JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Oil Quality and Sensory Evaluation of Almond (*Prunus amygdalus*) Stored after Electron Beam Processing

PALOMA SÁNCHEZ-BEL,[†] M. CONCEPCIÓN MARTÍNEZ-MADRID,[§] ISABEL EGEA,[#] AND FELIX ROMOJARO*,[†]

Department of Food Science and Technology, CEBAS-CSIC, Apartado 164, 3100 Murcia, Spain; Departamento de Agroquímica y Medio Ambiente, Escuela Politécnica Superior, Universidad Miguel Hernández, Ctra. Beniel, Km 3,2, 03312 Orihuela, Alicante, Spain; and Department of Food Science, Veterinary Faculty, Campus de Espinardo, University of Murcia, Apartado de Correos 4021, E-30008 Murcia, Spain

The changes in the lipid fraction and the deterioration of its quality were studied in almonds (*Prunus amygdalus*) of the variety Guara after treatment with accelerated electrons at doses of 3, 7, and 10 kGy, during a storage period of 5 months. In almond oil, the most significant difference from the nutritional point of view was seen in the fatty acid linolenic (18:3), which shows at 3 kGy a maintenance of the initial content during the whole storage period, whereas, at 7 and 10 kGy, the content in 18:3 disappears from the first moment. The quality indices of the oil (K_{232}, K_{270}) decreased at all doses and remained stable during the time of storage. The peroxide value did not show changes at the doses of 3 and 7 kGy, in non-irradiated samples, but significantly increased when the maximum dose of 10 kGy was applied. These changes were reflected in the sensory analysis, in which the tasters did not find sensory differences between the controls and those irradiated at doses of 3 or 7 kGy, whereas almonds irradiated at 10 kGy exhibited a rancid flavor and a significant decrease in general quality.

KEYWORDS: Almond; irradiation; electron beam; fatty acid; peroxide; UV; storage; oil quality

INTRODUCTION

According to the FAO estimates (*1*), ∼25% of world grain production is lost due to insects, bacteria, and rodents, and a similar percentage of dry fruit production is contaminated by mycotoxins, the most commonly contaminated being peanuts and pistachios (*2*).

Fumigants are now being phased out because they can, in some cases, affect consumer health and, therefore, the health authorities from different countries have established restrictions on their application; their use has even been banned by some countries (*3*).

Because the aflatoxins cannot be removed using conventional techniques, the microbial contamination must be avoided and, therefore, treatments for ensuring the product quality, while maintaining the sensory and nutritional quality presently demanded by consumers, must be used.

Recently, treatment with ionizing radiation has become more significant as a solution to these problems. It is a physical treatment that does not produce waste and allows a high degree of hygienization to be obtained while causing few changes in the chemical composition of the product (*4*, *5*). It involves exposure of foods to the direct action of certain electromagnetic radiation such as γ-rays, electrons, or X-rays, with sufficient energy to preserve them for long term while maintaining their organoleptic attributes, nutritional quality, and safety.

In Spain, the production, marketing, and import of foodstuffs and food ingredients treated with ionizing radiation will have, from now on, a legislative framework (Royal Decree 348/2001). At present, the list of foodstuffs that can be treated using ionizing radiation includes only dried aromatic herbs, spices, and dry vegetable seasonings. However, from now on, any person with domicile in the European Union will be able to apply for the introduction of a foodstuff on the mentioned list, with an application that must be accompanied by a scientific−technical report.

The commission in charge of the authorization of the treatments (*6*) has recently stated that although, at the moment, only one food category has been included in the community positive list, on a European scale, for the treatment by irradiation (dried aromatic herbs, spices, and dry vegetable seasonings), the process continues, and the scientific committee has issued a document stating that other products could be included on the positive list soon; among them, "dried fruits" were mentioned explicitly.

* Address correspondence to this author at the Department of Food Science and Technology, CEBAS-CSIC, Apdo. 4195, 3100 Murcia, Spain (telephone +34 968396328; fax +34 968396213; e-mail felix@cebas.csic.es).
[†] CEBAS-CSIC.
[§] Universidad Miguel Hernández.
[#] University of Murcia.

