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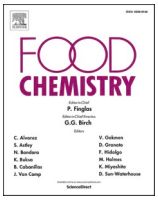

Effect of food processing on reduction and degradation pathway of pyrethroid pesticides in mackerel fillet (*Scomberomorus commerson*)

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ABSTRACT

Pyrethroid contamination in fish can contribute to the dietary uptake of pesticides. To mitigate this risk, the effects of frozen storage, thermal treatments (boiling and grilling), and non-thermal treatments (pickling and curing) on the reduction of bifenthrin, cypermethrin, deltamethrin, and permethrin in mackerel fillets were investigated. The curing process was the most effective method that significantly depleted 74.82–79.45% of pyrethroid residues from fish fillets, followed by the synergistic effect of eight weeks' frozen storage and grilling method (69.19–78.31%). Moreover, pyrethroid degradation pathways in processed fish were proposed into three major mechanisms of C1-C3 bond cleavage in cyclopropyl, dehalogenation, and double bond cleavage. These identical pathways incorporated with additional four mechanisms of dimerization, ester hydrolysis, oxidation, and reduction. This study recommended simple and effective processing practices for consumers and/or manufacturers to enhance food safety from the potential risks of consuming pyrethroid-contaminated fish.

1. Introduction

Fish is consumed as food in virtually all regions worldwide because of its high-quality protein with essential amino acids. Nevertheless, fish consumption can contribute significantly to dietary uptake of chemical contaminants such as heavy metals and pesticide residues (Milenkovic, Stajic, Stojic, Pucarevic, & Strbac, 2019).

Pyrethroids are one of the most widely used groups of synthetic pesticides in agriculture and aquaculture to prevent and control undesirable organisms. For instance, treatments of cypermethrin (5 mg/L) and deltamethrin (2–3 mg/L) solutions every 5–6 weeks are recommended in salmon farms to combat lice (Haya, Burridge, Davies, & Ervik, 2005). These chemical hazard compounds can be released from usage areas and, subsequently, accumulate in aquatic environments and aquatic organisms (Oliveira et al., 2019). Due to their hydrophobic property, bioaccumulation of pyrethroids in fish generally occurs through grill sorption and/or their food chains (Alonso et al., 2012). The contamination of pyrethroid residues in global fish and seafood products has been repeatedly detected, and it is increasingly recognized as a serious public health concern (Tang et al. 2018; Wongmaneepratip, Leong, & Yang, 2022). Ingestion of such contaminated food can cause negative effects on our reproductive, cardiovascular, immune, and neuronal systems (Chrustek et al., 2018; Kaneko, 2011). Therefore, in terms of food safety, it is crucial to estimate and manage pyrethroid levels at the point of fish consumption.

Before consumption, fishes are generally processed through various methods of thermal processing (blanching, boiling, drying, frying, grilling, and smoking), non-thermal processing (washing, fermenting, and salting) as well as freezing storage (Zhao, de Alba, Sun, & Tiwari, 2019). Among these processes, a number of researchers have reported that some methods may potentially alter concentration levels and degrade chemical structures of contaminants in food. The application of an individual process or the combination of processing methods differently affects the level of chemical contaminants (Yigit & Velioglu, 2020). For instance, the total arsenic concentration in seafood samples significantly decreased upon freezing storage for three months and their speciation pattern changed after frying (Dahl et al., 2010).

In particular to pyrethroid pesticides, the effect of post-harvest processing on residue levels in fruits and vegetables has been revealed. Low-temperature storage, which is generally practiced to maintain crop freshness, showed controversial results on pyrethroid concentrations in crops. Zhang, Luo, Wang, and Liu (2004) indicated that pyrethroid residues in fruits and vegetables decreased with increasing their storage time in refrigerators, whereas Albaseer (2019)

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presented that low-temperature storage expended pyrethroid lifetime and reduced their volatilization rate. It is interesting to investigate which scenario will happen to fish matrix. Besides the effect of cold storage, non-thermal and thermal processes were also taken into account. The combination of washing and boiling decreased pyrethroid concentrations in tomatoes, but the reduction was slightly less in refrigerated samples as compared to non-refrigerated tomatoes (Chauhan, Monga, & Kumari, 2012; Lin, Gerrard, & Shaw, 2005). Moreover, applying a 2% brine solution to okra samples for 10 min resulted in 31.58–94.67% pyrethroid reduction (Parmar, Korat, Shah, & Singh, 2012). Heat treatment of home roasting completely reduced pyrethroid residues in contaminated coffee beans (Mekonen, Ambelu, & Spanoghe, 2015). Although the previous studies mentioned above have demonstrated the effects of postharvest processing on the fate of pyrethroid residues in crops, the impact of commercial and household processing on these chemical hazards in the intricate matrix of fish remains unknown.

Lack of information on effective practices for handling pyrethroid residues in fish increases the possibility of pyrethroid exposure. Pyrethroid residues tend to persist in fish longer and more drastically than in crops because they can accumulate in lipophilic components and complex matrices of fishes (Tang et al., 2018). This accumulation trend may raise the risk of exceeding pyrethroid exposure to consumers. Thus, there is a need to demonstrate the effect of various processing methods on the mitigation of pyrethroid levels in fish fillets. Furthermore, how the processing methods alter parent pyrethroid compounds and which metabolites they will generate are important data for an in-depth understanding of pyrethroid degradation mechanisms. There has been little quantitative analysis describing the degradation pathway of pyrethroids. However, these studies were conducted in organic solutions under a designed laboratory system (Senneca, Scherillo, & Nunziata, 2007; Zhu et al., 2020) and in environmental media (Meyer, Lam, Moore, & Jones, 2013), but not in the manifold of real food sample.

Therefore, the aims of this study were to examine the effect of general fish processing on the reduction of four pyrethroid residues (bifenthrin, cypermethrin, deltamethrin, and permethrin) in fish fillets, and elucidate their possible degradation mechanisms in processed fish. In doing so, mackerel fillet whose consumption rate continuously increases year-on-year (Wongmaneepratip et al., 2022), and four pyrethroid residues that are frequently detected in seafood (Tang et al., 2018) were chosen as the fish sample and target compounds, respectively. This study particularly focused on detecting pyrethroid levels in fish samples during eight weeks of freezing storage and at the consumption point after processing with different treatments by using synthesized nanoparticles based on magnetic solid-phase extraction coupled with HPLC-PDA. Furthermore, LC-MS/MS analysis was applied to study altered compounds and possible degradation pathways of target pyrethroids. The results obtained from this study may help consumers and manufacturers identify effective processing methods that can be used to reduce the contamination level of pyrethroids in fish before consumption and also provide more understanding about pyrethroid degradation mechanisms affected by different food processing.

