# **Detection of Hydrocarbons in Irradiated Foods**

# Makoto Miyahara,<sup>\*, a</sup> Akiko Saito,<sup>b</sup> Tomomi Kamimura,<sup>b</sup> Taeko Nagasawa,<sup>b</sup> Yasuo Kobayashi,<sup>c</sup> Hitoshi Ito,<sup>c</sup> and Tamio Maitani<sup>a</sup>

<sup>a</sup>National Institute of Health Sciences, 1–18–1 Kamiyoga, Setagaya-ku, Tokyo 158–8501, Japan, <sup>b</sup>School of Allid Health Sciences, Kitasato University, 1–15–1 Kitasato, Sagamihara, Kanagawa 228–8555, Japan, and <sup>c</sup>The Japan Atomic Energy Research Institute Takasaki Radiation Establishment, 1233 Watanukimati, Takasaki City, Gunma 370–1207, Japan

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The hydrocarbon method for the detection of irradiated foods is now recognized as the international technique. This method is based on radiolysis of fatty acids in food to give hydrocarbons. In order to expand this technique's application, ten foods (butter, cheese, chicken, pork, beef, tuna, dry shrimp, avocado, papaya, and mango) were irradiated in the range from 0.5 to 10 kGy and the hydrocarbons in them were detected. Recoveries of the hydrocarbons from most foods were acceptable (38–128%). Some hydrocarbons were found in non-irradiated foods, particularly, in butter, cheese, tuna, and shrimp. Seven irradiated foods, butter, cheese, chicken, beef, pork, tuna, dry shrimp, and avocado were detectable at their practical doses by measuring the appropriate marker hydrocarbons. In most case, marker hydrocarbon will be 1,7-hexadecadiene. However, the marker hydrocarbons produced only in irradiated foods varied from food to food; therefore, it is necessary to check a specific irradiated food for marker hydrocarbons. On the other hand, two irradiated foods (papaya and mango which were irradiated at their practical doses) were difficult to distinguish from non-irradiated foods using this method.

Key words ------ hydrocarbon detection method, irradiated foods, GC/MS

# INTRODUCTION

In 2001, the hydrocarbon detection method became a standard international analytical technique. The Codex Aluminas committee decided to classify this method as type II, which can be used instead of regular detection methods when they are not available.<sup>1)</sup> It has been reported that this method can be applied to detect irradiated fatty foods such as meats, dairy products, seafoods, and fruits which have been treated at or above 1 kGy.<sup>2)</sup> Though the scope of this method is limited, it has the potential of detecting a wide range of irradiated foods which contain some fat.

Production of hydrocarbons to detect in irradiated sample can be affected by conditions of irradiation. Hydrocarbon production can also be affected by the components and contents of the fatty acids in the food. Those values depend on where they foods produced. Data in Japan are tabulated in Table 1. Eliminating those problems, we previously reported the production of hydrocarbons from fatty acid esters in *n*-hexane solutions, which was a model of fatty food.<sup>3)</sup> The results indicated the amount of hydrocarbons depended on kind of fatty acid esters, i.e., the yields of 1,7-hexadecadiene and 8heptadecene from oleic acid ester were higher than the other hydrocarbons from the other fatty acid esters. This means that detectable doses of irradiated samples are limited by the oleic acid content of in the sample. It also means ratio of produced hydrocarbons will not be related to their mother fatty acid ratios. In practical samples, it would be more difficult to estimate the ratio because the precise amounts accurate of oleic acid derivatives are usually unknown in specific samples.<sup>4,5)</sup> Therefore it is necessary to study practical samples that have been irradiated.

It has been reported that some of those hydrocarbons were found in non-irradiated foods.<sup>6)</sup> This means that detectable doses are also affected by background hydrocarbons. To avoid adverse effects of irradiation, the recommended/advised doses have been suggested as shown in Table 2. It is necessary for this detection method to detect marker hydrocarbons in each sample at the dose level.

