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ORIGINAL ARTICLE

Effect of sterilization conditions on the formation of furan and its derivatives in canned foods with different substrates

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Abstract

This study explored the effects of sterilization conditions on the formation of furan and its 10 derivatives in canned foods with a sterilizing value (F0) at 4. The contents of furans were determined by SPME arrow-GC-MS/MS, along with the furan precursors analyzed for elucidating the possible mechanism of furan formation. Results revealed that the total furan contents rose substantially in canned meat paste, tomato mackerel, chicken puree, tomato paste, pineapple slice, pineapple juice and carrot juice following sterilization. However, the total furan content did not change significantly ($p > 0.05$) in canned oily mackerel, but decreased significantly ($p < 0.05$) in canned apple puree after sterilization. With the exception of apple puree and pineapple slice, all the other canned foods showed a higher total furan content under low-temperature-long-time condition than that under high-temperature-short-time condition. Following heating, only the furan level showed a large increase in chicken puree, meat paste and tomato mackerel, whereas in canned fruit- and vegetable-based foods, the contents of furan and furfural showed a pronounced increase. The levels of alkylated furans were higher in sterilized samples containing high level of amino acid, while that of oxygenated furans were higher in sterilized samples containing high level of reducing sugar.

Keywords: Canning, Furan and its derivatives, SPME arrow-GC-MS/MS, Sterilization

1. Introduction

Furan is a highly volatile heterocyclic compound that comprises four carbon atoms and one oxygen atom. Most derivatives of furan are lipophilic and highly volatile, except oxygenated furans, processing a higher polarity than the other derivatives. Furan and its derivative furfuryl alcohol are listed in Group 2B by the International Agency for Research on Cancer (IARC), while furfural is listed in Group 3 [1]. Of the various furan derivatives, 2-methylfuran, 3-methylfuran, and 2,5-dimethylfuran have been reported to cause potential damage to organ cells and possess potential genetic toxicity [2,3].

The mechanisms underlying furan formation include degradation of ascorbic acid, protein, and carbohydrate, as well as lipid oxidation and Maillard reaction. In a heated food system, ascorbic acid will be rapidly oxidized to form dehydroascorbic acid, followed by hydrolysis to form 2,3-diketogulonic acid (DKG) for subsequent formation of xylosone and 2-deoxyaldotetrose via decarboxylation, leading to furan formation via cyclization. In contrast, ascorbic acid can be hydrolyzed and decarboxylated under non-oxidative conditions to generate 3-deoxypentosulose for furan formation through cyclization [4].

For proteins, it can undergo degradation to form amino acids for subsequent formation of ethanolamine via decarboxylation under continuous heating, followed by conversion to acetaldehyde following removal of ammonia or conversion to pyruvic acid via dehydration and deamination. Then acetaldehyde can also be produced from pyruvic acid via decarboxylation or glycolaldehyde. Finally, furan can be formed from the above intermediates during aldol condensation and cyclization [4].

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Polyunsaturated fatty acids such as linoleic acid can undergo oxidation in the presence of oxygen or lipoxygenase and are then cleaved to form 4-hydroxy-2-alkenals, followed by formation of 2,5-dihydro-2-furanol via cyclization and subsequent furan formation following dehydration [4].

During the Maillard reaction, hexose can undergo degradation to form aldose derivatives, followed by furan formation through degradation, cyclization and dehydration [4]. Amino acids are essential in the generation of methylfuran, as they can form aldehydes following the Strecker degradation step in the Maillard reaction. Then the generated aldehyde compounds and aldose can form methylfuran via aldol condensation [5].

Furan formation is a concerning topic for all worldwide health organizations due to its high toxicity. However, currently, most studies have only examined the levels of furan and few of its alkylated derivatives. As furan and its derivatives can be generated during food processing, commercial sterilized foods such as sauce, baby food, juice and meat can be expected to be rich in furan and its derivatives. However, most existing studies have investigated the levels of these compounds in commercial food products sold on the market. There is a lack of data regarding formation of furan and its derivative as affected by sterilization condition of canned foods. Therefore, this study aims to investigate furan formation and the potential underlying mechanism during sterilization of canned foods with different substrates including meat, fish, fruit, juice, tomato paste, and baby foods. To achieve this, food samples were processed into canned foods by controlling sterilization temperature and time length that would meet the sterilization target ($F0 = 4$) and the contents of furan and its 10 derivatives were analyzed by SPME arrow-GC-MS/MS. Finally, we analyzed and compared the contents of furan precursors before and after sterilization using a reliable method that was employed before [6].

2. Materials and methods

2.1. Materials

All the raw material and flavoring ingredients of canned foods were procured from a local market in New Taipei City, Taiwan. Containers used in this study were enemal tinplate cans (307 × 201 mm for solid foods and tomato paste; 202 × 504 mm for juice; and glass jar capacity 75 mL, height 50.7 mm, with cap for baby foods).

2.2. Chemicals and reagents

Furan standard was purchased from Alfa Aesar Co. (Ward hill, MA, USA), while 3-methylfuran was from Acros Co., (Carlsbad, CA, USA), and 2-pentylfuran from Tokyo Chemical Industry Co. (Tokyo, Japan). The other furan derivative standards including 2-methylfuran, 2,3-dimethylfuran, 2,5-dimethylfuran, 2-ethylfuran, furfural, furfuryl alcohol, 2-butylfuran and 2-acetylfuran were from Sigma–Aldrich (St. Louis, MO, USA). Internal standard d4-furan was from Dr. Ehrenstorfer GmbH Co. (Augsburg, Germany). The HPLC-grade solvents methanol and petroleum ether were from Merck (Darmstadt, Germany). Deionized water was produced by a Milli-Q water purification system (Bedford, MA, USA). Sodium chloride, ninhydrin, 3,5-dinitrosalicylic acid, D-dextrose, potassium sodium tartrate 4-hydrate, and glycine was purchased from Sigma–Aldrich (St. Louis, MO, USA).

2.3. Instrumentation

A model 7890B GC with 7000C triple quadrupole tandem mass spectrometer was from Agilent Technologies (Palo Alto, CA, USA). An SPME arrow system with a MPS robotic autosampler was from GERSTEL GmbH & Co.KG (Eberhard-Gerstel-Platz, Germany). An HP-5MS (30 m × 0.25 mm × 0.25 μm film thickness) column was from Agilent Technologies (Palo Alto, CA, USA). A carboxen/polydimethylsiloxane (CAR/PDMS) SPME arrow (phase thickness 120 μm, outer diameter 1.1 mm) and headspace vial (20 mL) with a silicone/PTFE septum was from CTC Analytics AG (Zwingen, Switzerland). A sprinkle water type auto retort (type CY-3000H-RD770-1P) was from CHANG YU Machinery Works (Changhua, Taiwan). A model HT1043 Soxhlet extractor was from FOSS Co. (Hillerod, Denmark).

2.4. Evaluation of sterilization temperature and duration for different canned foods using the heat distribution test

According to the regulation on good hygiene practice for food in Taiwan [7], an $F0 \geq 3$ is required for low-acid canned foods after sterilization. Thus, in this study the F0 was set at 4. Moreover, for commercial canned foods, the sterilization temperature generally depends on acidity and properties of foods. In other words, the temperature is usually set at about 120 °C for low-acid canned foods and 100 °C for acid foods and juice. Thus in this study we explored the effects of two sterilization temperatures (F0 = 4) on the levels of furan and its derivatives in canned foods during canning. Specifically, the sterilization temperature was controlled at 115 °C and 125 °C for low-acid foods, and 105 °C and 115 °C for acid foods and juice.

Ten cans each of pineapple slice (representative samples of acid foods and juice in tinplate cans), oily mackerel (representative samples of low-acid foods in tinplate cans) and chicken puree (representative samples of low-acid foods in glass jar) were prepared separately. Then these samples were placed in a sterilization retort and heated at the above-mentioned two temperatures. The product and retort temperatures were measured using a probe and a thermal distribution curve was plotted to obtain a F0 value at 4.

2.5. Preparation of canned foods

2.5.1. Canned meat paste

A raw pork sample of 2 kg (lean meat to fat meat, 3:1, w/w) was washed, ground and mixed thoroughly. Then, 200 g of soybean oil, 60 g of shallot and 20 g of garlic were mixed for stir-frying for 3 min, followed by adding ground pork for stir-frying for about 10 min. Then an appropriate amount of seasoning salt (20 g), sugar (190 g), monosodium glutamate (10 g), shrimp skin (12 g), pepper powder (2.6 g), spice powder (1.4 g), bean curd (190 g), and soy sauce (240 mL) was added for continuous stir-frying until half cooked. The cooked samples were then poured into tinplate cans (307 × 201 mm each) with a net weight of 200 g each, which were heated at 85 °C for 15 min for exhausting and cans were sealed, placed in a retort for sterilization at 115 °C for 60 min or 125 °C for 25 min. Following sterilization, cans were cooled to 35 °C in sterile water.