2. Materials and methods

2.1. Chemicals

Standards of four target pyrethroids, including bifenthrin, cypermethrin, deltamethrin, and permethrin, were purchased in a powder form with > 98% purity (Sigma Aldrich, MO, USA). Millipore water (18.2 MΩ cm^{-1}) prepared by a Milli-Q water purification system was used throughout the research. Acetonitrile (HPLC-grade) and glacial acetic acid (analytical-grade) were acquired from Macron Fine Chemicals, USA. Other chemicals, including hydrochloric acid, iron (II) chloride tetrahydrate, iron (III) chloride hexahydrate, methacrylic acid, oleic acid, potassium persulfate, sodium dodecylbenzenesulfonate, sodium hydroxide, and styrene, were obtained from Sigma Aldrich (St. Louis, MO, USA) for nano-adsorbent synthesis.

2.2. Sample preparation

Spanish mackerel (*Scomberomorus maculatus*) fillets were purchased from a local supermarket in Singapore. For each replication, fish fillets were divided into one control sample (non-fortified) and another group of fortified samples, consisting of fourteen specimens (50 ± 2 g each specimen). The mix-standard fortification of four pyrethroids (0.5 ng/g each compound) into fish fillets was carried out for 48 h in a dark environment at 4 °C. After that, each fortified sample was processed via different treatments based on household processing methods, as follows: (1) fresh-raw sample (non-processed sample), (2) fresh-boiling, (3) fresh-grilling, (4) fresh-pickling, (5) fresh-curing, (6) frozen two weeks, (7) frozen two weeks-boiling, (8) frozen two weeks-grilling, (9) frozen four weeks, (10) frozen four weeks-boiling, (11) frozen four weeks-grilling, (12) frozen eight weeks, (13) frozen eight weeks-boiling, and (14) frozen eight weeks-grilling. Processing details include: boiling in 100 °C water for 10 min using a stainless steel pot (diameter 20 cm); grilling at 100 °C for 10 min (5 min/side) in an aluminum fry pan covered with Teflon (diameter 20 cm); curing by soaking a fish fillet in a brine solution (pH 7.23 ± 0.01) of 10 g sodium chloride salt in 60 mL water for 1 h; pickling by immersed a fish fillet in an acidic solution (pH 2.45 ± 0.02), comprising 8 g sugar, 20 mL vinegar, and 40 mL water for 1 h; and frozen at −20 °C for two, four and eight weeks.

Pyrethroid concentrations were determined in fresh-raw and processed fish samples in accordance with treatments (1) to (14), and the results were reported as pyrethroid concentration per dry weight (DW) of sample for consistent comparison between fish samples obtained from different treatments.

2.3. Pyrethroid extraction in fish samples

Methods for nano-adsorbent synthesis and pyrethroid quantification followed our previous study (Wongmaneepratip et al., 2022). The extraction method was liquid–solid extraction, followed by low-temperature cleanup and magnetic solid-phase extraction using synthetic nano-adsorbents. Briefly, a homogenized sample (10 g) was extracted with 20 mL of acetonitrile through intense stirring for 10 min. After vacuum filtration, the supernatant was stored overnight at −20 °C. The obtained aliquot was diluted with 80 mL of Millipore water before adding 50 mg of synthetic nano-adsorbents and constantly stirring at 1250 rpm for 30 min. Then, adsorbents were collected and followed by the desorption process, which was performed with 5 mL of acidified acetonitrile (3% v/v acetic acid in acetonitrile) via stirring for 70 s. The supernatant was dried at 40 °C in a water bath under a nitrogen atmosphere. The extracts were reconstituted with 100 μL of acetonitrile and filtrated through 0.22 μm membrane filter before HPLC-PDA and LC-MS/MS analysis.

2.4. Matrix effect and recovery studies

The matrix effect was used to describe the consequences of sample components on the quality of obtained results under an analytical condition (Mao, Yan, Wan, Luo, & Yang, 2019). In current research, the matrix effect was studied by a calibration curve method in which the curves of standard solution and matrix-matched solution (post-spiked sample) were contributed in parallel at 0.2, 0.5, 1, 5, 10, 15, and 20 μg/L. Moreover, the efficiency of this analytical method was examined in terms of recoveries at 0.5 ng/g by comparing the pyrethroid concentrations in pre- and post-spike samples. Matrix effect and recovery test were calculated as follows (EC, 2019):

$$\%ME = \frac{Slope_{matrix-matched\ solution}}{Slope_{standard\ solution}} \times 100$$

$$\%Recovery = \frac{Pyrethroid\ concentration_{pre-spike}}{Pyrethroid\ concentration_{post-spike}} \times 100$$

2.5. HPLC analysis

Target pyrethroids were identified using a Phenomenex C18 column with 100 Å pore size and 150 × 4.6 mm id (Phenomenex, CA, USA). The injection was carried out at 20 μL with a flow rate of 1 mL/min by an autosampler of a Waters 2695 Alliance HPLC instrument. Its quaternary pump was set as a gradient system of acetonitrile (A) and Millipore water (B), starting at 68% of (A) for 30 min and increasing to 75% within 1 min. After 10 min of the 75% (A) constant proportion, solvent (A) was increased again to 85% within 1 min and continuously carried for 10 min (Wongmaneepratip et al., 2022). A photodiode array (PDA) detector was established at 230 nm. The quantification of each pyrethroid compound was calculated using external calibration curves obtained from the matrix effect study.

2.6. LC-MS/MS analysis

Based on HPLC results, effective processing methods that significantly reduced pyrethroid levels in fish samples were indicated and selected to be further analyzed with LC-MS/MS. The selected samples were obtained from fish fillets after treatments of (5), (12), (13), and (14). LC-MS/MS was used exclusively to examine altered compounds and possible degradation pathways of pyrethroids, not for quantification purposes. A Bruker AmaZon X (Bruker, Rheinstetten, Germany) was carried out for LC-MS/MS analysis. The LC system is an Agilent 1200 Series, and its running conditions were similar to the HPLC conditions presented in *Section 2.5*. Due to using a column size of 150 × 4.6 mm id (Phenomenex, CA, USA), the flow split device to mass spectrometer was applied. The mass spectrometer was configured with an electrospray ionization (ESI) source that was operated in both negative and positive ionization modes. High voltage (HV) capillary was maintained at −4500 V and 4500 V for negative and positive ion modes, respectively. Other acquisition parameters were set as follows: scan mode, a high voltage endplate offset of −500 V, a drying temperature of 200 °C, a dry gas flow of 6 L/min, and a nebulizing gas pressure of 29 psi. The obtained mass spectra were used to identify target pyrethroids and their degradation products based on the NIST Mass Spectral database, the PubChem database, and related references.

