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Relationship Between Hydrocarbon Content and Oxidative Stability in Irradiated Hazelnut Oils

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Keywords

Gamma Irradiation

Hydrocarbon(s)

Rancimat

Induction Time

Hazelnut Oil

Abstract

The hydrocarbon detection method, based on the detection of hydrocarbons formed during irradiation, is one of the internationally accepted detection methods for irradiated foods. Radiolysis products, formed due to breakdown of unsaturated fatty acids by irradiation, are detected in this method. While no hydrocarbons were not found in the unirradiated hazelnut oil, hydrocarbons, namely 1-7 hexa-decadiene, 1- hexa-decene, n-penta-decane and 1- tetra-decene, but they were detected after irradiation at doses of 5 kGy or higher. It was found that irradiation induced the formation of hydrocarbons and when irradiation dose increased, the amount of hydrocarbons increased. The Rancimat process is widely used to define the amount of oxidation in foods containing fat. Analysis time is short as it is a very fast method. The induction time, showing the oxidation resistance of oils, decreased as irradiation dose increased. The possible relationship between the detected hydrocarbons and oxidative stability was examined and a negative correlation was found between the hydrocarbon and rancimat methods.

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1. INTRODUCTION

Food irradiation is a technology applicable for all groups of foods, as nutritional, functional and sensory properties of food products are slightly affected. In a food system, there is an interaction between radiation and water and other biological systems, resulting in radiolytic products, acting as oxidizing agents and changes in the molecular structure of organic matter are observed. Deoksi-ribonükleik asit molecules are damaged by radiation and inhibit the reproduction of microorganisms, insects and gametes. Chauhan et al. (2009).

High-energy-photons sourses (Gamma rays with 60-Co and 37-Cs nuclei), X-rays is produced by machines with energies of 5 MeV and electron accelerator machines are used in food irradiation process. These sources are feasible for commercial use of irradiation as desired food preservative effects are achieved and no radioactivity is observed in foods or packaging materials Farkas (2004). Gray (Gy) is the international unit for the absorbed radiation dose; generally pasteurization doses are <10 kGy are and sterilization doses are >10 kGy. It can perform irradiation on packaged products, as it creates minimal temperature rise in the product and can be used through packaging materials, hereby preventing recontamination or reinfestation of the product.

The World-Health Organization, the Food and Agricultural Organization, the International- Atomic-Energy-Agency and many countries confirm food irradiation for producing better and safer foods. Space foods for astronauts are sterilized by irradiation (Acheson & Steele, 2001).

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Microbial decontamination of herbs and spices have been assured by irradiation for more than 40 years. CODEX and most countries have allowed the use of irradiation (WHO, 1994; Chmielewski & Migdal, 2005). Doses greater than 10 kGy should be used to a food, except for application of higher doses for technological doses. In Turkey, radiation processing of food is controlled by Food Irradiation Legislation of Republic of Turkey Ministry of Agriculture and Forestry (URL1, 2019).

In previous studies, irradiation was more effective than heat treatment against bacteria, while leaving no chemical residues (Tjaberg et al., 1972; Loaharanu, 1994; Thayer et al., 1996). While heat sterilization of spices causes the loss of causes thermally induced changes, thermolabile aromatic volatiles or, such as decomposition brought about by high temperatures or production of thermally induced radicals, food irradiation is less harmful to the spices and can be applied in place of ethylene oxide and methyl bromide treatment. Minimal modifications on the quality attributes of food are observed (Olson, 1998; Sádecká, 2007).

Hazelnut production in Turkey is very high due to the favorable weather conditions. Turkey is one of the main producer, as well as the largest hazelnut exporter in the world. Turkey accounts for 75% of the world hazelnut production and approximately 70-75% of this production is exported to more than 90 countries in the world (URL2, 2012).

Hazelnuts are commercially irradiated in the range of 1-5 kGy to control insects, reduce the number of microorganisms and extending the shelf life of food (URL3, 1999). Although appropriate labeling of irradiated foods is mandatory, there is the possibility that they have been irradiated without any notification on the shipment (EN 1784, 2003).