In this paper we discuss the minimum detectable doses of irradiated foods and the background

<sup>\*</sup>To whom correspondence should be addressed: National Institute of Health Sciences, 1–18–1 Kamiyoga, Setagaya-ku, Tokyo 158–8501, Japan. Tel.: +81-3-3700-1141; Fax: +81-3-3707-6950; E-mail: mmiyaha@nihs.go.jp

fatty acid	C <sub>14:0</sub>	C <sub>16:1</sub>	C <sub>16:0</sub>	C <sub>18:0</sub>	C <sub>18:1</sub>	C <sub>18:2</sub>	C <sub>20:5</sub>	C <sub>22 : 5</sub>
butter	12	b)	30	11	25	b)	b)	b)
cheese	10	b)	28	11	25	b)	b)	b)
beef	b)	5	27	13	45	b)	<u>b</u> )	b)
pork	b)	b)	26	13	43	9	b)	b)
chicken	b)	b)	23	8	42	15	<u>b)</u>	b)
tuna	b)	b)	21	<u>b)</u>	16	b)	12	15
dry	b)	8	18	6	18	b)	14	16
shrimp avocado	b)	8	19	59	13	b)	b)	b)

**Table 1.** Fatty Acid Composition<sup>*a*</sup>)

a) The standard tables of food composition in Japan 1990, unit: g/100 g fat. b) —: less than 5%.

East numara	dose (IrCri)	Def
Food purpose	dose (kGy)	Kel
butter	Reduction of microbial load	$1.5^{a)}$
cheese	Reduction of microbial load	$3-5^{b)}$
beef	Reduction of pathogenic microorganism	$2.5-7^{c)}$
pork	Reduction of pathogenic microorganism	$2.5 - 7^{d}$
chicken	Reduction of pathogenic microorganism	$3-7^{e)}$
tuna	Reduction of pathogenic microorganism	
	Control of infection parasites	$0.6 - 2^{f}$
dry	Reduction of pathogenic shrimp microorganism	
	Control of infection parasites	$0.5-2^{g)}$
avocado	Quarantine treatment	$0.3-0.8^{h,i)}$
mango	Quarantine treatment	$0.3-0.8^{h,i)}$
рарауа	Quarantine treatment	$0.3-0.8^{h,i)}$

 Table 2. Advised Dose (kGy) of Practical Irradiation

*a*) Hayashi, Tohru (1989) "Food Irradiation," Korin, Tokyo, p. 66. *b*) European Parliament, the Consultation Paper on Food Irradiation (2000). *c*) Nanke, K. E. (2000) Private communication, Sure Beam. *d*, *e*) IAEA (1994) "Analytical detection methods for irradiated foods," IAEA-TECDOC-587, Vienna, p. 7. *f*, *g*) Kilgen, M. B. (2001) "Chapter 7 Irradiation Processing of Fish and Shellfish Products," Edited by Molins, R. A., "Food Irradiation: Principle and Applications," John and Wiley & Sons, New York. *h*) APHIS (2002) "Irradiation Phytosanitary Treatment of Imported Fruits and Vegetables," Fed. Reg., 67, 11610–65029. *i*) Clark J. (2000) "Private communication," Hawaii Pride.

levels of hydrocarbons in non-irradiated samples.

# MATERIALS AND METHODS

#### Apparatus —

*Irradiation Apparatus*: A wet type <sup>60</sup>Co plate source irradiation apparatus at the Takasaki Establishment of Japan Atomic Energy Institute, Takasaki City, Gunma, and a table-type <sup>60</sup>Co rod source at the Tokyo Metropolitan Institute of Industrial Technology, Setagaya, Tokyo, were used for irradiation.

GC Equipment and Operating Conditions: The gas chromatograph used was a Hewlett-Packard model 5890 Ser.II equipped with a mass spectrometric detector (a Hewlett-Packard model 5971). Also used was a capillary column ( $25 \text{ m} \times 0.2 \text{ mm}$ 

i.d., film thickness, 0.33 um; Hewlett-Packard Ultra 1 (Hewlett-Packaged, Co.) or  $12 \text{ m} \times 0.2 \text{ mm i.d.}$ , Film thickness, 0.33 um; J & W DB-5). Injector temperature was 200°C. Detector temperature was 280°C. The carrier gas was helium, with a flow rate of 1 ml/min. The injection volume was 2  $\mu$ l. The injection mode was splitless. The column oven for the Ultra 1 column was controlled as follows: initially, the temperature was maintained at 40°C for 2 min, was raised to 170°C at 2.5°C/min, then to 200°C at 5°C/min, and was finally maintained at 200°C for 5 min. The column oven for the DB5 column was controlled as follows: initially, the temperature was maintained at 50°C for 2 min, was raised to 130°C at 10°C/min, then to 250°C at 5°C/min, and was finally maintained at 250°C for 5 min.