2.7. Statistical analysis

Sample preparation and pyrethroid detection were performed in triplicates with different batches of fish fillets to achieve reliable results. The recovery test was operated with six replicates. Pyrethroid concentrations (ng/g DW) and their percentage reductions were reported on either line chart or the form of mean values and their standard deviations (SD). The significant difference of results was assessed by an analysis of variance (one-way ANOVA) test with a confidence level of $P < 0.05$ and *t*-test with 95% confidence interval using IBM SPSS statistics software.

3. Results and discussion

3.1. Method validation

Target compounds of bifenthrin, cypermethrin, deltamethrin, and permethrin were detected between retention times of 25 and 45 min by HPLC-PDA, and examples of HPLC chromatograms are presented in Fig. S1. Calibration curves of standard solution and matrix-matched solution with regressions, correlation coefficients (R^2), root mean square values (RMSE), and matrix effect (%ME) are illustrated in Fig. S2. The R^2 values of standard and matrix-match calibration curves were all higher than 0.9990 for four target pyrethroids, which indicates satisfactory linearity of the curves. Concurrently, the RMSE values of both calibration curves were below 0.22, describing a small error of data points from these linear graphs. In addition, %ME of target pyrethroids varied from 97.96 to 99.79%, meaning that there was only a minor effect of sample components on the conduction of this analysis method (EC, 2019; Mao et al., 2019). Hence, the standard solution curves with a linearity of 0.20–20 μg/L were considered to use as external calibration curves for quantifying pyrethroid concentrations in all samples. Moreover, the limit of detection (LOD) and limit of quantification (LOQ) for four target PYs, evaluated as 3-fold and 10-fold of signal-to-noise ratios, were lower than 0.2 and 0.5 mg/L, respectively, indicating sufficient performance of the method for pyrethroid detection. Besides these analytical performances, the mean values of recoveries for bifenthrin, cypermethrin, deltamethrin, and permethrin were satisfactory at 82.96, 91.86, 89.91, and 90.43%, respectively, considered acceptable within the range of 70–120% (EC, 2019; Mao et al., 2020).

3.2. Effect of frozen storage on pyrethroid residues

Pyrethroid concentrations (bifenthrin, cypermethrin, deltamethrin, and permethrin) in fresh-raw samples (1) and frozen-raw samples (treatments: 6, 9, and 12) are shown as line graphs in Fig. 1. The concentrations of cypermethrin (0.40 ng/g DW), deltamethrin (0.33 ng/g DW), and permethrin (0.31 ng/g DW) in fresh-raw mackerel fillets significantly reduced to 0.31, 0.28, and 0.24 ng/g DW after two weeks of frozen storage; 0.31, 0.24, and 0.20 ng/g DW after four weeks of frozen storage; and 0.16, 0.17, and 0.14 ng/g DW after eight weeks of frozen storage. While bifenthrin in fresh-raw sample (0.23 ng/g DW) notably decreased to 0.12 ng/g DW only after eight weeks of frozen storage. These results suggest that frozen storage (−20 °C) has a greater impact on the reduction of cypermethrin, deltamethrin, and permethrin than bifenthrin.

Moreover, the overall result demonstrated the efficacy of eight weeks of frozen storage on pyrethroid removal (48.52–59.34%) (Fig. 1), suggesting that increasing storage time of frozen enhanced pyrethroid reduction in fish samples. This is consistent with findings from earlier studies that showed increasing storage time significantly reduced hazardous residues in food due to adequate time for alteration mechanisms (Dahl et al., 2010; Yigit & Velioglu, 2020). Dahl et al. (2010) demonstrated that the significant amount of total arsenic in blue mussels was reduced after frozen storage for one month (2.3–13.2%) and three months (7.8–14.7%), but this storage condition had no effect on the concentration of inorganic arsenic. These results point out the important role of storage duration and chemical structures of contaminants in the reduction effect. From another point of view, some researchers discussed that the dissipation of pyrethroid residues was slightly less when samples were stored at low temperature compared to room temperature storage (Chauhan et al., 2012; Jayakrishnan, Dikshit, Singh, & Pachauri, 2005). Although frozen storage may impede the degradation and other reactions of pyrethroid residues, it cannot fully inhibit their decomposition process, and the storage duration is a critical factor in the fate of pesticide residues in food (Yigit & Velioglu, 2020). It can be seen that frozen storage at −20 °C (two, four, and eight weeks), the most common storage method for food preservation, could significantly reduce pyrethroid residues from fish fillets, and the major factors here were storage time and the chemical structure of pesticides.

3.3. Effect of heat processing on pyrethroid residues

Pyrethroid residues in fresh and frozen samples of raw, boiled, and grilled fish fillets (treatments: 1, 2, 3, 6, 7, 8, 9, 10, 11, 12, 13, and 14) were examined and the results are indicated in Table 1. The effect of heat treatments (boiling and grilling) was assessed by comparing pyrethroid levels in boiled and grilled fish with their raw samples stored under similar conditions of fresh and frozen (two, four and eight weeks).