2.5.2. Canned tomato paste

A mixture of ketchup, soybean oil, sugar, salt, shallot, and garlic in a ratio of 100:15:7:3:7:1 (w/w) was heated in an iron pan at 100 °C for 10 min, followed by pouring into tinplate cans (307 × 201 mm each) with a net weight of 220 g each. The sterilization was then carried out using the same approach and condition as shown above.

2.5.3. Canned oily mackerel

The head, fin, and internal organs of mackerels were removed, washed with water and soaked in 0.18% saline solution for 10 min, followed by stewing at 100 °C for 30 min. After cooling, mackerels (150 g) were trimmed, poured into tinplate cans (307 × 201 mm each), and 60 g of soybean oil added with a net weight of 210 g each. Then mackerel samples were exhausted, sterilized and cooled following the same procedure shown above.

2.5.4. Canned tomato mackerel

Canned tomato mackerel was prepared and sterilized using the same approach as canned oily mackerel, with the exception that soybean oil was replaced with tomato paste.

2.5.5. Canned pineapple slice with sugar cover liquid

Pineapples were cleaned and both ends cut at about 10−20 mm from top and bottom, followed by coring, peeling, trimmimg to obtain a diameter of 81−83 mm, and slicing (0.5-cm thickness). The slices were then poured into tinplate cans (307 × 201 mm, approximately 170 g each), and 50 g of 40% sugar solution was added. Cans were heated at 85 °C for 15 min for exhausting, followed by sealing, placing in a retort for sterilization at 105 °C for 160 min and 115 °C for 40 min. After sterilization, cans were cooled to 35 °C in sterile water.

2.5.6. Canned pineapple juice

A portion of pineapple slices (1.5 kg) and cores (2 kg) was collected from canned pineapple slice with sugar cover liquid, and an equivalent volume of water was added. Then the mixture was pressed in a miller and passed through a filter to obtain juice, followed by filling into tinplate cans (202 × 504 mm each), with a net weight of 240 g each. Then cans were sterilized using the same approach as shown above (section 2.5.5).

2.5.7. Canned carrot juice

Carrrots were pressed in a miller and passed through a filter to obtain juice, followed by filling into tinplate cans (202 × 504 mm each) with a net weight of 240 g each. Then cans were sterilized using the same approach as shown above (section 2.5.5).

2.5.8. Canned chicken puree

For processing of commercial chicken puree products, chicken tenderloin was stewed at 90 °C for 30 min and water added at a water:chicken ratio of 3:10 (v/w), after which the mixture was homoginized in a homogenizer and filled into glass containers (capacity 75 mL and height 50.7 mm each) with a net weight of 80 g each. Following exhausting of cans at 85 °C for 15 min, cans were sealed, placed in a retort for sterilization at 115 °C for 30 min or 125 °C for 10 min, followed by cooling to 35 °C in sterile water.

2.5.9. Canned apple puree

For processing of commercial apple puree products, apple seeds were removed, homogenized in a homogenizer, filled into glass containers (capacity 75 mL and height 50.7 mm each) with a net weight of 80 g each, and sterilized using the same method as shown above (section 2.5.8).

2.6. Analysis of furan and its derivatives in canned foods

2.6.1. Extraction by SPME arrow

All the cans were precooled at 4 °C for 12 h before extraction of furan and its derivatives from canned foods. Briefly, 1 g of homogenized sample was collected from canned meat and 9 mL of saturated aqueous solution of sodium chloride added, after which the mixture was stirred, and 2 ng/g of internal standard (d4-furan) added. Similarly, 5 g of homogenized sample was collected from canned fruit and juice, and 5 mL of saturated aqueous solution of sodium chloride added, after which the mixture was stirred, 2 ng/g of internal standard (d4-furan) added, and placed in a sample tray at 4 °C for extraction. Before extraction, the test samples were transferred to a 30 °C heater for 15 min to reach an equilibrium, while the CAR/PDMS SPME arrows were desorbed at 285 °C for 5 min to avoid impurity interference before starting adsorption experiment. Test samples of canned juices were extracted by CAR/PDMS SPME for 5 min at 30 °C, while those of canned meat, canned tomato paste and canned fruits were extracted for 15 min at 30 °C. Following extraction, SPME arrows were inserted into the GC inlet and desorbed at 280 °C for 3 min to collect analytes for GC/MS/MS analysis. Following desorption, the SPME arrows were desorbed again at 285 °C for 5 min to remove residual analytes.

2.6.2. Determination of furan and its derivative in canned foods by GC–MS/MS

The GC–MS/MS conditions were as follows: carrier gas was helium with a flow rate at 1 mL/min, split mode with a spilt ratio at 1:10, split flow rate at 10 mL/min and injector temperature at 280 °C, with the following temperature programming condition: 32 °C in the beginning, maintained for 4 min, raised to 200 °C at 20 °C/min and maintained for 3 min. A triple-quadrupole tandem mass spectrometer with electron-impact ionization and MRM mode was used for detection with an ion source temperature of 230 °C and voltage of 70 eV, while nitrogen was collision gas at a rate of 1.5 mL/min and temperature of mass spectrometer at 150 °C.

The method validation was carried out as described in a previous study [6]. The recoveries of 11 furans were ranged from 75.9 to 114.6% in meat matrix, 86.1–113.9% in fruit and vegetable matrix, and 84.9–117.2% in juice matrix. The LOD and LOQ of the analytes were respectively 0.002–0.101 ng/g and 0.007–0.337 ng/g in meat samples, 0.001–0.204 ng/g and 0.003–0.675 ng/g in fruit and vegetable samples, as well as 0.001–0.048 ng/g and 0.003–0.160 ng/g in juice samples. For the intra-day and inter-day variability, the CV of the meat samples was 4–12% and 8–19%, respectively, while for the juice samples, the CV was 2–14% and 4–20%, as well as 3–11% and 5–14% for the fruit and vegetable samples.

The various furan and its 10 derivatives in samples was separated by an HP-5MS column and detected according to elution order and specific *m*/*z* (Table 1). Concentrations of furan and its derivatives were calculated by using the matrix matching calibration curves and the following equation: Concentrations of furan and its derivatives (ng/g) = {[(A/RRF)/Ai] × Ci}/weight of sample (g), where A is the peak area of furan and its derivative; RRF is the relative response factor, equal to (A/Ai)/(C/Ci); Ai is the peak area of internal standard, and Ci is the concentration of internal standard.

2.7. Analysis of precursors of furan and its derivatives

2.7.1. Reducing sugars

A method of Baskan et al. [8] with some modifications was used. All the canned foods were homogenized before analysis. Briefly, one gram of the test sample was weighed and added to 5 mL of deionized water in a tube, after which the mixture was shaken for 10 min and centrifuged at 3000 rpm for 15 min. The supernatant was collected for subsequent experiment. Then, 50 μL of D-glucose standard solution (1.5, 1.25, 1.0, 0.5, 0.25 and 0 mg/mL) was each mixed with 50 μL of the supernatant, followed by adding 150 μL of DNS reagent (3,5-dinitrosalicylic acid mixed with potassium sodium tartrate 4-hydrate) and heating in a boiling water bath for 5 min. After cooling, the mixture was diluted with 250 μL of deionized water and mixed thoroughly. Then the absorbance was measured at 540 nm, while a standard curve was prepared by plotting concentration against absorbance of the D-glucose standard for calculating reducing sugar concentration.

2.7.2. Amino acids

A method of Abernathy et al. [9] with some modifications was used. Briefly, 4 g of Na_2HPO_4, 6 g

Table 1. Operation parameters of furan and its 10 derivative standards and one internal standard (IS) in multiple reaction monitoring mode by GC–MS/MS.

Peak No.	Compound	Retention time (min)	Precursor ion (*m/z*)	Quantitation		Confirmation	
				Product ion (*m/z*)	Collision energy (V)	Product ion (*m/z*)	Collision energy (V)
IS	d_4-furan	2.6	72	42	20	44	15
1	furan	2.6	68	39	20	40	20
2	2-methylfuran	3.5	82	39	20	53	20
3	3-methylfuran	3.7	82	39	20	53	20
4	2-ethylfuran	5.3	81	53	10	50	50
5	2,5-dimethylfuran	5.4	96	53	10	81	25
6	2,3-dimethylfuran	5.6	96	53	10	81	25
7	furfural	7.6	96	39	30	68	20
8	furfuryl alcohol	7.9	98	42	20	39	40
9	2-butylfuran	8.3	124	81	20	53	20
10	2-acetylfuran	8.6	110	95	20	39	20
11	2-pentylfuran	9.4	138	81	20	53	35

of KH_2PO_4, 0.5 g of ninhydrin, and 0.3 g of glucose was dissolved in 100 mL of deionized water to prepare ninhydrin reagent. The supernatant from test samples was prepared using the same approach as shown above. Then, 50 μL of glycine standard solution (1.5, 1.25, 1.0, 0.5, 0.25 and 0 mg/mL) was each mixed with 50 μL of the supernatant and 25 μL of ninhydrin reagent, after which the mixture was heated in a boiling water bath for 5 min. After cooling, the mixture was diluted with 500 μL of deionized water and mixed thoroughly for absorbance measurement at 575 nm. A standard curve was prepared by plotting concentration against absorbance of the glycine standard for calculating amino acid concentration.