Homogenizer: Polytron PCU 11, Kinematica A

## G, Switzerland.

**Quantitative Determination** — The calibration curve was obtained by injecting 1.25, 2.5, 5, and 10  $\mu$ g/ml of standard solutions. Calibration curve for each hydrocarbon was reported.<sup>3)</sup> The internal standard method was used with the addition of 100  $\mu$ g of *n*-eicosan (C20).

**Reagents and Other Materials** —— Samples: Irradiating samples were purchased from local supermarket in Setagaya, Tokyo.

The hydrocarbon standards used are shown in the previous paper.<sup>3)</sup> The purities of the standard materials were over 98%. They were purchased from Tokyo Kasei Chemical Co., Inc., Tokyo, and Tela Chemicals, Germany.

All reagents for analysis were of the Japanese Industrial Standards (JIS) extra pure grade, which may be compatible with American Chemical Society (ACS, U.S.A.) grade. *n*-Hexane was of HPLC grade (Cica Merck, Co., Tokyo, Japan).

Standard solutions: One hundred milligrams of each hydrocarbon were dissolved in 100 ml of *n*-hexane.

Florisil for clean-up column: Florisil was activated in a muffle at 550 degree Celsius for overnight. Three per cent water of the activated was added to cool Florisil in order to deactivate the Florisil (for example, 3 g of water a 100 g activated Florisil). The prepared absorbent was kept in a flask with stopper at room temperature.

Irradiation procedure: Five grams of sample were placed in a 10 ml Pyrex tube equipped with a stopper. The sample was irradiated at 6 kGy/hr using a plate-type source for precision irradiation. A sample was routinely irradiated using a rod-type source at an appropriate dose rate.

**Temperature Control of Sample during Irradiation** — When the temperature of a sample needed to be maintained at 0°C, it was dipped in a bath containing a mixture of water and ice. After irradiation, the samples were stored at  $-20^{\circ}$ C.

Dosimetry Absorbed doses were measured using with GammaChrom YG (Hawell, U.K.), while a Radix RN-15 (Radie Kogyou, Japan) was used for calibration.

Caution: It should be noted that the gamma-irradiator should be operated with careful monitoring and supervision by someone experienced in irradiation. Some organic solvents used in this study are suspected carcinogens and should be handled with care. Recovery test: The mixture of 15 standard hydrocarbons in hexane and sodium sulfate were added to sample homogenate. The mixture was stirred for 5 min. Further process was carried out as described in extraction section. The recovery was not corrected by background hydrocarbon level.

# Extraction —

a) Butter and cheese: One gram of each sample was dissolved in 100 ml of *n*-hexane. The mixture was dried with 5 g of sodium sulfate overnight.

b) Chicken, pork, and beef: Five grams of chopped meat and 5 g of sodium sulfate with 100 ml of *n*-hexane were homogenized by means of a Polytron for 30 sec. The mixture was poured into a 300 ml flask which was equipped with a reflux condenser and was refluxed for 1 hr. After the mixture was cooled to room temperature, it was filtered into a 100 ml-graduated cylinder. *n*-Hexane was added up to 100 ml. The mixture was dried with 5 g of sodium sulfate overnight.

c) Tuna and dry shrimp: The extraction procedure for tuna and dry shrimp were the same as described in the section b.

d) Avocado: The sample's skin was peeled off, and the pulp was then cut into small pieces. Five grams of the cut pieces were homogenized with 100 ml *n*-hexane and 10 g of sodium sulfate by means of a Polytron. The mixture was refluxed for 1 hr. After the mixture cooled to room temperature, it was filtered into a 100 ml-graduated cylinder. *n*-Hexane was added up to 100 ml. The mixture was dried with 5 g of sodium sulfate overnight.