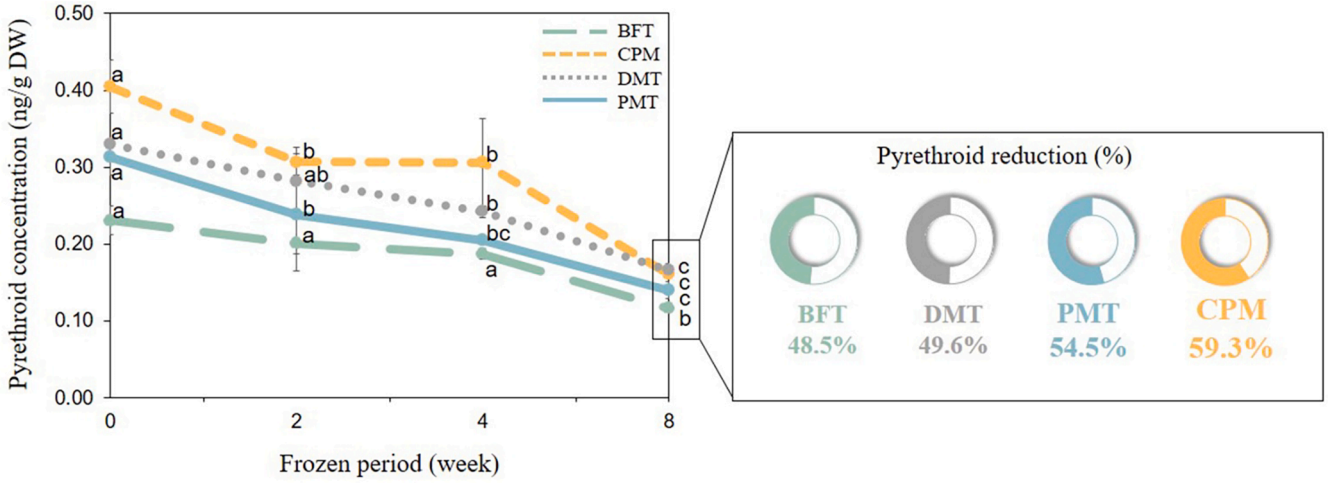

Fig. 1. Pyrethroid concentrations in fresh-raw and frozen samples (two, four, and eight weeks) of mackerel fillets. [a,b,c] Different lower case letters indicate significant differences between mean values of pyrethroid concentrations at different storage time ($P < 0.05$).

In other words, the percent reductions were calculated from the pyrethroid concentrations in boiled and grilled fish with the raw sample presented in the same row in Table 1. The results show that the boiling method was able to remove 5.01–24.90% of pyrethroid residues from mackerel samples, which is comparable to the reduction of chemical hazards (2.8–18.9%) in boiled salmon reported by Dahl et al. (2010). Although measurable reduction results were observed, more than half of the boiled samples demonstrated an insignificant difference in pyrethroid levels compared with their raw samples (Table 1). This finding is consistent with a previous report demonstrated by Aguilera, Valverde, Camacho, Boulaid, and García-Fuentes (2014) that the boiling process had little effect on pesticide reduction in green beans. The ineffective outcome of the boiling process may be influenced by the hydrophobic property of pyrethroids. Lipophilic pyrethroid compounds can accumulate and remain in fat tissue and/or other components of fish matrix (Kaczynski, Lozowicka, Perkowski, & Szabunko, 2017); thus, only a small amount of pyrethroids were released out or changed during the boiling process.

Compared to boiling, the grilling method provided significantly higher percentages of pyrethroid removal at 27.48–48.91% (Table 1), which estimated 2-fold to 10-fold of the percent reductions in boiled fish. This may be due to the heat generated from the cooking pan accelerating volatilization and thermal degradation of pyrethroid residues (Albaseer, 2019). The effectiveness of direct heat treatment from the cooking pan was also demonstrated by Mekonen et al. (2015) who found that home roasting process completely reduced residues of cypermethrin and permethrin in contaminated coffee beans. Thermal treatments have been found effective in the destruction of various pesticides, depending on their types and chemical structures (Bajwa & Sandhu, 2014).

3.4. Effect of non-heat processing on pyrethroid residues

Pickling fish in the vinegar-based solution (4) and curing fish in the salt-based solution (5) are traditional processes to preserve and contribute to extraordinary flavor and taste of fishes. The results of pyrethroid concentrations (bifenthrin, cypermethrin, deltamethrin, and permethrin) and their percent reductions in pickled and cured mackerel samples compared with fresh-raw samples are presented in Fig. 2A. In comparison to fresh-raw samples (0.23–0.41 ng/g DW), the concentrations of four target pyrethroids in pickled and cured fish fillets significantly decreased to 0.17–0.27 and 0.05–0.08 ng/g DW, respectively. Based on the percentage of pyrethroid reductions shown in Fig. 2A, the curing method (74.82–79.45%) showed a more robust effect of approximately 2-fold to 4-fold on the decrement of pyrethroid residues compared with the pickling process (19.65–36.78%). Our findings correspond to data reported by Cycoń and Piotrowska-Seget (2016), who observed that pyrethroid degradation was higher and faster under neutral and basic conditions than in acidic conditions.

Ester hydrolysis is a common pathway of pyrethroid degradation, which changes pyrethroid structures into by-products of acid compounds (chrysanthemic acid) (Zhu et al., 2020). This reaction generally occurs under both acidic and alkali conditions. The pH value of a solution is pertinent to pesticide hydrolysis, which they lose their integrity or break down into by-products (Albaseer, 2019). Under an acidic condition, acid compound acts as a catalyst in ester hydrolysis to alter the chemical structures of pyrethroids, but this mechanism is reversible (Radford, Panuwet, Hunter, Barr, & Ryan, 2018). Therefore, the rate of pyrethroid reduction under an acidic condition was inferior. In contrast, previous studies reported that, under neutral solution of sodium chloride (NaCl) and alkali solution of sodium hydroxide (NaOH), the percentages of pyrethroid reduction in crops achieved 27–91% and 40–60%, respectively (Abou-Arab, 1999; Ahmed, Randhawa, Yusuf, & Khalid 2011). Pyrethroid compounds were hydrolyzed under alkali conditions via an irreversible B_{AC2} mechanism in which hydroxide ion (OH^-) in solution attacks the acyl carbon in pyrethroid compounds to form a tetrahedral intermediate with acyl cleavage (Katagi, 2011). In this study, the curing process was conducted in the sodium chloride solution (pH ~ 7), resulting in neutral ester hydrolysis. da Silva, Guimaraes, and Pliego (2013) demonstrated that the hydrolysis of esters under a neutral condition could occur through the water autoionization mechanism, in which the second molecule of water acts as a catalyst. Therefore, the powerful effect of curing process on pyrethroid degradation in cured fish could be attributed to the neutral ester hydrolysis.

3.5. Identification of effective processing methods

To seek the most proficient treatments for pyrethroid reduction, percent removals with statistical analysis of target pyrethroids (bifenthrin, cypermethrin, deltamethrin, and permethrin) in mackerel fillets after processing (treatments 2–14) were analyzed in comparison to the fresh-raw sample (1), and the results are presented in Table 2. The results demonstrate that frozen storage at −20 °C for two, four, and eight weeks was able to remove pyrethroid residues from mackerel fillets by 13.59–30.34%, 18.30–35.47%, and 48.52–59.34%, respectively. Moreover, applying the heat treatments of boiling and grilling to fresh samples removed 15.06–24.09% and 40.12–48.45% of residues from the samples. Although the individual treatments of frozen storage and

Table 1
Pyrethroid concentrations in raw, boiled, and grilled fish with percentage reductions of processed fish samples in comparison to their raw samples.