2.7.3. Crude fat

A method of Thiex et al. [10] with some modifications was used. All samples were homoginized, lyophilized, and 1 g of sample was weighed and wrapped with a piece of filter paper No. 1, after which this mixture was placed in a cylindrical filter paper for double Soxhlet extraction. After extraction, the aluminum cup was dried at 103 °C for 1 h and then transferred to a dryer for cooling. After weighing, the crude fat content was calculated according to the following formula: Crude fat (%) = (B − C)/A × 100%, where A: sample weight (g); B: aluminum cup weight after extraction (g); and C: aluminum cup weight before extraction (g).

2.8. Statistical analysis

Two batches each of canned foods were prepared under two sterilization conditions, with one batch per condition and 10 cans per batch. Two cans were randomly sampled from each batch, and each can was tested in duplicate for determination of furan and its derivatives as well as the precursors including reducing sugar, amino acid and fat. All the data were subjected to ANOVA and Duncan's multiple rang test for significant difference ($P < 0.05$) in mean comparison by SAS [11].

3. Results and discussion

3.1. Evaluation of sterilization temperature and time length for different canned foods via heat distribution test

Figure 1 shows the shift in retort and sample temperatures and F0 value of each substrate over time under two sterilization temperatures. As shown in Figure 1A and B, the F0 of pineapple slice packed in 307 × 201 mm tinplate cans could reach 4 when heated at 105 °C for 160 min or 115 °C for 40 min. Similarly, the F0 of oily mackerel packed in the same cans could reach F0 = 4 when heated at 115 °C for 60 min or 125 °C for 25 min (Fig. 1C and D), while the F0 of chicken puree packed in glass jars could reach 4 when heated at 115 °C for 30 min or 125 °C for 10 min (Fig. 1E and F). Acid juice or low-acid vegetable juice in tinplate cans (pineapple slice, pineapple juice and carrot juice), low-acid food in tinplate cans (meat paste, oily mackerel, tomato mackerel and tomato paste) and low-acid infant food in glass jars (chicken puree and apple puree) were prepared using the abovementioned sterilization conditions separately.

The pH value of each canned food was measured and shown to be 5.6, 6.2, 5.5, 6.5, 3.6, 3.2, 3.5, 5.4 and 5.1 in meat paste, oily mackerel, tomato mackerel, chicken puree, apple puree, pineapple juice, pineapple slice, carotene juice and tomato paste, respectively.

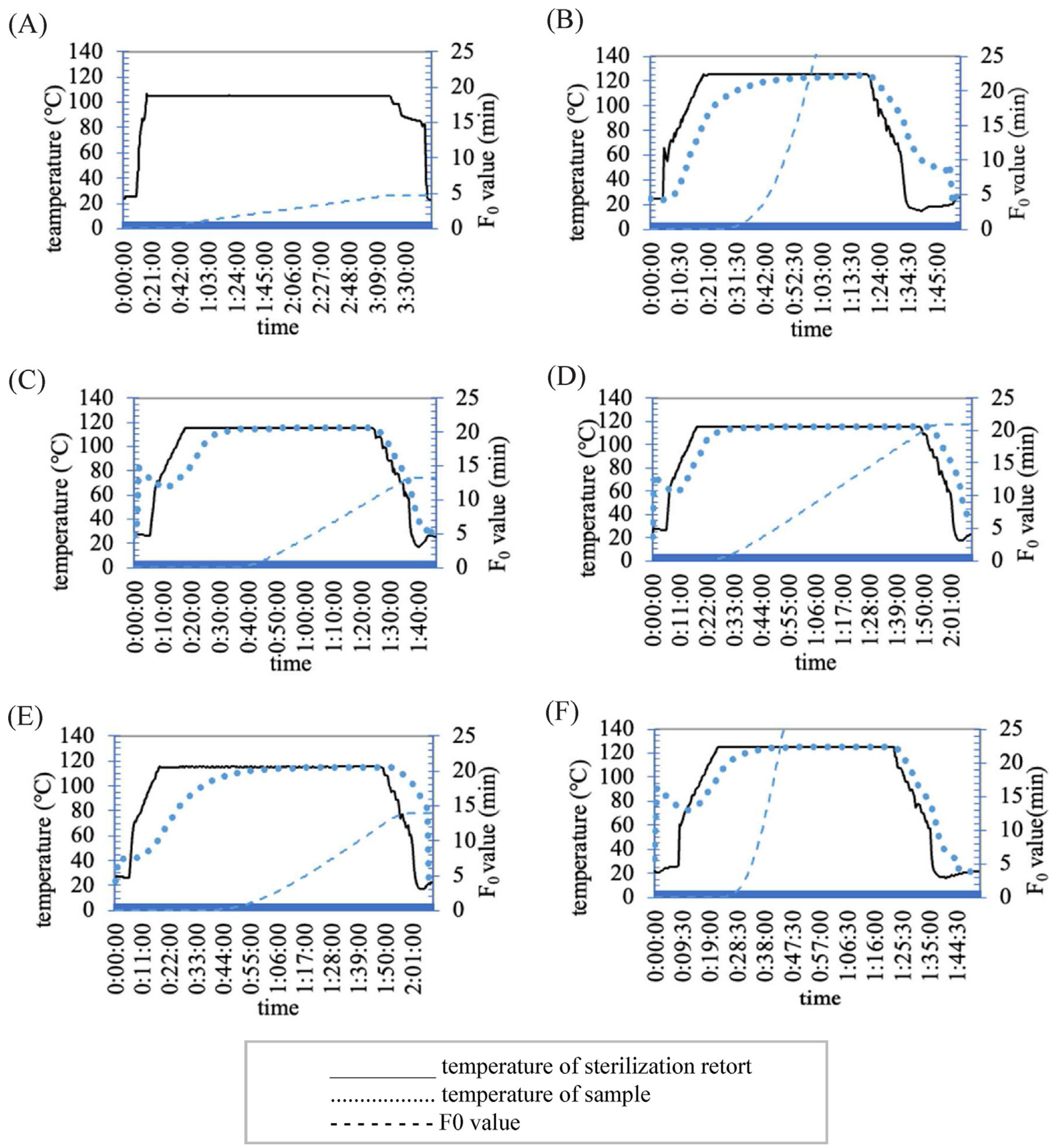

Fig. 1. F0 value test of canned foods with different substrates. (A) Canned pineapple slice at 105 °C. (B) Canned pineapple slice at 115 °C. (C) Canned oily mackerel at 115 °C. (D) Canned oily mackerel at 125 °C. (E) Canned chicken puree at 115 °C. (F) Canned chicken puree at 125 °C.

3.2. Levels of furan, furan derivatives, and furan precursors in canned foods with different sterilization temperature

3.2.1. Meat and fish products

3.2.1.1. Meat paste. Figure 2 shows GC-MS-MS chromotograms of furan and its derivatives in all canned food samples prepared under high-temperature-short-time condition and detected by MRM mode (Table 1). As shown in Table 2, furan and its 10 derivatives were detected in meat paste samples before sterilization, with the total furan content being 177.17 ± 5.03 ng/g, especially for furfuryl alcohol, which was present at the highest amount (96.64 ng/g, approximately 55% of total furan content). Regardless of sterilization conditions, the contents all the furan compounds increased significantly ($p < 0.05$) following heating with the exception of 2,5-dimethyfuran and 2,3-dimethylfuran. The content of furan rose by nearly 17-fold, while the total furan level also increased