e) Papaya seed: The pulp of a sample was removed and the seed was collected. The seed was cut using a knife and the hard skin of the seed was removed. Albumen in the embryo was homogenized with 10 g sodium sulfate and 100 ml of *n*-hexane for 30 sec. The mixture was refluxed for 1 hr. After the mixture cooled to room temperature, it was filtered into 100 ml-graduated cylinder. *n*-Hexane was added up to 100 ml. The mixture was dried with 5 g of sodium sulfate overnight.

f) Mango seeds: Seeds were collected from two mangos and the black skins covering seeds were removed. Five grams of peeled seeds were homogenized with 10 g of sodium sulfate and 100 ml of *n*hexane for 30 sec. The mixture was refluxed for 1 hr. After the mixture cooled to room temperature, it was filtered into a graduated cylinder. *n*-Hexane was added to the cylinder up to 100 ml. The mixture was dried with 5 g of sodium sulfate overnight.

Hydrocarbon	butter		cheese		chicken		pork		beef	
	mean b)	rsd <sup>c</sup> )	mean	rsd	mean	rsd	mean	rsd	mean	rsd
1-C <sub>12:1</sub>	35	18.2	41	13.8	58	3.1	83	12.5	55	20.8
C <sub>12:0</sub>	42	21.7	72	13.5	60	4.3	94	12.3	71	27.8
1-C <sub>13 : 1</sub>	51	15.3	53	4.6	61	5.7	84	5.6	53	13.9
C <sub>13:0</sub>	57	16.6	64	3.9	68	4.7	86	6.3	65	16.5
1-C <sub>14 : 1</sub>	67	9.6	103	4	66	5.6	82	6.8	86	29.1
C <sub>14:0</sub>	72	10.7	84	2.2	66	13.1	89	10.2	61	14.6
1-C <sub>15 : 1</sub>	81	5.1	66	0.9	91	11.9	96	8.9	55	13.8
C <sub>15:0</sub>	81	4.2	67	0.5	92	6.2	90	5.2	59	13.5
1,7-C <sub>16 : 2</sub>	87	4.8	69	0.4	85	6.1	91	4.1	57	11.4
1-C <sub>16:1</sub>	88	2.8	573	13.5	76	11.1	82	6.8	431	188
C <sub>16:0</sub>	91	3.7	86	3.8	93	7.4	94	4.9	66	14
6,9-C <sub>17 : 2</sub>	88	3.9	69	3	78	8.2	86	7.1	49	8.5
8-C <sub>17:1</sub>	90	4.7	66	1.4	81	8.6	85	3.4	54	9.9
1-C <sub>17:1</sub>	89	1.6	67	0.8	63	9.2	92	6.5	53	7
C <sub>17:0</sub>	95	2	71	1.2	93	5.3	95	3.8	59	10.6
Hydrocarbon	tuna		dry shrimp		avocado		mango		papaya	
	mean	rsd	mean	rsd	mean	rsd	mean	rsd	mean	rsd
$1 - C_{12 : 1}$	52	23.2	54	15.2	65	20	53	17.5	61	10
C <sub>12:0</sub>	53	23.5	75	14.7	73	15	70	23.5	73	12.5
$1 - C_{13 : 1}$	60	20.9	63	10.2	61	9.4	65	9.9	59	8.7
C <sub>13:0</sub>	60	20.6	58	15.3	59	14.2	67	10.7	68	9.7
$1 - C_{14:1}$	70	14.1	68	11.6	66	13.1	74	8.5	72	10.2
C <sub>14:0</sub>	75	13.4	73	12.1	77	11	80	14.1	76	8.3
$1 - C_{15:1}$	80	2.1	79	2.6	82	3.8	87	6.5	82	3.6
C <sub>15:0</sub>	117	7	81	5.2	79	7.4	95	9.4	84	6.9
1,7-C <sub>16 : 2</sub>	89	9.2	85	7.3	88	5.3	89	7.2	86	5.1
$1 - C_{16:1}$	97	10.7	152	20.8	93	17.3	92	12.7	96	7.6
C <sub>16:0</sub>	92	11.9	95	3.2	91	4.1	86	8.4	90	6.9
6,9-C <sub>17 : 2</sub>	129	83	86	11.6	84	9.7	83	7.9	89	7
8-C <sub>17:1</sub>	98	24.9	92	5.8	86	4.6	88	5.2	97	8.2
1-C <sub>17 : 1</sub>	93	14.4	73	7.7	82	8.3	77	9.9	91	5.8
C <sub>17:0</sub>	91	17.5	87	5.9	80	8	93	11.4	85	7.7