10.1021/jf040184r CCC: $30.25
Published on Web 03/11/2005

Table 1. Conditions Applied during the Irradiation Treatments and the Later Readings of the Dosimeters To Verify the Real Absorbed Dose

applied dose (kGy)	speed of conveyor belt (m/min)	beam current intensity (mA)	width of electron beam (cm)	dosimeter measurement (kGy)	optic abs	real absorbed dose (kGy)
3	5	2.15	103	3	0.413 ± 0.002	3.2 ± 0.17
7	4.7	4.38	103	7	0.720 ± 0.001	7.1 ± 0.12
10	3.47	5	103	10	1.003 ± 0.003	10.3 ± 0.4

High doses of radiation can sometimes cause undesirable changes in the food flavor, appearance, and texture, resulting in a product unfit for human consumption. This fact may limit the dose and, therefore, the number of microorganisms that can be removed. The combination of low radiation doses with other treatments can solve this problem. For this reason, other preservation methods, such as adjuvant systems, low temperatures, controlled or modified atmospheres, or just adequate storage conditions, are usually employed (*7*), but limited literature is available regarding the effects of ionizing radiation on dried fruits, particularly almonds (*8*−*14*).

This paper reports the effect of ionizing radiation treatments at doses of 3, 7, and 10 kGy on the whole shelled almonds, packed in air atmosphere and stored for 5 months at 20 °C. The influence of these doses on the quality of the lipid fraction and the organoleptic changes caused in the fruit also have been observed.

MATERIALS AND METHODS

Samples. Almonds (*Prunus amygdalus*) were supplied by Frutos Secos el Mañan (Pinoso, Alicante, Spain). Shelled Guara variety almond integuments—normal or contaminated by *Aspergillus*—were used in this work. The almonds contaminated by *Aspergillus* were obtained from the samples rejected by the firm due to the fungal contamination.

A total of 12 kg of almonds without mold and 2 kg of contaminated ones from the same harvest were packaged in high-barrier plastic bags (polypropylene polyethylene, PP.PE) (100 g each). Samples contaminated by *Aspergillu*s were used to determine the evolution of the level of aflatoxins after irradiation treatments.

Radiation Treatments. Irradiation was carried out using a Rhodotron (I.B.A.) circular electron accelerator (Ionmed, Tarancón, Spain) at an energy level of 10 MeV. Treatment lots were deposited in a transporting tape leading to the electron beam; the samples were arranged in a monolayer. The programmed irradiation doses were 3.0, 7.0, and 10.0 kGy; non-irradiated samples were separated as control lots. The treatment protocol and the number of dosimeters per treatment batch, as well as the determination of the real dose absorbed by the fruits, were carried out in the Research and Development Department of Ionmed. Radiochromic dosimeters FTW-60.0 (Far West Technology) were employed, and the absorbed dose was measured at 600 nm in a Genesis-5 spectrophotometer (Espectronic) with an uncertainty of $\Delta abs = 0.006$ for a level of confidence of 95%. An adequate number of dosimeters was randomly placed in both faces of the bags to verify the real dose absorbed by the fruits and to studiesy the penetration of the radiation.

The variability of the real dose of irradiation absorbed by the samples was <1% of the programmed dose applied. The dosimeters also verified the homogeneity of the dose and validated the irradiation process. The treatment conditions and the later readings of the dosimeters are shown in **Table 1**. After irradiation, samples were stored in controlled conditions (20 ± 1 °C and 75% relative humidity) for a period of 5 months, and periodic sampling was carried out.

The efficiency of treatments for avoiding the growth of fungi of the genus *Aspergillus* was verified. The lowest dose of radiation (3 kGy) was applied to samples already contaminated by the mold, and the formation of aflatoxins was observed in both control and treated samples.