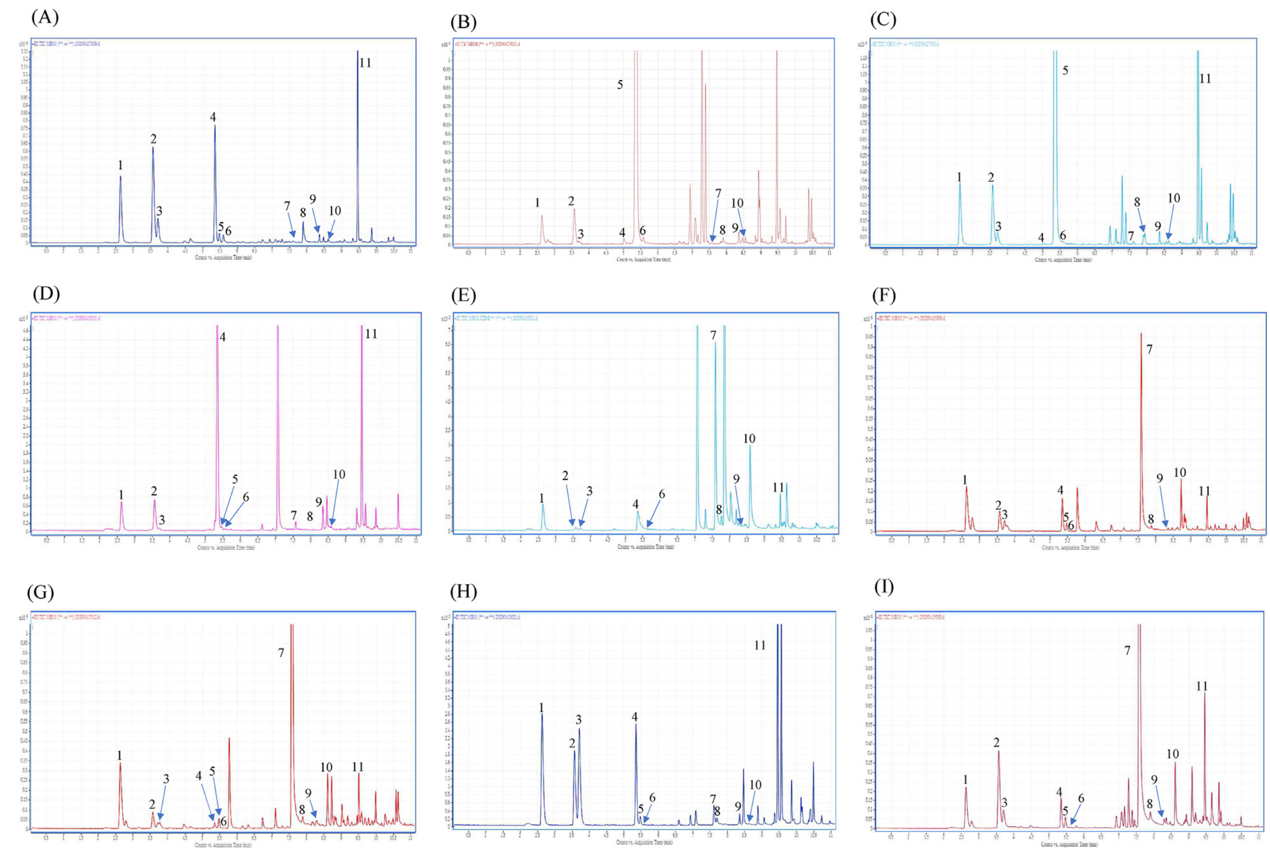

Fig. 2. GC−MS/MS chromatograms of furan and its 10 derivatives in sterilized canned foods detected by MRM mode. (A) Meat paste (125 °C, 25 min), (B) oily mackerel (125 °C, 25 min), (C) tomato mackerel (125 °C, 25 min), (D) chicken puree (125 °C, 10 min), (E) apple puree (125 °C, 10 min), (F) pineapple juice (115 °C, 40 min), (G) pineapple slice (115 °C, 40 min), (H) carrot juice (115 °C, 40 min), (I) tomato paste (125 °C, 25 min). Peaks: (1) furan, (2) 2-methylfuran, (3) 3-methylfuran, (4) 2-ethylfuran, (5) 2,5-dimethylfuran, (6) 2,3-dimethylfuran, (7) furfural, (8) furfuryl alcohol (9) 2-butylfuran, (10) 2-acetylfuran, (11) 2-pentylfuran.

significantly ($p < 0.05$). Only the levels of furan, 3-methylfuran, 2-ethylfuran, and furfuryl alcohol were higher for the treatment of low-temperature-long-time (115 °C, 60 min) compared to that of high-temperature-short-time (125 °C, 25 min), but the other derivatives and total furan did not show significant difference ($p > 0.05$) for both sterilization conditions. For the main precursors in meat paste, reducing sugar, amino acid and fat did not show a significant change ($p > 0.05$) following sterilization.

3.2.1.2. Oily mackerel. Likewise, furan and its 10 derivatives were detected in oily mackerel samples before sterilization, with the total furan content being 242.94 ± 11.72 ng/g, especially for 2,5-dimethylfuran, which was at the highest level (114.52 ng/g, 47% of total furan content) (Table 2). Following sterilization, both 2-methylfuran and furfuryl alcohol levels showed a slight decline, while that of 2-ethylfuran, 2,5-dimethylfuran, 2-butylfuran, and 2-acetylfuran remained unchanged, and the other derivatives showed a significant increase ($p < 0.05$). Similary, the total furan level remained unchanged, however, 2-methylfuran, 3-methylfuran, 2-butylfuran, and 2-pentylfuran showed a slight decrease for the samples sterilized at high temperature for short time (125 °C, 25 min) compared with that sterilized at low temperature for long time (115 °C, 60 min). Both reducing sugar and amino acid contents increased significantly ($p < 0.05$) after sterilization at 115 °C for 60 min or 125 °C for 25 min, while that of crude fat increased significantly ($p < 0.05$) in the samples sterilized at 125 °C for 25 min only.

3.2.1.3. Tomato mackerel. Similar to meat paste and oily mackerel, furan and its 10 derivatives were detected in tomato mackerel samples before sterilization, with the total furan content being 333.62 ± 7.36 ng/g, especially for 2,5-dimethylfuran, which was present at the highest level (102.98 ± 3.77 ng/g, approximately 31% of total furan content) (Table 2). Following sterilization, the furfural level decreased, whereas that of furan and

Table 2. Contents of furans and their precursors in canned meat paste, canned oily mackerel and canned tomato mackerel with different heating temperature and time length.

	Meat paste			Oily mackerel			Tomato mackerel		
	unsterilized	115 °C 60 min	125 °C 25 min	unsterilized	115 °C 60 min	125 °C 25 min	unsterilized	115 °C 60 min	125 °C 25 min
Precursor (mg/g)									
reducing sugar	78.44 ± 6.03^{A}	91.23 ± 0.78^{A}	91.23 ± 8.56^{A}	1.19 ± 0.12^{B}	8.61 ± 1.05^{A}	7.13 ± 0.58^{A}	31.00 ± 2.72^{A}	27.28 ± 0.97^{A}	29.48 ± 1.36^{A}
amino acid	248.05 ± 8.82^{A}	237.11 ± 21.96^{A}	245.34 ± 4.66^{A}	60.75 ± 2.16^{B}	136.05 ± 1.83^{A}	137.69 ± 5.16^{A}	107.06 ± 10.74^{A}	128.22 ± 0.92^{A}	116.13 ± 6.38^{A}
crude fat[c]	184.85 ± 8.98^{A}	168.67 ± 4.48^{A}	177.20 ± 0.14^{A}	596.90 ± 28.00^{B}	552.85 ± 12.09^{B}	673.30 ± 12.87^{A}	156.30 ± 13.19^{A}	116.40 ± 0.71^{A}	141.40 ± 1.27^{A}
Furans (ng/g)									
furan	4.94 ± 0.16^{C}	84.14 ± 0.22^{A}	79.25 ± 1.95^{B}	3.74 ± 0.28^{B}	5.29 ± 0.17^{A}	5.02 ± 0.05^{A}	5.58 ± 0.06^{C}	67.43 ± 0.58^{A}	51.11 ± 1.55^{B}
2-methylfuran	3.65 ± 0.02^{B}	6.95 ± 0.08^{A}	6.81 ± 0.23^{A}	2.12 ± 0.06^{A}	1.98 ± 0.02^{B}	1.49 ± 0.02^{C}	3.75 ± 0.00^{C}	5.27 ± 0.06^{A}	4.83 ± 0.09^{B}
3-methylfuran	4.48 ± 0.09^{C}	21.37 ± 1.19^{A}	18.81 ± 0.11^{B}	4.86 ± 0.13^{B}	5.54 ± 0.05^{A}	4.96 ± 0.23^{B}	4.72 ± 0.34^{C}	14.30 ± 0.05^{A}	10.68 ± 0.64^{B}
2-ethylfuran	5.45 ± 0.11^{C}	16.11 ± 0.00^{A}	12.37 ± 0.77^{B}	53.63 ± 3.57^{A}	48.91 ± 4.85^{A}	47.93 ± 2.77^{A}	67.50 ± 1.62^{C}	168.75 ± 4.89^{A}	126.90 ± 8.34^{B}
2,5-dimethylfuran	4.20 ± 0.03^{A}	5.48 ± 0.24^{A}	4.38 ± 0.13^{A}	114.52 ± 4.39^{A}	127.34 ± 20.76^{A}	105.41 ± 5.91^{A}	102.98 ± 3.77^{C}	341.69 ± 11.37^{A}	241.73 ± 19.94^{B}
2,3-dimethylfuran	4.50 ± 0.05^{A}	4.64 ± 0.14^{A}	4.58 ± 0.00^{A}	3.44 ± 0.42^{B}	8.15 ± 0.24^{A}	7.94 ± 0.32^{A}	4.55 ± 0.01^{C}	21.40 ± 0.71^{A}	14.67 ± 0.66^{B}
furfural	24.70 ± 1.76^{A}	9.69 ± 0.58^{B}	10.41 ± 0.71^{B}	4.48 ± 0.20^{A}	3.78 ± 0.06^{B}	3.77 ± 0.02^{B}	31.77 ± 1.63^{A}	15.34 ± 1.50^{B}	16.60 ± 0.09^{B}
furfuryl alcohol	96.64 ± 2.89^{C}	345.83 ± 5.82^{A}	316.64 ± 7.34^{B}	34.54 ± 3.88^{A}	21.31 ± 0.14^{B}	36.47 ± 1.39^{A}	74.17 ± 0.18^{C}	181.96 ± 4.67^{A}	148.09 ± 3.78^{B}
2-butylfuran	4.59 ± 0.10^{B}	4.89 ± 0.07^{A}	4.82 ± 0.08^{AB}	5.26 ± 0.03^{AB}	5.31 ± 0.07^{A}	5.18 ± 0.00^{B}	5.26 ± 0.17^{B}	6.45 ± 0.16^{A}	5.60 ± 0.27^{B}
2-acetylfuran	7.35 ± 0.22^{B}	12.00 ± 0.03^{A}	12.84 ± 0.69^{A}	4.73 ± 0.06^{A}	4.79 ± 0.06^{A}	4.70 ± 0.03^{A}	6.73 ± 0.08^{B}	11.94 ± 0.57^{A}	12.57 ± 0.33^{A}
2-pentylfuran	16.66 ± 0.48^{B}	39.20 ± 2.81^{A}	37.74 ± 3.09^{A}	11.63 ± 0.17^{C}	18.57 ± 0.61^{A}	13.28 ± 0.02^{B}	26.61 ± 0.14^{C}	94.79 ± 2.65^{A}	65.70 ± 6.97^{B}
Total furans (ng/g)	177.17 ± 5.03^{B}	550.30 ± 9.03^{A}	530.41 ± 9.48^{A}	242.94 ± 11.72^{A}	250.98 ± 16.13^{A}	236.15 ± 7.77^{A}	333.62 ± 7.36^{C}	929.32 ± 21.70^{A}	698.48 ± 42.00^{B}