**Table 3.** Recovery $^{a)}$ 

a) spiking level: 10 g of hydrocarbons in 5 g sample. b) Mean: average of three trials, %. c) rsd: relative standard deviation.

**Clean-Up by Florisil Column Chromatography** 

— Five milliliters of the extracted and dried solution was pipetted in order to determine the fat content in the solution. A volume of the solution which contained about 1 g of fat was filtered and evaporated up to about 20 ml. The concentrated solution was loaded into the top of a Florisil column (20 mm i.d.  $\times$  20 cm). Hydrocarbons were eluted with 100 ml of *n*-hexane.

#### **RESULTS AND DISCUSSION**

#### **Analytical Conditions**

Gas Chromatographic data were obtained bymodified conditions as described in our previous paper.<sup>3)</sup> Recoveries of hydrocarbons from foods were examined and the results are shown in Table 3. Recoveries of 1,7-C16 : 2, 8-C17 : 1, and 1-C14 : 1, which were main markers of hydrocarbons for detection of irradiated foods ranged from 57 to 91, 54 to 98, and 66 to 103%, respectively. Although the recoveries of hydrocarbons among foods were varied, they were sufficient for detection of irradiated foods. However, recoveries of hydrocarbons which have lower molecular weights and higher vapor pressures tended to be low. Such losses may occur during solvent evaporation for concentration.



Fig. 1. Flow Chart Describing Pre-Treatment

The clean-up procedure is shown in Fig. 1. The sample volume was adjusted in order to obtain 1 g of fat in the extracted solution, because the fat content differed from sample to sample.

#### **Detection of Irradiated Dairy Products**

Background levels of hydrocarbons were determined in non-irradiated products. Saturated hydrocarbons, C12 : 0, C13 : 0, C14 : 0, C15 : 0, C16 : 0, and C17 : 0 were determined. In butter, the level of most hydrocarbons ranged from 0 to 4.3  $\mu$ g/g. Cheese showed higher levels of many saturated hydrocarbons and unsaturated hydrocarbons of 1-tetradecene (5.5  $\mu$ g/g) than those seen in butter. The results means none of saturated hydrocarbons could be used as marker compound to identify the irradiated foods.

Butter and cheese were irradiated at several doses (1, 5, and 10 kGy) in order to determine the hydrocarbons produced in them. Seven unsaturated hydrocarbons (1-C12:1, 1-C13:1, 1-C15:1, 1-C16:1, 1,7-C16:2, 6,9-C17:2, and 8-C17:1)were not found in non-irradiated samples but were determined at 10 kGy in both foods (shown in Fig. 2). Close relationships between the amounts of those compounds formed in irradiated samples and given doses were observed as shown in Fig. 3. In butter, the marker hydrocarbons were 1,7-C16:2



Fig. 2. Gas Chromatographic Charts of Non- and 10 kGy-Irradiated Diary Products



Fig. 3. Dose-Response Curves of Hydrocarbons in Diary Products

and 8-C17 : 1 at 1.5 kGy. 1,7-C16 : 2 was detectable at 3 kGy, which is the recommended dose for Camembert cheese advised by the IAEA.