Analyte	Storage	Pyrethroid concentration ($\times 10^{-1}$ ng/g DW)			Reduction (%) compared to raw sample	
		Raw	Boiling	Grilling	Boiling	Grilling
Bifenthrin	Fresh	2.31 ± 0.19[b]	1.96 ± 0.30[b]	1.37 ± 0.08[a]	15.06 ± 2.28[A]	40.12 ± 5.02[B]
	Frozen 2 wks	2.01 ± 0.36[a]	1.88 ± 0.38[a]	1.28 ± 0.25[a]	6.37 ± 2.70[A]	35.79 ± 2.02[B]
	Frozen 4 wks	1.87 ± 0.07[c]	1.57 ± 0.13[b]	1.09 ± 0.16[a]	16.24 ± 3.71[A]	41.86 ± 6.20[B]
	Frozen 8 wks	1.16 ± 0.05[b]	1.11 ± 0.14[b]	0.68 ± 0.05[a]	5.01 ± 2.64[A]	40.97 ± 12.02[B]
Cypermethrin	Fresh	4.05 ± 0.35[c]	3.03 ± 0.45[b]	2.10 ± 0.13[a]	24.90 ± 3.02[A]	47.12 ± 7.69[B]
	Frozen 2 wks	3.07 ± 0.19[b]	2.32 ± 0.05[a]	2.01 ± 0.07[a]	24.01 ± 8.31[A]	34.44 ± 3.77[B]
	Frozen 4 wks	3.06 ± 0.57[b]	3.01 ± 0.96[b]	2.31 ± 0.16[a]	7.97 ± 3.61[A]	32.23 ± 9.36[B]
	Frozen 8 wks	1.61 ± 0.03[c]	1.46 ± 0.06[b]	0.85 ± 0.10[a]	9.12 ± 5.20[A]	47.03 ± 5.59[B]
Deltamethrin	Fresh	3.30 ± 0.03[c]	2.69 ± 0.15[b]	1.85 ± 0.09[a]	18.40 ± 4.89[A]	43.70 ± 4.43[B]
	Frozen 2 wks	2.82 ± 0.36[b]	2.65 ± 0.38[ab]	2.02 ± 0.08[a]	5.68 ± 1.64[A]	27.48 ± 8.86[B]
	Frozen 4 wks	2.42 ± 0.08[b]	2.29 ± 0.12[b]	1.62 ± 0.14[a]	5.49 ± 2.45[A]	33.08 ± 5.48[B]
	Frozen 8 wks	1.66 ± 0.08[b]	1.41 ± 0.17[b]	1.01 ± 0.01[a]	15.48 ± 0.75[A]	38.48 ± 7.84[B]
Permethrin	Fresh	3.13 ± 0.24[c]	2.59 ± 0.24[b]	1.62 ± 0.20[a]	17.05 ± 2.84[A]	48.45 ± 2.71[B]
	Frozen 2 wks	2.39 ± 0.51[b]	2.17 ± 0.55[b]	1.54 ± 0.31[a]	9.05 ± 0.51[A]	34.97 ± 4.39[B]
	Frozen 4 wks	2.05 ± 0.02[b]	1.93 ± 0.12[b]	1.38 ± 0.27[a]	5.88 ± 1.63[A]	32.68 ± 9.59[B]
	Frozen 8 wks	1.40 ± 0.11[b]	1.18 ± 0.15[b]	0.71 ± 0.03[a]	15.87 ± 3.72[A]	48.91 ± 5.69[B]

[a,b,c] Different lower case letters in a row indicate significant differences among processing conditions ($P < 0.05$).
[A,B] Different upper case letters in a row indicate significant differences between processing conditions (*t*-test, 95% CI).

thermal treatments showed significant effects on pyrethroid reduction, their combination presented a more powerful effect. As seen in Table 2, the implementation of frozen storage (two, four, and eight weeks) followed by the boiling process reduced 19.23–41.37%, 30.52–39.70%, and 51.19–62.81% of the residues, while the grilling of frozen samples (two, four, and eight weeks of frozen storage) achieved 38.71–51.22%, 50.68–60.42%, and 69.19–78.31% pyrethroid reductions. It can be concluded that there was a synergistic effect of frozen storage and heat treatment on the depletion of pyrethroid residues in fish fillets. In addition, among these implementations, the longest frozen storage of eight weeks and the pan grilling method were preferred due to their advantages mentioned in Sections 3.2 and 3.3. The combination of pretreatment and cooking methods was also recommended by Yang et al. (2012) to substantially reduce or eliminate pesticide residues in food samples. Outstandingly, the curing method, which immersed fish fillets into a brine solution of 16% sodium chloride, was the best strategy to decompose target pyrethroids in mackerel fillets by 74.82–79.45%.

Evidence from this study suggests that, among the tested processing methods (treatments 2–14), the curing process is the most powerful method for pyrethroid removal (74.82–79.45% reduction) from the intricate matrix of mackerel fillets, followed by the grilling of eight weeks' frozen sample (69.19–78.31% reduction), and the combination of eight weeks' frozen storage and the boiling process (51.19–62.81% reduction), respectively. Besides, frozen storage for eight weeks is considered as one of the effective methods of pyrethroid reduction (48.52–59.34%), whose performance was slightly less than its combination with the boiling process.

3.6. Degradation pathways of pyrethroids by effective processing methods

Apart from the reviewed degradation pathways of tested processing methods (frozen storage, thermal treatments, and non-thermal treatments) mentioned in Sections 3.2, 3.3, and 3.4, the target pyrethroids may be decomposed through other possible mechanisms. Therefore, based on the discussion in *Section 3.5*, fish samples from the effective processing methods: curing (5), eight weeks of frozen storage (12), the combination of eight weeks of frozen storage and boiling (13), and the integration of eight weeks of frozen storage and pan grilling (14), were further examined by LC-MS/MS to investigate altered structures and possible degradation mechanisms of target pyrethroids (bifenthrin, cypermethrin, deltamethrin, and permethrin). LC-MS/MS identifications of pyrethroid degradation products are presented in Tables S1–S4, and their chromatograms are illustrated in Figs. S3–S6. Chemical structures of these altered compounds were identified based on the NIST Mass Spectral database, the PubChem database, and related references (Gopal, Niwas, & Devakumar, 2015; Jeong et al., 2019; Zhu et al., 2020). The degradation compounds and possible alteration mechanisms of four target pyrethroids that occurred under different processing methods (treatments: 5, 12, 13, and 14) are displayed in Fig. 3. The results elaborate that the four target pyrethroids in fish samples were decomposed through the major seven pathways, including (a) C1-C3 bond cleavage in cyclopropyl, (b) dimerization, (c) dehalogenation, (d) double bond cleavage, (e) ester hydrolysis, (f) oxidation, and (g) reduction. In addition, the loss of particular structures of aromatic benzene, hydroxybenzene, and cyano groups on pyrethroid compounds was also observed.