[a] Results are presented as mean ± SD (n = 8).
[b] Different capital letters in the same row within each food category are significant different at $p < 0.05$.
[c] Crude fat calculated by dry weight.

Table 3. Contents of furans and their precursors in canned chicken puree and canned apple puree with different heating temperature and time length.

	Chicken puree			Apple puree		
	unsterilized	115 °C 30 min	125 °C 10 min	unsterilized	115 °C 30 min	125 °C 10 min
Precursor (mg/g)						
reducing sugar	ND[d]	ND	ND	79.68 ± 0.39[B]	97.83 ± 4.28[AB]	102.37 ± 9.53[A]
amino acid	122.33 ± 2.26[A]	146.72 ± 7.27[A]	136.64 ± 14.31[A]	2.98 ± 0.24[A]	1.75 ± 0.27[B]	1.88 ± 0.24[B]
crude fat[c]	24.00 ± 0.42[A]	24.95 ± 1.06[A]	24.60 ± 0.42[A]	0.05 ± 0.21[A]	0.10 ± 0.71[A]	0.15 ± 0.07[A]
Furans (ng/g)						
furan	0.99 ± 0.14[C]	24.28 ± 0.31[A]	16.39 ± 0.00[B]	0.23 ± 0.00[B]	5.33 ± 0.47[A]	5.21 ± 0.13[A]
2-methylfuran	4.79 ± 0.01[C]	10.68 ± 0.21[A]	7.12 ± 0.40[B]	0.10 ± 0.00[B]	0.16 ± 0.00[A]	0.17 ± 0.00[A]
3-methylfuran	3.54 ± 0.03[C]	9.16 ± 0.21[A]	5.69 ± 0.40[B]	0.08 ± 0.01[B]	0.10 ± 0.00[A]	0.11 ± 0.01[A]
2-ethylfuran	4.64 ± 0.11[C]	9.63 ± 0.11[A]	7.26 ± 0.03[B]	0.38 ± 0.03[A]	0.39 ± 0.00[A]	0.40 ± 0.01[A]
2,5-dimethylfuran	5.18 ± 0.26[C]	18.02 ± 0.63[A]	12.07 ± 0.06[B]	ND	ND	ND
2,3-dimethylfuran	4.47 ± 0.00[A]	4.51 ± 0.01[A]	4.49 ± 0.00[A]	0.17 ± 0.00[A]	0.13 ± 0.00[B]	0.13 ± 0.00[B]
furfural	3.88 ± 0.19[A]	4.45 ± 0.16[A]	4.28 ± 0.41[A]	ND[d]	113.23 ± 3.96[A]	65.65 ± 0.51[B]
furfuryl alcohol	8.47 ± 0.39[B]	9.03 ± 0.79[B]	10.84 ± 0.29[A]	6917.28 ± 59.27[A]	4577.63 ± 247.85[C]	5601.42 ± 312.07[B]
2-butylfuran	5.03 ± 0.02[B]	5.10 ± 0.01[A]	5.07 ± 0.01[AB]	0.14 ± 0.00[A]	0.14 ± 0.00[A]	0.14 ± 0.00[A]
2-acetylfuran	5.39 ± 0.01[A]	5.43 ± 0.01[A]	5.45 ± 0.05[A]	0.18 ± 0.02[C]	0.67 ± 0.01[A]	0.60 ± 0.00[B]
2-pentylfuran	5.67 ± 0.23[B]	8.46 ± 0.71[A]	8.27 ± 0.16[A]	0.25 ± 0.00[B]	0.36 ± 0.01[A]	0.28 ± 0.02[B]
Total furans (ng/g)	52.05 ± 0.07[C]	108.76 ± 1.35[A]	86.93 ± 0.30[B]	6918.94 ± 59.25[A]	4698.14 ± 244.35[C]	5674.10 ± 311.67[B]

[a]Results are presented as mean ± SD (n = 8).
[b]Different capital letters in the same row within each food category are significant different at $p < 0.05$.
[c] Crude fat calculated by dry weight.
[d] ND: not detected, lower than detection limit.

the other derivatives rose, particularly for furan, showing an increase by nearly 12-fold. Comparatively, with the exception of furfural and 2-acetylfuran, the contents of furan and the other derivatives showed an increased trend following sterilization at 115 °C for 60 min. In addition, the contents of reducing sugar, amino acid and crude fat, the main furan precursors in tomato mackerel, did not show significant change ($p > 0.05$) following sterilization.

3.2.2. Baby foods

3.2.2.1. Chicken puree. Likewise, furan and its 10 derivatives were detected in chicken puree samples before sterilization, with the total furan content being 52.05 ± 0.07 ng/g. By comparison, the furan level was lower than the other derivatives, while furfuryl alcohol showed the highest level (8.47 ng/g, approximately 16% of total furan content) (Table 3). After sterilization, with the exception of 2,3-dimethylfuran, furfural and 2-acetylfuran, the other derivative contents increased, especially for furan, showing a rise by 24-fold. Furthermore, the furfuryl alcohol content showed a slight increase following heating at high temperature for short time (125 °C, 10 min), while most furan derivatives rose at low temperature for long time (115 °C, 30 min), compared to the unsterilized samples. In addition, the contents of amino acid and crude fat, the main furan precursors in chicken puree, did not show significant change ($p > 0.05$) after sterilization, while reducing sugar remained undetected before and after sterilization.

3.2.2.2. Apple puree. For apple puree, with the exception of 2,5-dimethylfuran and furfural, furan and its 8 deviratioves were detected before sterilization, with the total furan content being 6918.94 ± 59.25 ng/g. Interestingly, furfuryl alcohol was present at the highest level (6917.28 ng/g, 99%) (Table 3). After sterilization, a high amount of furfural (113.23 ng/g) was formed, but that of furfuryl alcohol was reduced substantially, and the other derivatives slightly increased. Furthermore, no significant change ($p > 0.05$) in 2-ethylfuran and 2-butylfuran contents was observed, while that of 2,3-dimethylfuran showed a slight drop. As furfural underwent a higher loss than furfuryl alcohol during heating at 125 °C for 10 min, the total furan content was higher than that heated at 115 °C for 30 min. In addition, reducing sugar, amino acid, and crude fat, the main furan precursors in apple puree, were present at a low level before sterilization. But after heating, the animo acid content declined significantly ($p < 0.05$), while that of reducing sugar and crude fat did not change significantly ($p > 0.05$).