Determination of Aflatoxins. The extraction and determination of aflatoxins were carried out in the facilities of the Farming Cooperative Frutos Secos del Mañan. The extractions was carried out on defatted almonds using methanol/water, and they were separated using antibody affinity columns. The quantification and detection were carried out by high-performance liquid chromatography (HPLC) and fluorescence detection with iodine derivatization. Extraction, determination, and quantification of aflatoxins were made according to the AOAC official methods of analysis (*15*).

Lipid Extraction. The fat was extracted in a six-unit extractor (Det-Gras J. P. Selecta S.A., Barcelona, Spain), using petroleum ether (40−60 °C) as extractant; to avoid fat oxidation during the extraction, ether evaporation was carried out in a vacuum.

Fatty Acid Methyl Esters (FAMEs). The FAMEs were obtained according to the *Official Methods of Analysis* (*16*), with some modifications. The preparation of the FAMEs was carried out by direct interesterification of the fat in two stages: formation of free fatty acids by saponification with methanolic NaOH and a later free fatty acids esterification with methanolic HCl.

The methyl esters were analyzed in a gas chromatograph (CG14A; Shimadzu Corp., Kyoto, Japan) with a FID and a TR-Wax capillary column, 0.25 mm × 25 m (Technokroma, S. Coop. C. Ltda., Barcelona, Spain); the carrier gas was nitrogen with a flow rate of 0.8 mL/min, the temperature of the column was isothermal at 200 °C, the temperature in the detector and in the injector was 275 °C, and the identification of the fatty acids was carried out using the retention times relative to commercial standards of Supelco fatty acids (Sigma-Aldrich Quimica, S.A., Madrid, Spain). The results were expressed as a percentage of each fatty acid with regard to the total fat.

Peroxide Value. The peroxide value was determined on the extracted fat, estimated as the iodine released as a product of the oxidation of potassium iodide by the peroxides, or other similar products of fat oxidation. The value obtained was expressed as milliequivalents of O_2 per kilogram of seed; the procedure was carried out according to the methods described by the AOAC (*17*).

Oil Ultraviolet Absorption Coefficients (UV Index). Oil quality was evaluated as the absorbance of a solution containing 0.05 g of oil in 10 mL of cyclohexane under UV light (K_{230}, K_{270}), using a spectrophotometer (model Uvikon 930; Kontron Instruments Ltd.). The value of the UV index was expressed as $R = (K_{232}/K_{270})$ according to the methods described by the AOAC (*17*).

Sensory Determination. Sensory evaluation was conducted by a selected and trained panel comprising five judges with some expertise in tasting other foods. The evaluation was done using 5-point structured scales, 5 being the best and 1 the worst quality. To evaluate the capacity of examination and the sensitivity of the tasters, sucrose was used as a standard for the sweet flavor, bitter almond for the bitter flavor, and oxidized oleic acid for rancidity. The general acceptance quality attribute was assessed as measurement of the acceptability of the product by the consumer using a scale from "very unpleasant" (level 1) to "very pleasant" (level 5). The tasters' selection and training, as well as the fitting-out of the tasting room, were carried out according to UNE 87 (*18*).

Statistics. Tests for significant differences were carried out using the General Linear Model of the SPSS (version 11.0) statistical package. Analysis of variance (ANOVA) was conducted for irradiation doses and storage as factors. When differences were significant, multiple comparisons were made using Tukey's test (*19*), which compares the samples on the basis of the mean of the factors' variances.