To prevent this, there are ten current methods used to identify the irradiated foods. The European Standard EN 1784:2003 is used for the determination of hydrocarbons formed as a result of irradiation of oil-containing foods. It is a method based on gas chromatographic detection of hydrocarbons formed by radiation (Kader, 1986). When food is irradiated, different hydrocarbons are formed by the breakdown of fatty acids, some of them are found excessively, one with one fewer carbon than the main-fatty acid (n-1), and the other with two fewer carbons with an extra doubl-bond at position 1 (n-2, 1-ene) (Spiegelberg et al., 1994).

Hazelnut oil, its high content (more than 40%), is widely consumed in diet. Since the level of unsaturated fatty acids is high in hazelnut oils, irradiation causes oxidation of these fatty acids. These poly-unsaturated fatty acids are attacked by oxygen to yield peroxides, which then further decompose (Mexis et al., 2009). Oxidative stability is the main factor for determining the shelf life of high fat containing foods, such as hazelnuts. The Rancimat method is one of the most widely used methods, as it can detect oxidation easily and quickly in a very short time (Mendez et al., 1996). The oxidative stability depends on the acyl-glycerol composition and on the amount and type of minor components in oil (Mateos et al., 2005). In addition, this method does not require periodic work and chemicals (Hasenhuettl & Wan, 1992).

The aim of our study was to detect the formation of hydrocarbons in gamma irradiated hazelnut oils by gas chromatography (GC). Meanwhile, the Rancimat Method was used to determine the oxidative stability of the samples. The existence of possible correlation between the hydrocarbon method and Rancimat method was evaluated to examine the effect of irradiation in hazelnut oils.

2. MATERIALS AND METHODS

2.1. Samples

Hazelnut samples (Corylus avellana L.-Ordu variety, unshelled) used in this study were obtained from a regional market in Ankara, Turkey. Hazelnut samples were individually weighed into polyethylene bags for irradiation. Polyethylene bags were used because they are light, irresponsive to biological agents, robust to chemical substances and atmospheric conditions, unaffected by temperature changes between 60 and 200°C. All samples were stored in the refrigerator (± 4°C) until and after irradiation.

Lipid extraction

Finely chopped hazelnuts (10 g) were extracted by shaking the seeds with 30 mL of hexane/isopropanol (3:2, v/v) for 1 hour in steel tubesThe solutions were filtered under vacuum and the residues washed twice with 20 mL of the same solvent. 35 mL of sodium sulfate (6.72%) was added and the top layer was evaporated under vacuum at 40°C. The oils were stored at 4°C (Thayer et al., 1996).

2.2. GC Analysis of Hydrocarbons

Analysis of hydrocarbons in the samples, obtained by extraction of irradiated hazelnut oils, was performed using gas chromatograph (6980 series Hewlett-Packard Co. Wilmington, DE). The gas chromatography detector used in the analysis was a flame ionization detector (FID) with splitless injection. Carrier gas was helium, flow rate was set to 2.6 mL/min. The column in the analysis was a DB-5[(phenyl-5%)-methyl-polysiloxane] of 0.25mm i.d.x30m with a 0.25 µm film thickness. The column temperature was initially set at 50°C for 2 minutes and programmed at 10°C/min to 70°C, 2.5°C/min to 170°C, and 10°C/min to 280°C and 5 minute final hold. The detector and injector temperatures were respectively 250°C and 200°C. Samples (1 µL) diluted with hexane were injected into the instrument.

All experiments were repeated three times. Identification of hydrocarbon peaks was based on retention time as compared to hydrocarbon standards of 1-tetradecene, n-pentadecane and 1,7-hexadecadiene (Fluka Analytical), and 8-hexadecen (Sigma-Aldrich Corporation). The results were calculated by using the standard curves obtained for each of four hydrocarbons (Choi & Hwang, 1997).

2.3. Measurement of Oxidative Stability

Rancimat (Metrohm apparatus model 743, Switzerland, Herisau) was used to measure the oxidation level of oils in irradiated hazelnut samples. The operating temperature range of this device is 50-200°C. The processing temperature is set to 120°C. The airflow rate was set at 20 L/h for all analyses. Each oil sample was weighed 3.5±0.1g into the reaction vessel and placed on the heating block. It was filled with 60 mL of distilled water. The volatile compounds resulting from the breakdown of oils were gathered in a receiving flask during measurement.