Examples of mass spectra of deltamethrin in standard solution and in cured fish are illustrated in Fig. 2B and C. It can be seen that the mass spectral pattern of the deltamethrin standard changed after the curing treatment. The crucial degradation pathway under the curing process was dehalogenation, as all target pyrethroids broke down via this mechanism (Fig. 3). Dehalogenation is a common pathway for degrading or transforming hazardous halogenated compounds into other less harmful products. It can occur through different reactions of hydrolysis, oxidation, and reduction (Zhu, Wang, Li, Wang, & Liao, 2022). This finding further supports the previous finding by Zhu et al. (2020) that reductive dehalogenation is one of the major degradation mechanisms of pyrethroid compounds (deltamethrin, permethrin, and dihaloacetylated heterocyclic pyrethroids).

Moreover, available literature has indicated the potential degradation effects of thermal conditions (Lin et al., 2005; Mekonen et al., 2015; Takahashi, Mikami, Yamada, & Miyamoto, 1985). The researchers demonstrated that enhancing the cooking temperature accelerated the thermal degradation of pyrethroids in food samples. Under synergistic treatments in this study, pyrethroids decomposed through various routes such as C—C bond cleavage, dehalogenation, and double bond cleavage. In addition, dimerization and oxidation were the remarkable mechanisms, differentiating these synergistic processes (13 and 14) from other discussed methods (5 and 12). This result is consistent and inconsistent with previous reports. Thermal treatments of boiling and

A

Analyte	Pyrethroid concentration ($\times 10^{-1}$ ng/g DW)			Reduction (%) compared to raw sample	
	Fresh-raw	Pickling	Curing	Pickling	Curing
Bifenthrin	2.31 ± 0.29^{c}	1.69 ± 0.37^{b}	0.52 ± 0.15^{a}	27.45 ± 7.53^{A}	77.52 ± 4.08^{B}
Cypermethrin	4.05 ± 0.74^{c}	2.53 ± 0.32^{b}	0.78 ± 0.23^{a}	36.78 ± 6.84^{A}	79.45 ± 10.31^{B}
Deltamethrin	3.30 ± 0.12^{c}	2.65 ± 0.17^{b}	0.72 ± 0.18^{a}	19.65 ± 5.89^{A}	78.00 ± 6.32^{B}
Permethrin	3.13 ± 0.34^{c}	2.39 ± 0.44^{b}	0.80 ± 0.27^{a}	23.97 ± 7.65^{A}	74.82 ± 5.67^{B}

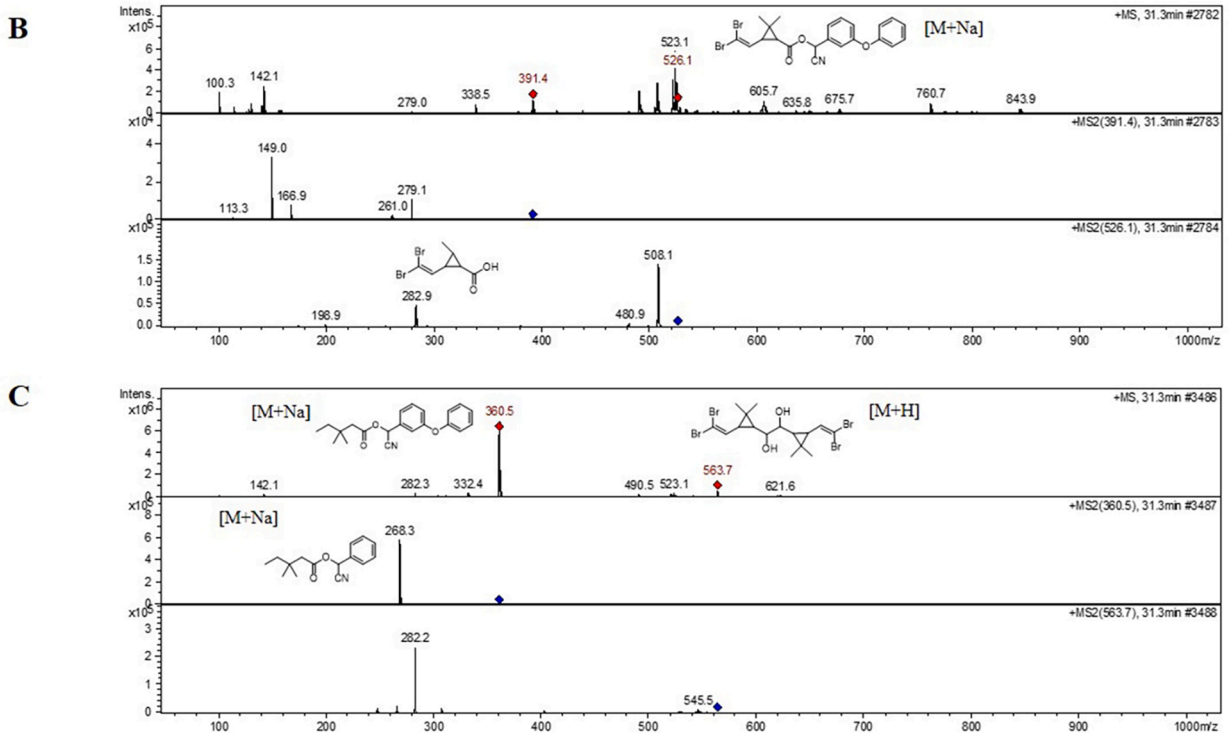

Fig. 2. Pyrethroid concentrations in fresh-raw, pickled, and cured fish with their percentages of reduction (A); MS chromatograms of deltamethrin in standard solution (B) and in cured fish sample (C). ^{a,b,c} Different lower case letters in a row indicate significant differences among processing conditions ($P < 0.05$). ^{A,B} Different lower case letters in a row indicate significant differences between processing conditions (*t*-test, 95% CI).

Table 2
The reductions (percentage) of pyrethroid residues in frozen and processed fish compared to the fresh-raw sample.