#### **Detection of Irradiated Meats**

The background levels of hydrocarbons in nonirradiated sample solutions of beef, pork, and chicken were very low as shown in Fig. 4. C12:0 (1.5- $2 \mu g/g$  and C13 : 0 (4.2–2.2  $\mu g/g$ ) were found in the three meats, while irradiated beef also showed C17 : 0 (1.1  $\mu$ g/g). Background hydrocarbons in beef were higher than those in chicken and pork. Therefore, cleanup of beef sample should be done carefully to eliminate interferences of gas chromatographic analysis. 1,7-C16 : 2, 8-C17 : 1, 6,9-C17 : 2, and 1-C14:1 were marker hydrocarbons for the three meats at 10 kGy. These hydrocarbons were not detected in non-irradiated meats. 1,7-C16: 2 and 1,8-17:1 were detectable in irradiated beef and chicken at 2 kGy which is a practical dose for the sterilization of meats in the United States. The amount of 1,7-C16 : 2 at this dose was estimated as 2–4  $\mu$ g/g, which was calculated based on the results shown in Fig. 5. However, only one marker hydrocarbon (1,7-C16:2) was detectable at 1 kGy in pork.

#### **Detection of Irradiated Seafoods**

In non-irradiated tuna and shrimp, as many saturated hydrocarbons were detected as in butter and cheese, but no unsaturated hydrocarbons were found (see Fig. 6). The levels of hydrocarbons in non-irradiated tuna were high  $(3-19 \ \mu g/g)$ , but in non-irradiated shrimp, they were at the same levels as in meats (less than  $2 \ \mu g/g$ ).

1,7-C16: 2 and 8-C17: 1 were marker hydro-

carbons for detection of irradiated tuna at 10 kGy. The amount of 1,7-C16 : 2 was estimated as 0.7–1.8  $\mu$ g/g (which was calculated based on the results shown in Fig. 7) at a dose of 1.5–3 kGy, which was suggested by Kilgen. However, the amount of 8-C17 : 1 was below LOD at the dose range.

6,9-C17 : 2, 8-C17 : 1, and 1-C15 : 1 were marker hydrocarbons for detection of irradiated shrimp but 1,7-C16 : 2 was not a marker hydrocarbon at 10 kGy. The amounts of 6,9-C17 : 2, 8-C17 : 1, and 1-C15 : 1 were 2.5, 0.7, and 0.3  $\mu$ g/g, respectively, at 1 kGy. This result demonstrates that only 6,9-C17 : 2 can be a marker at a practical dose range from 0.75 to 2 kGy.

Thus, marker hydrocarbons for the detection of irradiated seafoods differs from those of dairy products and meats. These results illustrated the difference of fatty acid composition between these foods and seafood. Thus, it is necessary to confirm which is a marker hydrocarbon in each type of irradiated seafood.

#### **Detection of Irradiated Fruits**

In non-irradiated avocado and papaya, no target hydrocarbons were detected. In non-irradiated papaya, and mango, many unknown peaks appeared in their GC chromatograms (Fig. 8) (the results regarding mango are not shown). This result means that the cleanup procedure for analysis is not sufficient to detect the hydrocarbon levels in some irradiated fruits. In 10 kGy-irradiated avocado and papaya, several unsaturated hydrocarbons (1-C14 : 1, 1,7-C16 : 2, 6,9-C17 : 2, and 8-C17 : 1 in avocado; 1-C14 : 1, 1-C15 : 1 and C15 : 0, in papaya) were detected. (Fig. 9)



Fig. 4. Gas Chromatographic Charts of Non- and 10 kGy-Irradiated Meats

The amounts of 1-C17 : 1 and 1,7-C16 : 2 were estimated as 0.9 and 0.5  $\mu$ g/g, respectively, in irradiated avocado at 0.5 kGy which were recommended for the quarantine of fruits by the IAEA. The amounts of 1-C15 : 1 and 1-C14 : 1 were 1.8 and 0.5  $\mu$ g/g in irradiated papaya at 0.5 kGy.

Thus, marker hydrocarbons for detection of ir-

radiated fruits differed among the type of fruits. Therefore, it is necessary to determine which hydrocarbon is marker for detection of irradiated fruit. Unfortunately, no hydrocarbon was detected in 1kGy-irradiated mango. The final sample solution contained a large amount of co-extractives, which interfered with the analysis. It is necessary to reno-



Fig. 5. Dose-Response Curves of Hydrocarbons in Meats



Fig. 6. Gas Chromatographic Charts of Non- and 10 kGy-Irradiated Seafoods



Fig. 7. Dose-Response Curves of Hydrocarbons in Seafoods



Fig. 8. Gas Chromatographic Charts of Non- and 10 kGy-Irradiated Fruits

vate the cleanup procedure in order to eliminate coextractives for the analysis of irradiated fruits.