3.2.3. Fruit and vegetable products

3.2.3.1. Pineapple slice. With the exception of 3-methylfuran and furfural alcohol, present in trace

Table 4. *Contents of furans and their precursors in canned pineapple juice, canned pineapple slice, canned carrot juice and canned tomato paste with different heating temperature and time length.*

	Pineapple juice			Pineapple slice			Carrot juice			Tomato paste		
	unsterilized	105 °C 160 min	115 °C 40 min	unsterilized	105 °C 160 min	115 °C 40 min	unsterilized	105 °C 160 min	115 °C 40 min	unsterilized	115 °C 60 min	125 °C 25 min
Precursor (mg/g)												
reducing sugar	8.29 ± 0.85^{A}	8.89 ± 0.85^{A}	8.14 ± 0.21^{A}	67.68 ± 0.72^{C}	177.02 ± 1.48^{B}	191.21 ± 2.07^{A}	30.15 ± 1.27^{C}	51.86 ± 2.75^{B}	60.24 ± 2.75^{A}	88.37 ± 0.25^{B}	138.22 ± 11.64^{A}	121.00 ± 9.91^{A}
amino acid	16.88 ± 0.99	trace[e]	trace	17.90 ± 0.72^{A}	12.53 ± 0.21^{B}	12.15 ± 0.91^{B}	21.79 ± 1.40^{A}	19.51 ± 0.43^{AB}	17.43 ± 0.48^{B}	43.13 ± 23.52^{A}	14.86 ± 2.39^{B}	11.52 ± 0.35^{B}
crude fat[c]	0.85 ± 0.35^{A}	0.40 ± 0.14^{A}	0.35 ± 0.07^{A}	0.80 ± 0.12^{A}	0.44 ± 0.14^{A}	0.50 ± 0.14^{A}	13.20 ± 4.53^{A}	15.50 ± 0.42^{A}	9.10 ± 2.97^{A}	81.85 ± 1.48^{A}	56.60 ± 1.41^{B}	64.85 ± 6.01^{B}
Furans (ng/g)												
furan	0.52 ± 0.12^{B}	31.96 ± 0.96^{A}	29.94 ± 0.75^{A}	0.40 ± 0.01^{C}	24.66 ± 0.04^{B}	51.40 ± 4.90^{A}	0.24 ± 0.03^{C}	37.00 ± 0.03^{A}	26.52 ± 11.61^{B}	5.66 ± 0.21^{C}	116.31 ± 2.47^{A}	78.14 ± 1.17^{B}
2-methylfuran	0.08 ± 0.03^{C}	0.91 ± 0.03^{A}	0.80 ± 0.00^{B}	0.10 ± 0.03^{C}	0.52 ± 0.03^{B}	0.93 ± 0.06^{A}	0.10 ± 0.02^{C}	1.19 ± 0.01^{A}	0.94 ± 0.56^{B}	1.16 ± 0.01^{C}	18.81 ± 0.70^{A}	14.13 ± 0.26^{B}
3-methylfuran	ND[d]	0.15 ± 0.00^{A}	0.15 ± 0.00^{A}	trace	0.08 ± 0.01^{A}	0.07 ± 0.01^{A}	0.21 ± 0.07^{B}	1.23 ± 0.05^{A}	1.12 ± 0.60^{A}	0.57 ± 0.01^{B}	1.33 ± 0.06^{A}	1.32 ± 0.03^{A}
2-ethylfuran	0.11 ± 0.02^{B}	0.46 ± 0.03^{A}	0.47 ± 0.04^{A}	0.04 ± 0.02^{B}	0.06 ± 0.01^{B}	0.10 ± 0.00^{A}	0.08 ± 0.01^{B}	0.64 ± 0.00^{A}	0.53 ± 0.29^{A}	0.29 ± 0.00^{C}	1.68 ± 0.05^{A}	1.41 ± 0.03^{B}
2,5-dimethylfuran	0.13 ± 0.02^{A}	0.13 ± 0.00^{A}	0.16 ± 0.00^{A}	0.15 ± 0.02^{B}	0.18 ± 0.01^{A}	0.10 ± 0.01^{B}	0.07 ± 0.01^{B}	0.10 ± 0.00^{A}	0.10 ± 0.01^{A}	0.23 ± 0.00^{C}	0.83 ± 0.07^{A}	0.70 ± 0.02^{B}
2,3-dimethylfuran	0.05 ± 0.00^{A}	0.05 ± 0.00^{A}	0.05 ± 0.00^{A}	0.01 ± 0.00^{A}	0.02 ± 0.01^{A}	0.01 ± 0.01^{A}	0.05 ± 0.00^{B}	0.05 ± 0.00^{AB}	0.06 ± 0.01^{A}	0.13 ± 0.00^{B}	0.15 ± 0.00^{AB}	0.16 ± 0.02^{A}
furfural	37.73 ± 0.10^{C}	470.45 ± 24.19^{A}	403.42 ± 22.15^{B}	7.29 ± 1.54^{C}	1025.99 ± 13.99^{B}	1271.63 ± 97.99^{A}	32.81 ± 0.22^{B}	47.80 ± 0.08^{A}	46.95 ± 7.02^{A}	546.82 ± 28.65^{C}	6385.07 ± 119.05^{A}	4269.38 ± 407.52^{B}
furfuryl alcohol	70.55 ± 7.23^{A}	66.93 ± 1.53^{A}	70.42 ± 3.19^{A}	trace	17.54 ± 1.78^{B}	42.18 ± 4.11^{A}	64.66 ± 0.36^{A}	65.03 ± 0.91^{A}	64.89 ± 2.54^{A}	40.18 ± 3.77^{C}	450.79 ± 22.90^{A}	137.06 ± 18.51^{B}
2-butylfuran	7.13 ± 0.00^{A}	7.13 ± 0.00^{A}	7.12 ± 0.00^{A}	0.03 ± 0.00^{A}	0.03 ± 0.00^{A}	0.03 ± 0.00^{A}	7.12 ± 0.00^{A}	7.13 ± 0.00^{A}	7.13 ± 0.01^{A}	0.21 ± 0.01^{C}	0.32 ± 0.01^{A}	0.26 ± 0.00^{B}
2-acetylfuran	0.28 ± 0.05^{B}	9.41 ± 0.41^{A}	9.09 ± 2.23^{A}	0.08 ± 0.02^{C}	15.17 ± 0.40^{B}	27.83 ± 7.09^{A}	ND	0.48 ± 0.00^{A}	0.41 ± 0.31^{A}	21.35 ± 0.83^{C}	103.97 ± 7.92^{A}	69.78 ± 7.88^{B}
2-pentylfuran	7.72 ± 0.00^{A}	7.78 ± 0.01^{A}	7.79 ± 0.03^{A}	0.05 ± 0.00^{C}	0.09 ± 0.01^{B}	0.12 ± 0.00^{A}	7.77 ± 0.02^{B}	8.20 ± 0.01^{A}	8.12 ± 0.20^{A}	0.83 ± 0.05^{C}	4.20 ± 0.05^{A}	2.92 ± 0.23^{B}
Total furans (ng/g)	124.15 ± 7.10^{B}	595.34 ± 27.17^{A}	532.45 ± 26.73^{A}	9.87 ± 0.69^{C}	1084.33 ± 16.15^{B}	1384.95 ± 90.03^{A}	113.10 ± 0.73^{C}	168.86 ± 3.50^{A}	156.76 ± 4.98^{B}	617.43 ± 33.38^{C}	7083.45 ± 151.74^{A}	4575.26 ± 435.56^{B}

[a]Results are presented as mean ± SD (n = 8).
[b]Different capital letters in the same row within each food category are significant different at $p < 0.05$.
[c] Crude fat calculated by dry weight.
[d] Not detected, lower than detection limit.
[e] Lower than quantitation limit.

amount, furan and its 8 derivatives were detected in pineapple slice before sterilization, with the total furan content being 9.87 ± 0.69 ng/g, especially for furfural, which was present at the highest level (7.29 ± 1.54 ng/g, approximately 74% of total furan content) (Table 4). Compared to meat and fish cans, furan derivatives were present at a lower level in unsterilized pineapple slice. However, after sterilization, with the exception of 2,3-dimethylfuran and 2-butylfuran, all the other derivatives rose significantly ($p < 0.05$) with the highest content being observed mainly for the treatment of high temperature for short time (115 °C, 40 min). Compared to that before sterilization, the contents of furfural and furan increased by approximately 174-fold and 129-fold, respectively, after sterilization at 115 °C for 40 min. It is worth pointing out that furfuryl alcohol showed a pronounced increase from trace to 42.18 ng/g following sterilization at 115 °C for 40 min. Collectively, the total furan content in pineapple slice was lower when heated at 105 °C for 160 min that at 115 °C for 40 min. In addition, the content of reducing sugar, the main furan precursor in pineapple slice, increased significantly ($p < 0.05$) by over 2-fold, while that of amino acid decreased significantly ($p < 0.05$) and crude fat did not show significant change ($p > 0.05$) following sterilization.

3.2.3.2. Pineapple juice. For pineapple juice, with the exception of 3-methylfuran, furan and its 9 derivatives were detected before sterilization, with the total furan content being 124.15 ± 7.10 ng/g, especially for furfuryl alcohol, which was present at the highest level (70.55 ± 7.23 ng/g, approximately 57% of total furan content) (Table 4). After sterilization, with the exception of 2,5-dimethylfuran, 2,3-dimethylfuran, furfuryl alcohol, 2-butylfuran, and 2-pentylfuran, the contents of all the other derivatives increased significantly ($p < 0.05$), especially for furan and furfural, both of which rose by approximately 60- and 12-fold, respectively. Furthermore, the levels of 2-methylfuran, 3-methylfuran, 2-ethylfuran and 2-acetylfuran were slightly higher when heated at 105 °C for 160 min, while most furan derivatives did not show significant change when heated at 115 °C for 40 min. Also, the total furan content did not show significant change ($p > 0.05$) for both sterilization conditions. In addition, all the furan precursors were present in pineapple juice before sterilization, however, following sterilization, amino acid, the main furan precursor in pineapple juice, declined to trace amount, while both reducing sugar and crude fat did not show significant change ($p >0.05$).