Storage	Processing method (Treatment No.)	Reduction (%) of pyrethroid in mackerel fillet			
		Bifenthrin	Cypermethrin	Deltamethrin	Permethrin
Fresh	Boiling (2)	15.06 ± 2.28^{ab,A}	24.09 ± 3.02^{a,B}	18.40 ± 4. 89^{a,A}	17.05 ± 2.84^{a,A}
	Grilling (3)	40.12 ± 5.02^{de,A}	47.12 ± 7.69 ^{cd,A}	43.70 ± 4.43^{de,A}	48.45 ± 2.71^{de,A}
	Pickling (4)	27.45 ± 7.53^{bc,AB}	36.78 ± 6.84^{abc,B}	19.65 ± 5.90^{a,A}	23.97 ± 7.65^{ab,AB}
	Curing (5)	77.52 ± 4.08^{g,A}	79.45 ± 10.31^{e,A}	78.00 ± 6.32 ^{h,A}	74.82 ± 5.67^{g,A}
Frozen 2 wks	Raw (6)	13.59 ± 8.54^{a,A}	30.34 ± 8.52^{ab,B}	21.54 ± 4.66^{ab,B}	24.62 ± 10.62^{ab,B}
	Boiling (7)	19.23 ± 5.86^{abc,A}	41.37 ± 11.50^{bc,B}	22.49 ± 9.24^{ab,A}	31.45 ± 9.56^{bc,AB}
	Grilling (8)	44.63 ± 3.74^{e,A}	48.93 ± 12.50 ^{cd,AB}	38.71 ± 4.69 ^{cd,A}	51.22 ± 4.62^{ef,B}
Frozen 4 wks	Raw (9)	18.30 ± 7.85^{ab,A}	35.47 ± 10.38^{abc,B}	26.44 ± 3.83^{ab,AB}	34.31 ± 5.24^{bc,B}
	Boiling (10)	31.54 ± 7.85 ^{cd,A}	39.70 ± 9.57^{abc,A}	30.52 ± 3.09^{bc,A}	38.12 ± 6.02 ^{cd,A}
	Grilling (11)	52.57 ± 6.17^{e,A}	60.42 ± 5.31^{d,A}	50.68 ± 6.19^{ef,A}	56.03 ± 4.03^{ef,A}
Frozen 8 wks	Raw (12)	48.52 ± 12.15^{e,A}	59.34 ± 7.75^{d,A}	49.60 ± 3.76^{ef,A}	54.50 ± 10.90^{ef,A}
	Boiling (13)	51.19 ± 11.21^{e,A}	62.81 ± 9.21^{d,A}	57.38 ± 3.51^{f,A}	61.92 ± 8.19^{f,A}
	Grilling (14)	70.58 ± 2.04^{f,AB}	78.31 ± 5.69^{e,C}	69.19 ± 1.57^{g,A}	77.17 ± 3.20^{g,BC}

^{a,b,c,d,e,f,g} Different lower case letters in a column indicate significant differences among processing conditions ($P < 0.05$).
^{A,B} Different upper case letters in a row indicate significant differences among pyrethroid compounds ($P < 0.05$).

grilling could damage native pyrethroid structures and, simultaneously, initiate dimerization or polymerization of their fragment compounds (Albaseer, 2019; Amvrazi, 2011). A controversial result was presented by González Audino, Licastro, and Zerba (2002) that pyrethroid compounds resisted polymerization under thermal treatment at 210 °C. This argument could be because González Audino et al. (2002) performed the experiment in inorganic salt samples but not in intricate matrices of food, which have many different compositions that may

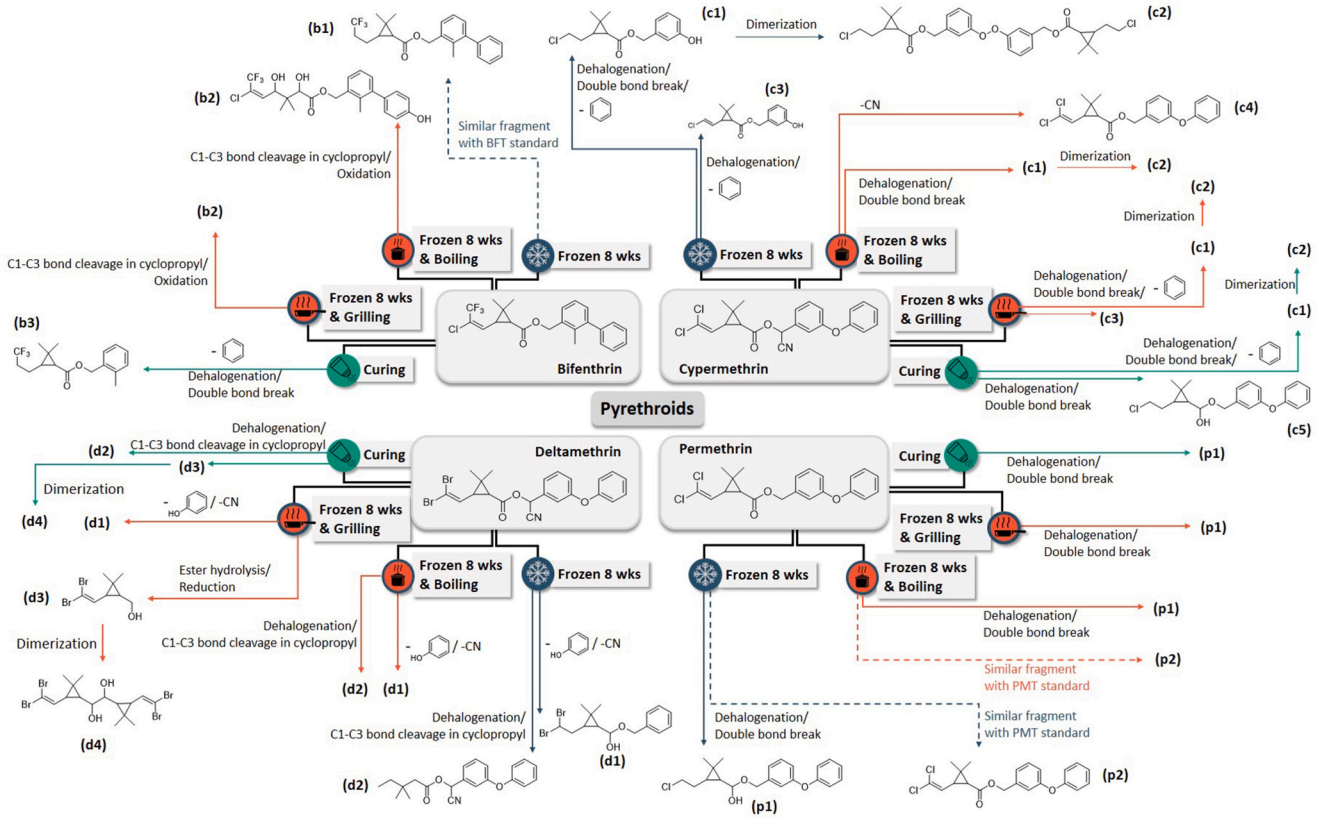

Fig. 3. Degradation compounds of target pyrethroids based on LC-MS/MS analysis and their possible degradation mechanisms in mackerel fillets.

involve or accompany dimerization. Moreover, a few numbers of studies suggested that the major process of thermal degradation was evaporation, associated with some decomposition and oxidation (Senneca et al., 2007; Yigit & Velioglu, 2020).

