They are not only persistent but also lipophilic and thereby accumulate in plant, animal, and human tissues. An increasing public concern about their ubiquitous occurrence and possible long-term effects in human health resulted in their use being banned in most industrialized countries (Concon 1988).

The study of the contamination of organochlorine pesticides in meat and meat products is very important because of their high fat content and increasing rate of consumption worldwide. Most research carried out in European countries as Italy (Cantoni et al. 1985), France (Richou-Bac and Venant 1980), and Spain (Conchello et al. 1993a; 1993b; Lázaro et al. 1991), showed a widely distributed contamination in animal products at levels generally below the maximum residue limits. Some other countries with possibility of exporting meat and meat products are exceptions, like Chile, where Pinto et al.(1986; 1987) detected heptachlor, DDT, chlordane, toxaphene and metoxychlor in bovine meat in higher quantities than the established tolerances. Likewise, in Brazil, Carvalho et al. (1984) detected pesticide residues in the 95,4% of the bovine fat samples analysed, and almost 5% exceeded the maximum limits; in Iraq, Al-Omar et al. (1985) found that 2,6% of ovine samples exceeded the tolerances established for heptachlor, and nearly 5% of beef samples contained dieldrin above the respective MRL.

Many studies on pesticide residues have revealed that certain factors significantly reduce their levels in the course of food processing. Consistently, both technological and kitchen processes can partially or fully remove or degrade chlorinated residues to other compounds often less toxic, which renders safer products to man (Kubacki and Lipowska 1980). Regarding to thermal degradation of pesticides in meat, most papers describe a reduction in the residual amounts (Kubacki and Lipowska1980; Gonzalez and Visweswariah1984; Conchello et al. 1993a; 1993b).

In this study we have determined the content of some highly-persistent organochlorine pesticides in three retail cuts of ovine meat (chop, leg, and breast), and the resulting metabolites and conversions between isomers during a like number of culinary treatments (grilling, roasting, and cooking).

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MATERIAL AND METHODS

We have determined the contamination of organochlorine pesticide residues in three commercial cuts (chop, leg and breast) of 21 ovine carcasses and the effect of grilling, roasting and pressure cooking on these residues. Culinary treatments were previously described by Conchello et al.(1993a): chop samples were grilled without oil or dressing and heated at 85ºC for 5 min; leg samples were roasted for 45 min in a conventional electric oven, reaching an internal temperature of 100±1ºC as indicated by a penetration thermometer, and breast samples were subjected to cooking at 130ºC for 10 min.

Extraction and clean-up of residues were performed in our laboratory using the method by Telling et al. (1977) as described elsewhere (Conchello et al. 1993a). The eluted extracts (n=126) were concentrated and stored in glass vials at -18ºC until their analysis by gas-liquid chromatography using electron capture detector and capillary columns. The organochlorine pesticides investigated were pp'DDT, op' and pp'DDD, op' and pp'DDE, heptachlor epoxide, endosulphan I and II, metoxichlor, α-chlordane, γ-chlordane, α-chlordene and trans-nonachlor.

The chromatographic analysis was performed with two apparatus Hewlett-Packard models 5890A and 5890 Series II, equipped with two fused silica capillary columns: SPB-608 (30 m x 0.25 mm ID and 0.25 μm of film thickness) and SPB-5 (30 m x 0.32 mm ID and 0.25 μm of film thickness). After a study of the resolution of each column, we used the SPB-608 for identification and quantification of residues in both raw and treated samples, while the SPB-5 was used for confirmatory analysis. Operating parameters are given in Table 1.

Table 1. Operation parameters of the two capillary columns employed.

Parameter	SPB-5	SPB-608
Injector temperature (ºC)	250	210
Initial oven temperature (ºC)	50	50
Rate (A) 1º C/min	8	25
Oven temperature after rate A (ºC)	250	150
Rate (B) 2 ºC/min	10	8
Final oven temperature (ºC)	290	290
Temperature of ^{63}Ni detector (ºC)	300	300
Carrier gas	N_2	N_2
Flow (mL/min)	1.5	0.84

The peaks were identified by comparison of retention times with those of the standards on the two capillary columns. The pesticide concentrations in the samples were obtained by comparing peak areas from sample extracts with those recorded for the standards, which were made in μg/kg of hexane. A three-level multicalibration table (5, 20, and 40 ppb) was created and stored in the integrator daily. The amount of injected sample was 3 mL.