3.2.3.3. Carrot juice. With the exception of 2-acetylfuran, furan and its 9 derivatives were detected in carrot juice before sterilization, with the total furan content being 113.10 ± 0.73 ng/g, especially for furfuryl alcohol, showing the highest level (64.66 ± 0.36 ng/g, approximately 57% of total furan content) (Table 4). After sterilization, with the exception of 2,3-dimethylfuran, furfuryl alcohol, and 2-butylfuran, the contents of all the other derivatives increased, in which furan increased most (154-fold). Also, furan was generated at a higher level when heated at low temperature for long time (105 °C, 160 min) than that at high temperature for short time (115 °C, 40 min). However, the contents of most furan derivatives did not show significant change ($p > 0.05$) for both sterilization conditions, and thus the total furan contents in carrot juice heated at 105 °C for 160 min was slightly higher than that at 115 °C for 40 min. In addition, following sterilization, the content of reducing sugar, the main furan precursor in carrot juice, rose significantly ($p < 0.05$), while that of amino acid declined and crude fat did not show significant change ($p > 0.05$).

3.2.3.4. Tomato paste. For tomato paste, furan and its 10 derivatives were detected before sterilization, with the total furan content being 617.43 ± 33.38 ng/g, especially for furfural, showing the highest level (546.82 ± 28.65 ng/g, approximately 89% of total furan content) (Table 4). Following sterilization, with the exception of 2,3-dimethylfuran, all the furan and its derivative contents increased, prominently for furan, 2-methylfuran and furfural, which were raised by 20-, 16-, and 12-fold, respectively. Comparatively, the contents of most derivatives and total furan in tomato paste were higher when heated at low temperature for long time (115 °C, 60 min) than at high temperature for short time (125 °C, 25 min). In addition, tomato paste was found to possess the highest total content of furan and its derivatives among all the canned food samples.

Following sterilization, the contents of reducing sugar increased significantly ($p < 0.05$), while that of amino acid and crude fat decreased significantly ($p < 0.05$).

3.3. Effect of sterilization conditions on the formation of furan and its derivatives in canned foods

Collectively, the 2-butylfuran content in all the canned samples remained unaffected during sterilization, whereas the furan content in all the canned samples was significantly increased ($p < 0.05$). For the total content of furan and its derivatives, a total of 4 canned products including tomato mackerel, chicken puree, carrot juice and tomato sauce were found to be higher following low-temperature-long-time sterilization, while 3 canned products (meat paste, oily mackerel, pineapple juice) showed insignificant change, and 2 canned products (apple puree and pineapple slice) were higher following high-temperature-short-time sterilization. This outcome indicated that furan formation can be affected by many factors. In addition to heating temperature and time length, some other factors such as the original furan content, pre-preparation method, precursor content and packaging materials can also affect the variety and amount of furan derivatives formed. Thus, further studies are needed to elucidate the formation mechanism of furan and its derivations as affected by various factors. Nevertheless, in this study we demonstrated that a large amount of furan and its derivatives was generated in canned foods during sterilization with the exception of apple puree, showing a decreased furan content.

In a previous study Palmers et al. [12] reported that following sterilization under high pressure, the contents of furan, 2-methylfuran, and 3-methylfuran in vegetable puree decreased compared to sterilization under standard pressure, probably caused by a higher heating and cooling capacity of the former, and thus resulted in a shorter heating time. In some other studies, a high-pressure and high-temperature-short-time sterilization treatment was also shown to decrease formation of 2-methylfuran in spinach and 3-methylfuran in carrots and bell peppers, probably due to retardation of Maillard reaction under high-pressure treatment. Nevertheless, the high-pressure treatment may also speed up oxidative reaction and thermal degradation of both ascorbic acid and unsaturated fatty acid, and thus the test samples did not consistently show a less amount of furan and its derivatives formed after heating for a short period of time [13,14].

3.4. Effect of precursors on the formation of furan and its derivatives

The precursor content in test samples before and after heating was measured in this experiment. The reducing sugar content in samples of oily mackerel, carrot juice, tomato paste, apple puree and pineapple slice increased following heating, which should be due to conversion of disaccharides such as sucrose to monosaccharides such as glucose and fructose during heating. However the amount of individual furan derivative formed during heating did not correlate well with that of reducing sugar and amino acid content. In this study, individual derivatives were classified into a sub-set and the total content of a sub-set derivatives was calculated and compared to that of the precursors. Apparently, samples containing a higher level of reducing sugar generated more oxygenated furans, while that containing a higher level of amino acids produced more alkylfurans (Fig. 3). Of the various test samples, both vegetables and fruits are rich in reducing sugars and vitamin C, the main precursors in furfural formation. Thus, compared to meat products, vegetables and fruits could produce more furfural from vitamin C through catabolization during heating [15]. Additionally, it was reported that in an amino acid system, vitamin C was more readily degraded to form pyrazines rather than furfuryl alcohol under roasting condition, which should explain a higher level of furfural and furfuryl alcohol generated in canned fruits and vegetables [16]. Although vitamin C is not analyzed in this study, its content is obviously higher in canned fruits and vegetables. Therefore, the formation of oxygenated furans in canned fruits and vegetables during heating correlated well with the contents of reducing sugar and vitamin C.

Furthermore, the furan formation may be correlated with variety of reducing sugar. For example, Palmers et al. [12] reported that pumpkin puree contained more sucrose than carrot puree and thus resulted in a higher level of furan generated during heating, which can be attributed to decomposition of sucrose into glucose and fructose. In the same report dealing with a model system containing free sugar and vitamin C during heating, the heat treatment condition significantly correlated well with the furan concentration formed in vegetable puree [12]. Comparatively, vitamin C showed the highest correlation, followed by fructose, sucrose, and glucose. The difference in furan formation between simple model system and food product system may be explained by the presence of some other ingredients present in the latter, resulting in a competitive reaction in a complex substrate between reducing sugar and amino acids. Therefore, the precursors do not lead to furan formation following degradation.

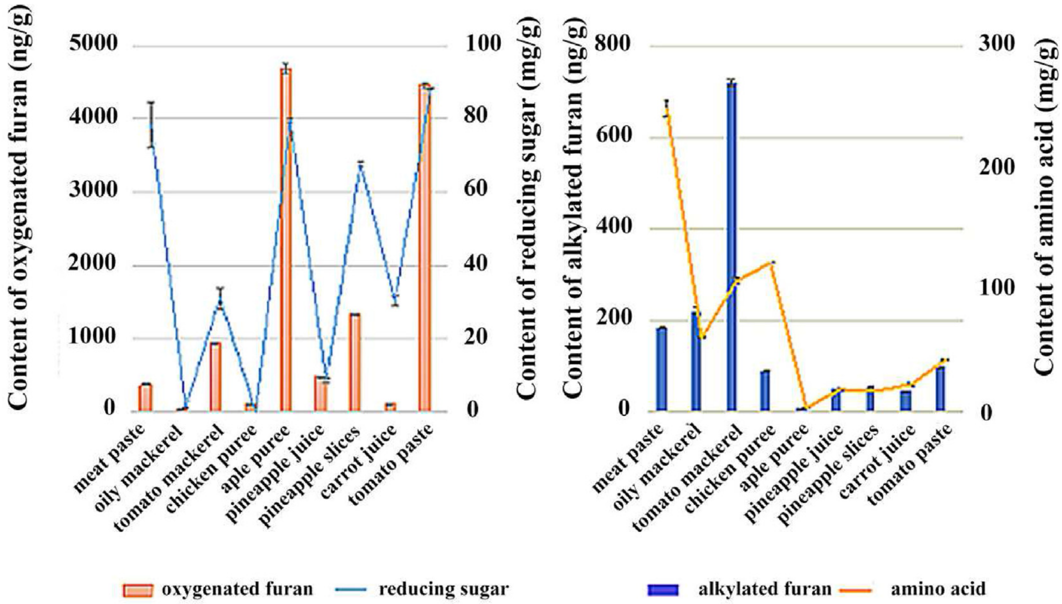

Fig. 3. Contents of furan precursors including reducing sugar and amino acid as well as furans in canned foods sterilized at 115 °C for varied time length. Results are presented as mean ± SD (n = 8).

In addition to precursors, the environmental conditions in a model system can also affect furan formation. For instance, in a low acidic system, the furan content generated from carbohydrate cleavage was shown to rise, and the furan formation followed a concentration-dependent increase of oxygen [17]. Therefore, the effect of reaction condition as well as the interaction of various factors on furan formation should be taken into account in addition to change in precursors.