RESULTS

The irradiation of samples contaminated with fungus *Aspergillus* showed a clear effect on the formation of aflatoxins

Table 2. Percentages of Fatty Acids Contents [Palmitic Acid (C16:0), Estearic Acid (C18:0), Oleic Acid (C18:1), Linoleic Acid (C18:2), and Linolenic Acid (C18:3)] at Different Ionization Doses and Storage Times[a]

dose (kGy)	storage (days)	C16:0	C18:0	C18:1	C18:2	C18:3	dose (kGy)	storage (days)	C16:0	C18:0	C18:1	C18:2	C18:3
0	0	6.37 ± 0.31	2.46 ± 0.12	68.25 ± 0.45	19.88 ± 0.52	0.28 ± 0.06	7	0	6.88 ± 0.71	2.24 ± 0.13	71.06 ± 0.14	17.67 ± 0.87	tr
	7	6.44 ± 0.01	2.50 ± 0.26	66.78 ± 0.69	19.75 ± 0.96	0.12 ± 0.07		7	6.63 ± 0.12	2.14 ± 0.10	70.11 ± 0.38	18.33 ± 1.57	tr
	14	6.20 ± 0.08	2.20 ± 0.05	70.03 ± 0.53	19.67 ± 0.04	tr		14	6.65 ± 0.19	2.18 ± 0.24	71.06 ± 0.35	17.68 ± 0.17	tr
	21	6.54 ± 0.03	2.48 ± 0.07	69.62 ± 0.05	19.69 ± 0.04	tr		21	6.66 ± 0.46	2.06 ± 0.00	71.46 ± 0.03	18.36 ± 1.50	tr
	28	6.42 ± 0.06	2.35 ± 0.12	69.55 ± 0.27	19.34 ± 0.19	tr		28	6.69 ± 0.17	2.32 ± 0.27	67.97 ± 0.55	18.27 ± 0.06	tr
	43	6.52 ± 0.05	2.41 ± 0.01	69.21 ± 0.33	19.74 ± 0.45	tr		43	6.91 ± 0.31	2.05 ± 0.18	71.14 ± 0.52	18.02 ± 0.93	tr
	58	6.58 ± 0.18	2.38 ± 0.05	68.38 ± 0.76	20.24 ± 0.78	tr		58	6.65 ± 0.04	2.06 ± 0.04	70.71 ± 0.40	20.08 ± 0.39	tr
	74	6.38 ± 0.10	2.33 ± 0.08	66.69 ± 0.09	21.94 ± 0.38	tr		74	7.02 ± 0.37	2.29 ± 0.16	69.89 ± 0.15	18.95 ± 1.11	tr
	121	6.29 ± 0.10	2.20 ± 0.16	69.61 ± 0.20	19.17 ± 0.13	tr		121	6.74 ± 0.10	2.12 ± 0.04	70.74 ± 0.06	18.89 ± 0.10	tr
	157	6.41 ± 0.24	2.25 ± 0.06	69.33 ± 0.39	19.41 ± 0.37	tr		157	6.76 ± 0.16	2.11 ± 0.20	71.22 ± 0.40	18.53 ± 0.31	tr
3	0	7.48 ± 0.39	2.32 ± 0.10	69.10 ± 1.08	18.74 ± 0.80	0.31 ± 0.04	10	0	6.58 ± 0.03	2.38 ± 0.15	69.54 ± 0.44	18.10 ± 0.67	tr
	7	7.01 ± 0.07	2.09 ± 0.06	71.03 ± 0.78	17.16 ± 1.56	0.30 ± 0.03		7	6.50 ± 0.10	2.34 ± 0.12	71.09 ± 0.11	18.37 ± 0.16	tr
	14	6.99 ± 0.22	2.21 ± 0.03	69.29 ± 0.83	18.64 ± 0.35	0.38 ± 0.09		14	6.57 ± 0.26	2.45 ± 0.07	71.00 ± 0.32	18.32 ± 0.88	tr
	21	6.79 ± 0.17	2.28 ± 0.28	69.75 ± 0.24	18.16 ± 0.06	0.28 ± 0.01		21	6.63 ± 0.09	2.38 ± 0.05	69.72 ± 0.17	18.97 ± 0.83	tr
	28	7.04 ± 0.44	2.25 ± 0.12	68.37 ± 0.05	18.34 ± 1.04	0.43 ± 0.46		28	6.53 ± 0.41	2.62 ± 0.03	70.59 ± 0.32	18.55 ± 1.10	tr
	43	7.06 ± 0.31	2.28 ± 0.16	69.24 ± 0.80	18.66 ± 0.28	0.34 ± 0.04		43	6.59 ± 0.28	2.46 ± 0.02	71.40 ± 0.24	18.58 ± 1.69	tr
	58	7.19 ± 0.24	2.36 ± 0.18	68.38 ± 0.14	18.65 ± 1.67	0.33 ± 0.03		58	6.64 ± 0.26	2.47 ± 0.39	71.20 ± 0.17	18.89 ± 0.34	tr
	74	7.00 ± 0.14	2.23 ± 0.01	68.81 ± 0.18	17.55 ± 1.23	0.44 ± 0.02		74	6.09 ± 0.25	2.23 ± 0.01	71.42 ± 0.45	17.12 ± 0.31	tr
	121	7.16 ± 0.67	2.32 ± 0.09	68.15 ± 0.11	18.74 ± 1.69	0.37 ± 0.03		121	6.77 ± 0.16	2.55 ± 0.20	70.84 ± 0.01	19.15 ± 1.27	tr
	157	6.83 ± 0.21	2.19 ± 0.04	70.52 ± 0.48	18.29 ± 0.09	0.10 ± 0.04		157	6.63 ± 0.05	2.41 ± 0.09	71.94 ± 0.60	18.27 ± 0.46	tr
dose		**	**	**	**	**	dose		**	**	**	**	ns
storage		ns	ns	ns	ns	ns	storage		ns	ns	ns	ns	ns
dose × storage		ns	ns	ns	ns	ns	dose × storage		ns	ns	ns	ns	ns