Since no interfering peaks were observed in the blanks, the detection limit of the pesticides was set to the minimum concentration of each one that had a linear response in the ECD, and ranged from 0.5 (γ-chlordane, and trans-nonachlor) to 10 ppb (metoxychlor). The detection limit of DDT and metabolites was around 1.0-2.0 μg/kg on a fat basis.

RESULTS AND DISCUSSION

Table 2 summarises the results obtained in raw and treated samples. No op'DDE, op'DDD, heptachlor epoxide, metoxychlor, endosulphan I and II, α-chlordane, γ-chlordane, α-chlordene and trans-nonachlor residues were detected. 83% Of the samples contained DDT residues ranging from 8 ppb to 91 ppb (on a fat basis); the average contamination was 25 ppb (29 ppb in the positive samples). From all the isomers of DDT, pp'DDE was the most frequently detected, followed by pp'DDT and pp'DDD. The levels of these compounds were always below the EC-MRL established in 1000 ppb for meat and meat products.

Our results confirm the high persistence and chemical stability of these pesticides in agreement with data reported in Chile by Pinto et al. (1986) and Montes et al. (1988) in beef. Our percentage of DDTs' detection is somewhat lower than that of 100% reported in beef in Italy by Cantoni et al. (1985), or the 90% and 100% reported in Iraq by Al-Omar et al. (1985) in ovine and bovine meat, respectively.

Table 2. Organochlorine residues in 63 samples of ovine meat expressed as μg/kg fat (ppb).

Pesticide	% Detected	Mean of positive samples	Range	Mean of total samples
pp'DDE	81	20	8 - 47	16
pp'DDD	6	7	6 - 9	<1
pp'DDT	38	21	11 - 40	8
ΣDDTs*	83	29	8 - 91	25

* DDT+DDE+DDD (op'+pp' isomers)

Our results of DDT contamination are lower than those given by different Spanish authors during the 80's. Thus, Sánchez et al. (1982) detected 350 ppb in ovine fat and between 50 ppb and 60 ppb in bovine and pork fats. Pozo Lora et al. (1982) observed a higher contamination by pp'DDT (100 ppb) in canned pork products. Both authors detected pp'DDE residues, but unlike our results, no pp'DDD data were reported. In Italy, Cantoni et al. (1985) also detected a higher contamination by total DDT in bovine meat samples (49 ppb), and in France, Richou-Bac and Venant (1980) detected a DDT average content of 40 ppb in bovine, ovine and pork fats.

On the other hand, in Ireland, Harper (1980) detected a lower contamination of this type of residue in samples of bovine, ovine and pork, reporting a decrease in the DDTs' concentration from 90 ppb to 2 ppb during the period of time between 1972 and 1978.

In our study, the leg samples were the most contaminated by total DDT followed by chop and breast samples (Table 3). The same order is observed for its principal isomer pp'DDE. Regarding to other isomers, leg samples were more contaminated with pp'DDD whereas chop samples contained more pp'DDT. Statistical analysis by Wilcoxon's nonparametric test showed significant differences ($p < 0.05$) in pp'DDE residues between leg and breast cuts. These two cuts also showed significant differences ($p < 0.01$) in the contamination by total DDT.

Table 3. Contamination by organochlorine pesticide residues in three commercial cuts from 21 ovine carcasses. Results expressed as µg/kg fat (ppb).