In this study, alkylated furans, including 2-methylfuran, 3-methylfuran, 2,3-dimethylfuran, 2,5-dimethylfuran, 2-ethylfuran, 2-butylfuran, and 2-pentylfuran, were found to be higher in canned meat paste, oily mackerel, tomato mackerel, and chicken puree, than in canned fruit and vegetable, which should be due to presence of a higher level of amino acid of the former. Similar results were observed in some other studies where the contents of furan, 2-methylfuran, and 3-methylfuran were found to be higher in commercial squid, meat paste, and meatball products than that in fruits and vegetables [18]. By comparison, the model system composed of alanine, threonine and glucose was shown to produce a higher level of 2-methylfuran than the simple carbohydrate model system, as some more cleavage and recombination reactions were involved in the formation of alkylated furan compounds when compared to furan [5].

It is worth pointing out that in this study an unique sample of canned fruits and vegetables is tomato paste, as 2-methylfuran was detected at an equivalent level as in canned meat (18.81 ng/g). This result is consistent with the findings of some other studies, reporting that in some commercial canned ketchups, 2-methylfuran and 3-methylfuran were detected at an equivalent level as in canned meat, presumably because tomatoes, the raw material of making ketchup, contained a high level of isoprene compounds [18]. Likewise, a model system containing β-carotene and the other isoprenoid compounds of similar structure was shown to generate 2-methylfuran and 3-methylfuran during heating [19]. Also, the crude fat content in tomato paste showed a significant decrease ($P < 0.05$) during heating, while the other samples did not show significant change ($P > 0.05$). Although fat oxidation was presumed to be one of the major pathways of furan formation as indicated in the literature, the degree of fat oxidation remains unknown in canned foods as only crude fat was measured in our study.

3.5. Safety evaluation of canned foods

For the currently available regulations worldwide, no safety limits have been set regarding the levels of furan and its derivatives in foods. However, based on the minimum dose (1.34 mg/kg body wight/day) leading to a rise in the incidence of liver cancer by 10% in mouse fed with furan, the dose required for the lowest incidence of liver cancer for adults based on an average weight of 60 kg was calculated to be 80.4 mg. In this study, the highest furan content of 116 ng/g was found in tomato paste samples after sterilization at 115 °C for 60 min, that is, an intake of over 690,000 g tomato paste per day is required to increase the incidence of liver cancer by 10% in adults.

Additionally, according to JACFA, the upper limit of the total ADI of furfuryl alcohol and furfural as food additives is 0.5 mg/kg bw, that is, the ADI is 30 mg for an adult with an average weight of 60 kg. In this study, the content of furfuryl alcohol and furfural was the highest (6835 ng/g) in tomato paste samples after sterilization at 115 °C for 60 min, revealing an intake of >4300 g tomato paste per day is required to reach the upper limit of the ADI in adults. But for a 4-month-old infant with complementary foods being allowed for consumption, the ADI is 3.92 mg based on the weight of 7.85 kg. In this study, among baby foods, apple puree samples after sterilization at 125 °C for 10 min were shown to contain the highest level of furfuryl alcohol and furfural (5666 ng/g). Therefore, the intake of 690 g of apple puree (approximately 8 cans of apple puree, with 80 g each) in infants can reach the upper limit of the ADI. Collectively, the intake of foods containing high level of furan and its derivatives should be cautiously controlled especially for infants since they have relatively simpler diets and processess immature immune system.

Although the levels of furan and its derivatives in canned foods reported in the present study were far lower than that may cause human disease, furan and some of its derivatives were detected in all the test samples. Therefore, the total intake of furan and its derivatives from canned foods must be given with caution. Additionally, JACFA states that when furfuryl alcohol and furfural in samples are generated during food processing, their levels must be controlled as low as possible. Thus, the processing condition of canned foods should be carefully controlled to minimized formation of furan and its derivatives.

The margin of exposure (MOE) approach was widely used for risk assessment by EFSA, which is the ratio of a benchmark dose lower limit ($BMDL_{10}$) relative to dietary exposure [20]. The daily canned foods consumption by adults (age 19–64) in Taiwan was reported to be respectively 32.7, 39.6, 39.6, 78.0, 128.5, 188.8, 188.8, 44.8 and 53.5 g/day for meat paste, oily mackerel, tomato mackerel, chicken puree, apple puree, pineapple juice, pineapple slice, carrot juice and tomato paste, while for infants (age 0–3), the daily canned foods consumption was 32.7, 17.8, 17.8, 37.2, 77.2, 70.3, 70.3, 18.2, and 29.9 g/day [21]. Therefore, the exposure of furan to adults through canned foods with two different sterilization conditions, based on a reference 60 kg body weight for adults, was estimated to be 43.2–45.9, 3.3–3.5, 33.7–44.5, 21.3–31.6, 11.2–11.4, 94.2–100.6, 77.6–161.7, 19.8–27.6 and 69.7–103.7 ng/kg BW/day for meat paste, oily mackerel, tomato mackerel, chicken puree, apple puree, pineapple juice, pineapple slice, carrot juice and tomato paste, respectively. Likewise, the exposure of furan to infants

Table 5. Margins of exposure values of furan in canned foods for the incidence of non-neoplastic and neoplastic effects in adults and infants age groups.

Canned foods	Sterilization condition	MOE[a] (non-neoplastic effect)		MOE (neoplastic effect)	
		Adults	Infants	Adults	Infants
Meat paste	115 °C/60 min	1396	349	28,568	7142
	125 °C/25 min	1482	370	30,330	7583
Oily mackerel	115 °C/60 min	18,331	10,195	375,208	208,683
	125 °C/25 min	19,317	10,744	395,388	219,907
Tomato mackerel	115 °C/60 min	1438	800	29,436	16,372
	125 °C/25 min	1897	1055	38,835	21,599
Chicken puree	115 °C/30 min	2028	1063	41,503	21,756
	125 °C/10 min	3004	1575	61,482	32,229
Apple puree	115 °C/30 min	5607	2333	114,760	47,755
	125 °C/10 min	5736	2387	117,404	48,855
Pineapple juice	105 °C/160 min	636	427	13,026	8746
	115 °C/40 min	679	456	13,095	9336
Pineapple slice	105 °C/160 min	825	554	16,882	11,335
	115 °C/40 min	396	266	8099	5438
Carrot juice	105 °C/160 min	2317	1426	47,418	29,180
	115 °C/40 min	3232	1989	66,156	40,712
Tomato paste	115 °C/60 min	617	276	12,631	5650
	125 °C/25 min	919	411	18,802	8410

[a] MOE: margin of exposure, the MOE was calculated by dividing the $BMDL_{10}$ (benchmark dose lower confidence limit) value by the dietary exposures, where $BMDL_{10}$ adopted from EFSA (2017) and used for non-neoplastic effect and neoplastic effect are 0.064 and 1.31 mg/kg body weight/day, respectively.

(based on a reference 15 kg body weight) through canned foods was estimated to be 172.8−183.4, 6.0−6.3, 60.7−80.0, 40.6−60.2, 26.8−27.4, 140.3−149.8, 115.6−240.9, 32.2−44.9 and 155.8−231.8 ng/kg BW/day for meat paste, oily mackerel, tomato mackerel, chicken puree, apple puree, pineapple juice, pineapple slice, carrot juice and tomato paste, respectively. The $BMDL_{10}$ of furan was selected as 0.064 mg/kg bw/day and 1.31 mg/kg bw/day for non-neoplastic effect and neoplastic effect, respectively [2], both of which were used as a basis to determine the MOE (non-neoplastic effect) and MOE (neoplastic effect) in various samples as shown in Table 5. An MOE of 100 or higher (for non-neoplastic effect) and 10,000 or higher (for neoplastic effect) would be sufficient to be designated as a low health concern. The calculated MOEs for the incidence of non-neoplastic effect were >100 in Table 5, which can be deemed to be a low health concern. However, the calculated MOEs <10,000 were shown in a number of dietary surveys, particularly meat paste, pineapple juice, pineapple slice and tomato paste for infants and pineapple slice for adults, Thus, it may be concluded that the MOEs shown in our study indicate a health concern with a neoplastic effect. This outcome is in agreement with a report from EFSA [2], suggesting a health concern for carcinogenic furan due to MOEs <10,000 in a number of dietary surveys, particularly for the high percentile exposure estimates for the younger age groups.

4. Conclusions

During canning, samples with fruits and vegetables as the raw materials including apple puree, carrot juice, pineapple juice, pineapple slice and tomato paste resulted in a higher level of furfural and furfuryl alcohol, while samples rich in amino acids including meat paste, oily mackerel, tomato mackerel, and chicken puree resulted in a higher level of alkylated furan. In most test samples, the contents of total furan and its derivatives were lower under high-temperature-short-time treatment, suggesting that a short heating-time length may reduce furan formation. Based on the precursor contents, the correlation between the precursor content and furan formation cannot be drawn to a conclusion. However, the precursor content can be correlated well to the variety of furan and its derivatives formed. The MOE data suggested a health concern with a neoplastic effect of furan intake from selected canned foods by infants. Moreover, furan and some of its derivatives were detected in all the test samples. Thus, the food processing condition should be carefully controlled to reduce the formation of furan compounds.

Conflict of interest

The authors declare that they have no conflicts of interest.

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