[a] Statistical differences were analyzed by ANOVA ($p < 0.05$); ns, not significant; **, significance at 99%; tr, trace, <0.1.

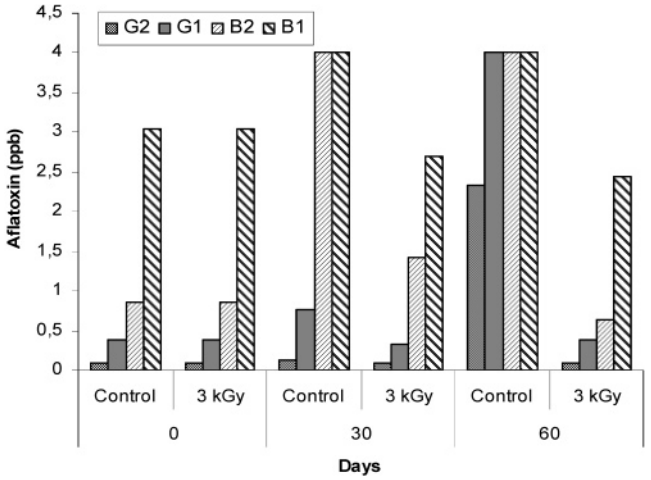

Figure 1. Evolution of the level of aflatoxins G_1, G_2, B_1, and B_2 with storage period for control and irradiated at 3 kGy samples.

G_1, G_2, B_1, and B_2 (**Figure 1**). In control samples, the aflatoxin levels increased over time, whereas, in ionized samples, it remained constant during the whole storage period. Therefore, the ionization at minimum doses of 3 kGy showed a great efficacy for the destruction of the existing colonies of *Aspergillus* (*20*, *21*), but it could not eliminate the already formed aflatoxins in the sample.

Effect of Irradiation on Fatty Acids Composition The effects of irradiation on the samples were not expressed in the physical characteristics as in the lipid content (*20*, *22*, *23*) (data not shown). A significant factor, in assessing the effect of the irradiation treatments, is the fatty acids composition of the lipid fraction. In almond, the main fatty acids are oleic and linoleic acids (*23*−*26*), both being unsaturated with one and two double bonds, respectively, a fact favoring the relative speed of oxidation in comparison to other plant foods with a lower content of these fatty acids.