The conductivity and the induction times were measured automatically by apparatus software. Induction time was taken as the time that corresponded to the point of sharp increase in conductivity, where the baseline tangent to the conductivity curve starts, and expressed in hours (Frank et al., 1982). All analyses were repeated in duplicate**.**

RESULTS AND DISCUSSION

As with other oil seeds, hazelnut oil contains mono-unsaturated fatty acids, oleic acid. İt is usually found the highest. This is followed by ***linoleic acid***, which is a binary unsaturated fatty acid (Choi & Hwang, 1997). For this reason, oxidative deterioration occurs easily in hazelnut oils. The presence of hydrocarbons in oil-containing foods is the most important indicator of the irradiation process applied to the food.

In our studies, no hydrocarbons were detected in the oil extracted from the naturel hazelnuts (Table 1). As shown in the Table 1, ***1-7 hexadecadiene*** reached a very high value (10.42 ppm) in hazelnut oil irradiated at 5 kGy. ***n-pentadecane*** and ***1-tetradecene***, possibly from palmitic acid, were not found in unirradiated hazelnuts but were found in hazelnuts irradiated at 0.5 kGy or higher. When oil irradiated 5 kGy doses they reach the value of 1.02 and 0.89 ppm, respectively. ***1-hexadecene***, was found at fairly high levels in the samples irradiated at 0.5 kGy or higher. The value of the analysis results are given in Figure 1.

In parallel with the increase in the irradiation dose, a linear increase occurred especially in the amount of *1-tetradecene* (R^2=0.990) and *n-pentadecane* (R^2=0,982). The highest increase in the amount of hydrocarbons in the irradiated oils was determined at 5 kGy dose. As seen in the table, the amount of hydrocarbons increased in parallel with the increase in the irradiation dose (Table 2). Also, the increases of the hydrocarbons as a result of irradiation are given in Figure 1.

This finding concurs with those found by Hwang (1999) that 1-hexadecene, *1-7 hexadecadiene*, *n-pentadecane* and *1-tetradecene* were prominently detected in the irradiated sesame seeds after 0.5 kGy. Hwang (1999). Also, hydrocarbons *1-hexadecene*, *1-7 hexa-decadiene, n-penta-decane* were detected in pork, bacon and ham irradiated at 0.5 kGy or higher, but not in un-irradiated samples except for *1-hexadecene* (Park & Hwang, 1999).

Furthermore, hydrocarbon 1-tetradecene was not detected in un-irradiated peanuts, but was detected in nuts irradiated at 0.5 kGy or higher (Mexis & Kontominas, 2009a).

The authors found that the amount of stearic and palmitic acids increased while there was a decrease in the amount of oleic acid in parallel with the irradiation dose in walnuts (Mexis & Kontominas, 2009b). Irradiation doses applied to peanuts, pistachio nuts and hazelnuts resulted in an decrease in unsaturated fatty acids and parallel increase in saturated fatty acids. (Cam & Kilic, 2009; Mexis & Kontominas, 2009b).

Table 1. *Hydrocarbon contents of the irradiated hazelnut oils determined by gas chromatography*

Hydrocarbons	0kGy	0.5kGy	1kGy	3kGy	5kGy
1-tetradecene (ppm)	0.00	0.11	0.14	0.35	0.89
n-pentadecane (ppm)	0.00	0.12	0.26	0.51	1.02
1-7 hekzadecadiene (ppm)	0.00	1.61	2.76	5.32	10.42
1-hekzadecene (ppm)	0.00	0.16	0.52	0.71	2.01
n-eikosan (Internal standard)	4.00	4.00	4.00	4.00	4.00

Table 2*. The relation between irradiation and hydrocarbon content for hazelnut oils*

Hydrocarbon	**Linear equation**	**R^2**
1-tetradecene	$y = 0.065\ x + 0.05$	0.990
n-pentadecane	$y = 0.193\ x + 0.015$	0.982
1-7 hexadecadiene	$y = 0.95\ x + 1.24$	0.947
1-hekzadecene	$y = 0.36\ x + 0.01$	0.918

y : amount of hydrocarbons(ppm)
x : irradiation dose (kGy)