# Comparison of Radiolytic Products with Pyrolytic Products

As discussed in former section, prominent product in irradiated food was 1,7-hexadecadiene (Cn-2:m+1) from oleic acid ester (Cn:m, n = 18, m = 1) as shown in Fig. 10. On the other hand, heat treatment of glycerin trioleiate produced butyl cyclohexene (Cn-8:m). Same result also was obtained regarding to ethyl stearate (Cn:m, n = 18, m = 0). Major radiolytic products were heptadecane (Cn-1:m), 1-hexadecene (Cn-2:m+1) and major pyrolytic products were decane (Cn-8:m).<sup>7,8)</sup> Those results were explained that main radiolytic degradation pathway involves attack of radical species on carbonyl group at initial stage of reaction; hence main pyrolytic degradation includes self-fission of C–C bond at center of molecule. Thus, components of radiolytic hydrocarbons in irradiated food were somewhat different from those of pyrolytic hydrocarbons in heated oil. Therefore, those marker hydrocarbons for irradiated food detection were useful to identify irradiated foods.

In conclusion, the hydrocarbon detection method



Fig. 9. Dose-Response Curves of Hydrocarbons in Fruits



Fig. 10. Radiolytic and Pyrolytic Products of Oleic Esters

food	marker		
butter	1,7-C16:2,8-C17:1		
cheese	1,7-C16 : 2,		
beef	1,7-C16:2,8-C17:1		
pork	1,7-C16 : 2		
chicken	1,7-C16:2,8-C17:1		
tuna	1,7-C16 : 2		
dry shrimp	6,9-C17 : 2, 8-C17 : 1		
avocado	1,7-C16 : 2, 1-C17 : 1		
рарауа	1-C15:1,1-C14:1		
mango	not available		

Table 4. Marker Hydrocarbons at Practical Dose

for irradiated foods were applicable to butter, cheese, beef, pork, chicken, tuna, dry shrimp, avocado, and papaya at their practical doses. The amounts of background hydrocarbons of those samples from nonirradiated foods were negligible, and the production of marker hydrocarbons was eminent at their minimum doses of practical irradiation. In order to achieve the best performance from this method, it is necessary to check particular irradiated foods for hydrocarbons because marker hydrocarbons will vary from food to food as shown in Table 4. On the other hand, this method could hardly distinguish one types of irradiated food (mango which were irradiated at their practical doses) from non-irradiated foods. More study is required to detect them by this method.

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# REFERENCES

- 1) ALINORM (2001) 01/41, para, 197–200, Vienna.
- 2) British Standard Institute (1997) Foodstuffs. Detection of irradiated food containing fat. Gas chromatographic analysis of hydrocarbon, EN1784, Brussels.
- Miyahara, M., Saito, A., Kamimura, T., Nagasawa, T., Ito, H. and Toyoda, M. (2002) Hydrocarbons Production in Hexane Solutions of Fatty acid Methyl Esters Irradiated with Gamma Ray. *J. Health Sci.*, 48, 418–426.
- Goto, M., Tanabe, H. and Miyahara, M. (2001) Detection of electron beam irradiated beef by hydorcarbon method. *Food Irradiation Japan*, 36, 13–22.
- 5) Tanabe, H., Goto, M. and Miyahara, M. (2002) Detection Method of Irradiated Chicken by GC Analysis of 2-Alkylcyclobutanones and Hydrocarbons Using Soxhlet Extraction and Florisil Chromatography. *Radioisotopes*, **51**, 109–119.
- 6) Ito, H. (2001) Principles and Safety of Irradiated Food, In *JAERI-Review 2001-029*, The Japan Atomic Energy Institute, Takasaki, Japan.
- Elias, P. S. and Cohn, A. J. (1977) *Radiation Chemistry of Major Food Component*, (Japanese Edition), Elsevier/North-Holland Biomedical Press, New York, pp. 52–53.
- 8) Nawar, W. (1986) Volatiles from Food Irradiation. *Food Reviews International*, **2**, 45–78.