Table 2 shows the results obtained from the determination of the percentage composition of the oleic, stearic, linoleic, linolenic, and palmitic fatty acids, with respect to the total lipids, according to the storage period and the dose applied. The contents of saturated palmitic (C16:0) and stearic (C18:0) fatty acids changed but, whereas for palmitic acid the change was at all doses, only stearic acid showed a significant variation when the maximum dose of 10 kGy was applied.

Table 3. Homogeneous Subset from the Multiple-Comparisons Test (Tukey's Test) for Each Fatty Acid after Irradiation[a]

dose (kGy)	C16:0	C18:0	C18:1	C18:2	C18:3
0	6.41 a	2.35 a	68.7 a	19.7 b	tr a
3	7.06 c	2.2 a	69.2 ab	18.49 a	0.33 b
7	6.76 b	2.1 a	70.5 bc	18.98 ab	tr a
10	6.55 ab	2.5 b	70.8 c	19.0 ab	tr a

[a] Statistical differences were analyzed by ANOVA ($p < 0.05$); tr, trace, <0.1; subset, c > b >a.

With regard to unsaturated fatty acids, the content of linoleic acid (18:2) in the irradiated samples was slightly lower than that in the control samples, whereas the content of linolenic acid (18:3) showed significant differences, in comparison to control samples, only in the samples irradiated at 3 kGy. The statistical analysis shows that significant differences only appear according to the irradiation treatment applied and, therefore, the differences during the storage period for the same irradiation doses are not statistically significant. **Table 3** shows the homogeneous subsets into which the samples are distributed according to the applied irradiation dose.

The irradiated samples showed an oleic acid content significantly higher than that of the control samples; these differences were higher at the highest dose, maybe due to a delay in the desaturation of oleic to linoleic acid caused by the treatment (*27*). During the 5 months of storage, no significant changes were observed in the lipid composition, which was modified at the precise moment of the treatment or immediately after, but remained constant during the whole storage period.

The contents of other fatty acids did not show significant changes with the doses irradiated or during the period after the

Table 4. Variation of Total Fatty Acids Saturated, Unnsaturated, and Ratio of Unnsaturated/Saturated Based on Ionization Dose and Storage Time[a]

		storage									
	dose (kGy)	0 days	7 days	14 days	21 days	28 days	43 days	58 days	74 days	121 days	157 days
% saturated	0	8.83 ± 0.44	8.94 ± 0.26	8.40 ± 0.03	8.95 ± 0.10	8.76 ± 0.06	8.93 ± 0.04	8.96 ± 0.14	8.71 ± 0.02	8.49 ± 0.26	8.66 ± 0.29
	3	9.79 ± 0.29	9.09 ± 0.01	9.20 ± 0.25	9.07 ± 0.45	9.29 ± 0.56	9.34 ± 0.47	9.55 ± 0.42	9.23 ± 0.15	9.48 ± 0.76	9.02 ± 0.26
	7	9.12 ± 0.59	8.77 ± 0.02	8.83 ± 0.43	8.72 ± 0.46	9.01 ± 0.44	8.95 ± 0.50	8.71 ± 0.00	9.31 ± 0.52	8.86 ± 0.05	8.87 ± 0.36
	10	8.96 ± 0.18	8.85 ± 0.02	9.02 ± 0.33	9.71 ± 0.44	9.15 ± 0.44	9.05 ± 0.30	9.11 ± 0.65	8.33 ± 0.24	9.32 ± 0.35	9.03 ± 0.13
% unsaturated	0	88.13 ± 1.08	86.53 ± 0.65	88.70 ± 0.49	88.91 ± 0.00	88.89 ± 0.46	88.54 ± 0.12	88.63 ± 0.02	88.64 ± 0.47	88.78 ± 0.33	88.73 ± 0.02
	3	87.83 ± 0.89	88.19 ± 1.22	87.93 ± 1.48	88.90 ± 1.18	86.71 ± 1.00	88.90 ± 1.09	87.03 ± 1.53	86.37 ± 1.05	86.90 ± 0.58	88.81 ± 0.58
	7	88.73 ± 1.01	89.44 ± 1.95	88.74 ± 1.18	90.83 ± 0.53	88.24 ± 0.61	89.16 ± 1.46	90.7 ± 0.091	88.84 ± 1.27	90.63 ± 0.05	89.75 ± 1.71
	10	90.23 ± 0.23	90.46 ± 0.05	90.32 ± 0.44	88.69 ± 0.66	90.13 ± 0.22	90.38 ± 0.54	90.09 ± 0.50	88.54 ± 1.14	89.99 ± 0.26	90.20 ± 0.14
unsat/saturated	0	9.98 ± 0.37	9.69 ± 0.69	10.55 ± 0.02	9.94 ± 0.11	10.14 ± 0.12	9.92 ± 0.03	9.89 ± 0.15	10.18 ± 0.07	10.46 ± 0.36	10.25 ± 0.35
	3	8.97 ± 0.46	9.70 ± 0.13	9.56 ± 0.42	9.82 ± 0.62	9.35 ± 0.46	9.53 ± 0.60	9.11 ± 0.24	9.35 ± 0.04	9.19 ± 0.67	9.85 ± 0.35
	7	9.76 ± 0.96	10.20 ± 0.24	10.07 ± 0.85	10.43 ± 0.61	9.82 ± 0.88	9.98 ± 0.83	10.42 ± 0.00	9.56 ± 0.78	10.23 ± 0.07	10.13 ± 0.61
	10	10.07 ± 0.23	10.22 ± 0.02	10.03 ± 0.41	9.15 ± 0.49	9.87 ± 0.50	9.99 ± 0.39	9.92 ± 0.76	10.63 ± 0.07	9.66 ± 0.39	9.99 ± 0.16
dose		**	**	**	**	**	**	**	**	**	**
storage		ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
dose × storage		ns	ns	ns	ns	ns	ns	ns	ns	ns	ns