Pesticide	Descriptive statistics	Chop	Leg	Breast
pp'DDE	% detected	81	90	71
	Total mean (ppb)	17	19	14
pp'DDT	% detected	49	38	33
	Total mean (ppb)	9	8	6
pp'DDD	% detected	5	10	5
	Total mean (ppb)	0.3	0.7	0.3
ΣDDTs	% detected	81	90	76
	Total mean (ppb)	26	28	20

After the culinary treatments of the meat cuts, the overall concentration of DDT residues decreased by an average of 44% while the number of positive samples were almost halved (table 4). The most effective treatment was the grill that decreased the total DDT by 56%, whereas roasting and cooking reduced total DDT by nearly 40%. Grilling reduced the pp'DDE and pp'DDT levels by 48% and 72%, respectively, roasting by 21% and 87%, and cooking by 29% and 70%. Statistical analysis by Wilcoxon's test showed a significant reduction of pp'DDE after grilling ($p < 0.001$), and roasting ($p < 0.01$), while cooking did not affect pp'DDE levels significantly ($p > 0.05$). In the same way, grilling and roasting significantly reduced pp'DDT levels ($p < 0.01$), unlike cooking ($p > 0.05$).

Most authors who have investigated the effect of processing of meat and meat products on the DDT content observed decreases of the residue levels after treatment. Thus, Kubacki and Lipowska (1980) reported 5-15% of losses after curing, pasteurization (25-36%), and sterilization (26-29%) of canned meat products. More recent data were given by Conchello et al. (1993a; 1993b) and Ariño et al. (1992; 1993) that obtained significant reductions of the fungicide HCB (hexachlorobenzene) and the pesticide HCH (hexachlorocyclohexane) between 25-40% after kitchen treatments of ovine meat, and processing of pork sausage and dry-cured ham. Despite the lack of significant increase observed in the pp'DDD levels after the three culinary treatments in our samples (Table 4), it should be noted that this fact may be due to the few number of pairs involved in the statistical analysis since this metabolite was the less frequently detected in raw samples. There was, however, a mean increase of nearly 150% of DDD so that some of the DDT lost was simply converted to the dechlorinated isomer reducing the loss of total DDT compounds to 37-56%. Ritchey et al. (1967) reported that frying and baking in chicken meat converted some of DDT to DDD, as did Abd-Rabo et al. (1989) during the thermal processing of milk.

To evaluate total distribution of the three DDT metabolites before and after cooking, the relative proportion of each pesticide was calculated (Table 5). The relative proportion of pp'DDE and pp'DDD increased while the proportion of pp'DDT decreased, likely due to the conversion of DDT to its metabolites by the thermal process. In raw chop samples the proportion of DDT was 35%, decreasing to 22% in the treated samples; DDE increased from 64% to 76%, respectively. Furthermore, DDD proportion also increased from 1% before treatment to 2% in grilled samples. In samples of leg and breast the proportion of DDT decreased as long as that of its metabolites DDD and DDE increased. According to this, Maggi et al. (1979) also reported such conversion of DDT to its metabolites in cooked and canned bovine meat

Table 4. Effect of grilling, roasting and cooking on the percentage of detection and mean values of organochlorine residues in ovine meat expressed as μg/kg fat (ppb). Wilcoxon's nonparametric test applied to seek significant differences after treatments.

Pesticide	Descriptive statistics	Grilling	Roasting	Cooking
pp'DDE	% of detection in treated samples	48	52	62
	Total mean after treatment (ppb)	9	15	10
	% of decrease (-) or increase (+)	-48***	-21**	-29
pp'DDT	% of detection in treated samples	14	10	14
	Total mean after treatment (ppb)	2	1	2
	% of decrease (-) or increase (+)	-72**	-87**	-70
pp'DDD	% of detection in treated samples	5	19	19
	Total mean after treatment (ppb)	0.3	1	1
	% of decrease (-) or increase (+)	+4	+106	+321
ΣDDTs	% of detection in treated samples	48	57	67
	Total mean after treatment (ppb)	11	17	13
	% of decrease (-) or increase (+)	-56	-38	-37

Significant differences at 99% (**; $p < 0.01$), and 99.9% (***; $p < 0.001$).

Table 5. Proportional distribution of DDT and metabolites (DDD and DDE) in the samples before and after the culinary treatments.

Sample	DDT	DDD	DDE	ΣDDTs
Raw chop	35	1	64	100
Grilled chop	22	2	76	100
Raw leg	30	3	67	100
Roasted leg	6	8	86	100
Raw breast	31	1	68	100
Cooked breast	15	9	76	100

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