Furthermore, the less significant reduction effect of eight weeks of frozen storage (12) was supported by the mass spectra shown in Figs. S3–S6. It can be seen that the mass spectral patterns of bifenthrin and permethrin after frozen storage for eight weeks are similar to their standards. However, the altered compounds of pyrethroid residues were also detected. The target pyrethroids under this storage treatment were changed through a few routes such as dehalogenation and double bond break (Fig. 3). These proposed mechanisms after the long storage duration may be influenced by photo-degradation in which the light was the key factor for pyrethroid degradation mechanisms (Zhu et al., 2020). Among the discussed processing methods (treatments: 5, 12, 13, and 14), overall results demonstrate that some degradation pathways of target pyrethroids are only involved under specific processing, but most of the mechanisms are overlapped (Fig. 3).

In terms of pyrethroid compounds used in this study, the chemical structures of bifenthrin, cypermethrin, deltamethrin, and permethrin were altered through the proposed seven pathways (a–g) mentioned before. However, based on Fig. 3, each target pyrethroid was decomposed via different combinations of mechanisms under a similar processing method. This may be because of unpredicted side reactions caused by other compositions in the fish fillets. In addition, different degradation patterns of pyrethroid compounds are common and can also occur, even though the degradation experiment was performed in an uncomplicated mix-solution of water and organic solvents under controlled laboratory conditions (Zhu et al., 2020).

Although the degradation pathways of different pyrethroid compounds were varied and could be complicated under similar food processing, the integrated mechanisms of the effective processing methods (treatments: 5, 12, 13, and 14) were observed and a summary is presented in Fig. 4. Our findings propose that the degradations of four target pyrethroids undergo three identical degradation mechanisms of (a) C1-C3 bond cleavage in cyclopropyl, (c) dehalogenation, and (d) double bond cleavage with the assistance of additional four pathways, including (b) dimerization, (e) ester hydrolysis, (f) oxidation, and (g) reduction. Furthermore, evidence from this current study suggests that the composition of sample matrix, as well as the chemical structures of pyrethroids, may play an important role in their degradation patterns. Therefore, the effect of food compositions such as fat and protein on pyrethroid degradation is highly emphasized for future research.

4. Conclusion

Fish is regarded as an important source of high-quality proteins; however, reports from different areas across the world have indicated the risk of pyrethroid contamination. Beyond the need to regulate the application of pyrethroid pesticides in agriculture and aquaculture, methods for reducing pyrethroid levels in fish at the consumption point are indispensable. This study has examined the effects of various household processing methods on pyrethroid reduction in the intricate matrix of fish fillets. It was found that the curing process in sodium chloride solution (~16%) and the combination of frozen storage (eight weeks) and pan grilling were the most effective methods for pyrethroid removal. This finding is significant as it provides powerful strategies of simple and effective food processing for consumers and/or manufacturers to reduce the level of pyrethroid contaminants in fish before consumption.

Furthermore, the current study provides new insights into pyrethroid degradation mechanisms. Among seven proposed pathways, the predominant degradation routes of pyrethroid residues in fish after processing were identified as C1-C3 bond cleavage in cyclopropyl, dehalogenation, and double bond cleavage. These pathways may aid in the development of the proper method(s) and/or artificial agents for

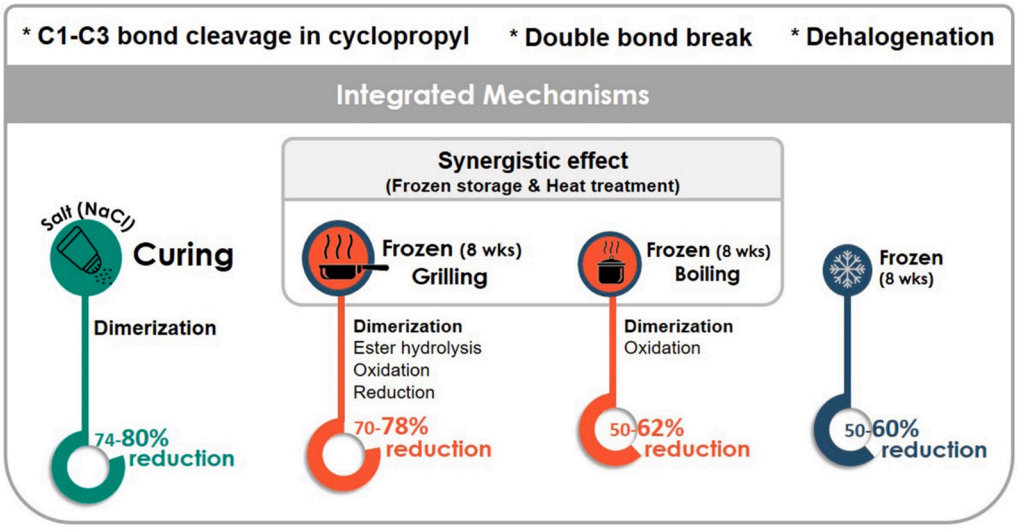

Fig. 4. Summary of proposed degradation pathways occurred under four effective processing methods with percentages of pyrethroid reduction.

decomposing pyrethroid residues in fish and other foods to ensure food safety. Nevertheless, this information was demonstrated for a specific matrix of mackerel sample that may or may not be applicable for other seafood as each species has different matrix compositions such as fat, protein, and water. Therefore, it would be interesting to apply the effective processing methods proposed in this study to other seafood samples or food commodities to investigate the possible effect of matrix composition on pyrethroid reduction.

CRediT authorship contribution statement

Wanwisa Wongmaneepratip: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Validation, Writing – original draft. **Xianfu Gao:** Formal analysis, Methodology. **Hongshun Yang:** Resources, Writing – review & editing, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.foodchem.2022.132523.

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