[a] Statistical differences were analyzed by ANOVA ($p < 0.05$); ns, not significant; **, significance 99%.

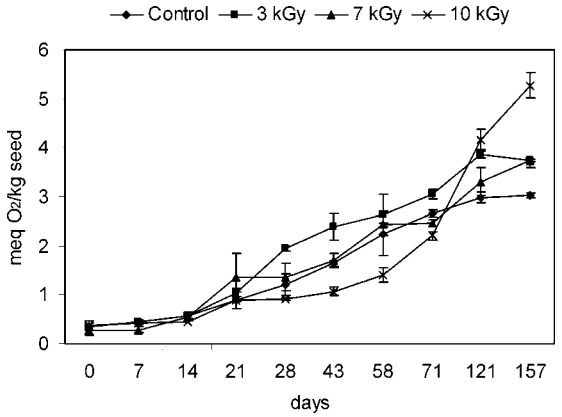

Figure 2. Peroxide values at different doses and storage.

storage; their average contents are <0.1% except palmitoleic acid (0.4−0.5%).

Table 4 shows the total contents of saturated and unsaturated fatty acids and the ratio of unsaturated/saturated fatty acids. The results indicate that there is a significant change ($p < 0.05$) in these percentages in samples exposed to irradiation; thus, the percentage of saturated fatty acids increased with the treatments, whereas the percentage of unsaturated fatty acids decreased. Thus, the unsaturated/saturated ratio decreased with the treatments, and this influence was higher at 3 kGy than at the other doses, resulting in a decrease in the nutritional quality of the oil.

Effect of Irradiation on Peroxide Value. Both the applied irradiation treatments and the storage period had a significant influence on the peroxide index, and a significant interaction between the two factors was also observed. These statistical differences are clearly seen in **Figure 2**, where an increase in fatty acids oxidation during storage, both in the control and in the irradiation treatments, was observed; the peroxide value went from 0.34 to 3 mequiv of O_2/kg in control fruits, to 3.7 mequiv of O_2/kg in those treated at 3 or 7 kGy, and to 5 mequiv of O_2/kg in fruits treated at the maximum dose of 10 kGy.