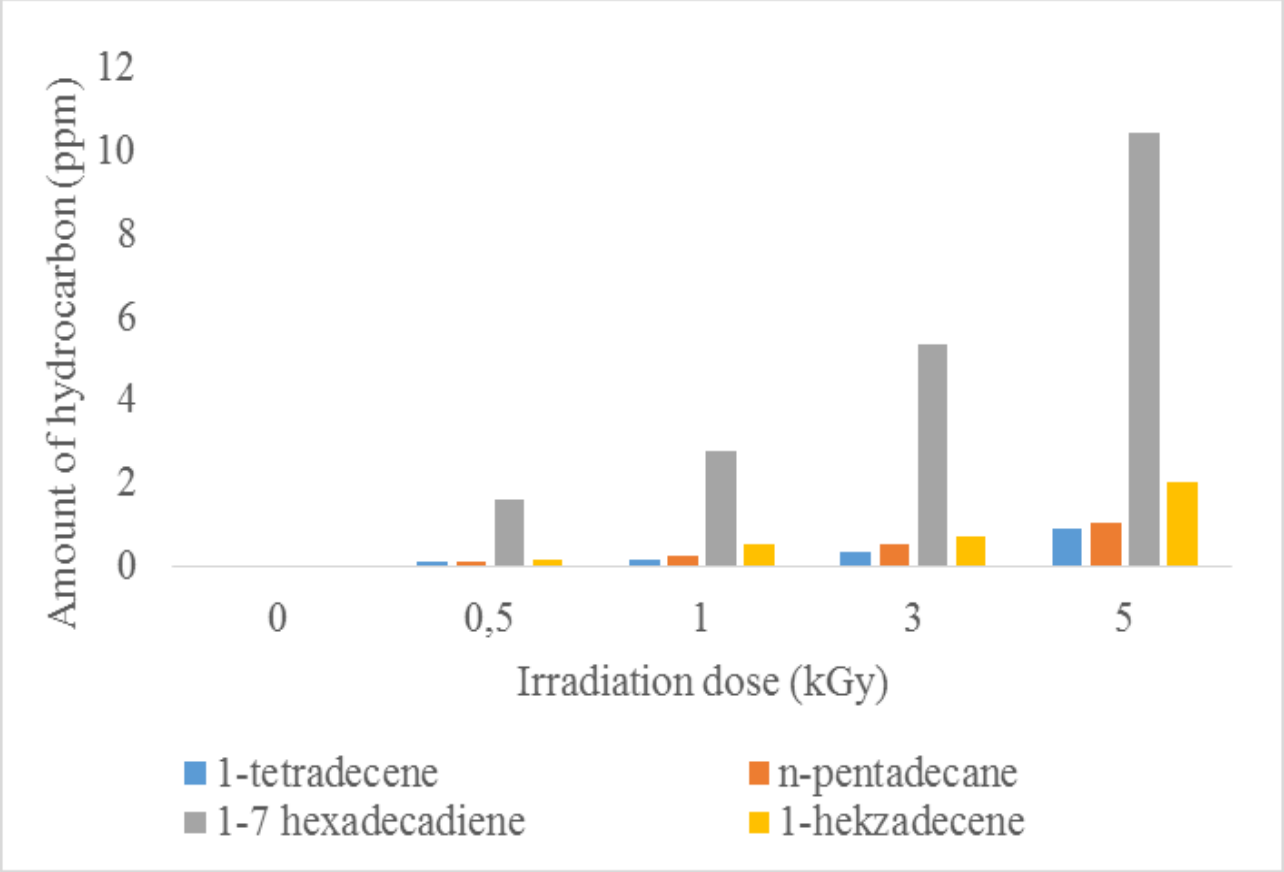

Figure 1. *Hydrocarbon contents of the irradiated hazelnut oils determined by gas chromatography*

The Rancimat prosess is generally used to measure the oxidative stability in oils. The stability of oils decreases as the amount of unsaturated fatty acids increases. The increase in the number of double bonds in the fatty acid makes it easier for free radicals to break the double bonds. Therefore, the excess of un-saturated fatty acids reduces the stability of oils.

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The effects of gamma irradiation at various levels on the Rancimat values of hazelnut oils are shown in Table 3. The graph of the change in conductivity (mS/cm) against IT in hazelnut oils irradiated at different doses is given in Figure 2. As can be seen from the figure, when nut oils irradiated 5kGy, conductivity increase occurred in a shorter time compared to other irradiation doses.

In a study with oils, it was shown that, heat application, which causes oxidation in oils, increases the conductivity value (Yaşkıran, 2020). Also, while induction time detected in non-irradiated oils was 11.6 hours and induction time decreased 9.25 hours after 5 kGy irradiation (Figure 1). An induction time of 14.5 hours was reported in hazelnuts (Gecgel et al., 2011). The concentration of the total saturated fatty acids increased while the total amount of mono-unsaturated and poly-unsaturated fatty acids decreased with the different irradiation dose applied to black cumin seeds (Arici et al., 2007).

Table 3. *Determination of oxidative stability of irradiated hazelnut oils by the Rancimat Method*

Dose (kGy)	**Induction time (h)**
0.0	11.60
0.5	11.14
1.0	10.90
3.0	10.31
5.0	9.25
Regression equation	$y = 0.432\ x + 11.461$
Regression coefficient	$r^2 = 0.9785$

y : induction time(hour)
x : irradiation dose (kGy)

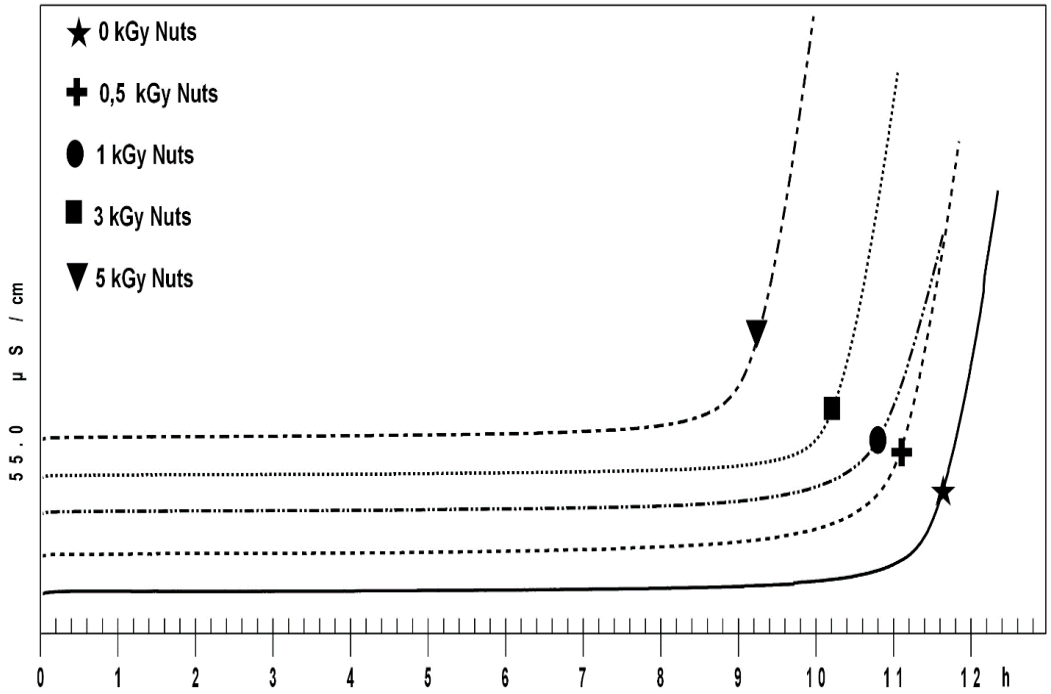

Figure 2. *Determination of oxidative stability of irradiated hazelnut oils by the Rancimat Method*

4. CONCLUSION

It was shown that the hydrocarbon content and oxidative stability of hazelnut oils depend on the irradiation dose applied. An adverse effect of gamma irradiation on induction times was observed. When irradiation dose increased, IT of the oil was decreased. Hydrocarbon formation was observed in the irradiated oils. The amount of hydrocarbon formed increased with increasing dose.

When oily foods are irradiated, the amount of hydrocarbons increases in parallel with the decrease in IT. There is a negative correlation between these two features.

Also, the results show that if the irradiation dose applied to hazelnut oils is known, IT, which is an important criteria for oils, can be determined by the formula given Table 1. In addition, If the irradiation dose applied to hazelnut oils is known, the amount of hydrocarbons in the oil can be determined by the formula given Table 2.

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CONFLICT OF INTEREST

No conflict of interest was declared by the author.

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