The interaction of the factors time and treatment is reflected in the fact that the increase in the peroxide index was not linear with time, but showed well-distinguished slopes according to the irradiation dose and the storage period. Thus, immediately after the application of the treatments, there were no significant differences in the peroxide index among the studied samples; however, from day 28, this index significantly increased in the samples treated at 3 kGy and, to a lesser extent, in those treated at 7 kGy and in control fruits. Samples treated at 10 kGy showed a less-pronounced tendency to increase than the other samples during the period between 28 and 71 days; this tendency was observed until month four, when the samples treated at 10 kGy showed a significant increase while the rest remained relatively stable.

Uthman et al. (*11*) found a similar behavior when irradiating shelled and toasted almonds at doses of 6 and 10.5 kGy; with the lowest dose they showed, at the beginning and until 8 weeks of storage, a higher peroxide value than those irradiated at 10.5 kGy.

The results found in this study indicate that the peroxide value of the fat in almonds stored for 5 months at 20 °C is not affected by irradiation with accelerated electrons at doses lower than 7 kGy, because after 157 days, levels of peroxides were similar to those found in non-irradiated control fruits. It seems that for higher doses (10 kGy) the induction period is extended for up to 8 weeks and, therefore, a delay in the start of the peroxidation is observed in comparison to control samples.

Effect of Irradiation on UV Index. Polyunsaturated fatty acids, such as linolenic and linoleic acid, have their double bonds placed according to the system called "malonic". One of the reactions occurring during the lipid oxidation implies the transformation of the malonic systems into conjugated systems, which are less stable against later oxidations. These conjugated systems can be detected by UV spectrophotometry, and they tend to break down and result in carbonylic compounds, aldehydes, and ketones, which, together with other compounds, give the food the "rancid smell" that is disliked by the consumer (*28*). The index R (K_{232}/K_{270}), which compares the absorbances at 232 and 270 nm, is employed for evaluation of the fat oxidation (the higher the oxidation, the lower the value of the index) and, together with the peroxide value, it is a good indicator of the oil quality (*29*, *30*).

Table 5 shows the evolution of this index in the almonds; it significantly decreased from the first moment for all treatments applied and then remained constant during the whole storage period. The greatest decrease in R was obtained when the samples had been treated at 3 kGy, from an initial value of 28, similar to that of non-irradiated samples, to 16. When 7 or 10 kGy was applied, the decrease was lower, values of 18 being reached in both cases.

Table 5. UV Index Variation at Different Ionization Doses and Storage Times[a]

dose (kGy)	storage (days)	R (K_{232}/K_{270})	K_{232}	K_{270}	dose (kGy)	storage (days)	R (K_{232}/K_{270})	K_{232}	K_{270}
0	0	28.60 ± 0.99	2.12 ± 0.34	0.07 ± 0.01	7	0	18.93 ± 1.41	1.96 ± 0.06	0.11 ± 0.02
	7	28.09 ± 0.09	1.84 ± 0.01	0.07 ± 0.00		7	18.89 ± 0.06	2.22 ± 0.15	0.12 ± 0.01
	14	28.58 ± 0.61	1.82 ± 0.20	0.06 ± 0.01		14	19.17 ± 0.56	2.08 ± 0.19	0.11 ± 0.00
	21	27.06 ± 0.70	1.91 ± 0.05	0.07 ± 0.00		21	18.38 ± 1.27	1.96 ± 0.03	0.11 ± 0.01
	28	27.45 ± 0.37	1.84 ± 0.13	0.07 ± 0.00		28	19.61 ± 0.35	2.30 ± 0.06	0.12 ± 0.01
	43	27.45 ± 0.09	1.84 ± 0.17	0.07 ± 0.01		43	19.61 ± 0.62	2.30 ± 0.11	0.12 ± 0.01
	58	28.58 ± 1.66	1.89 ± 0.08	0.07 ± 0.00		58	19.63 ± 0.88	2.27 ± 0.13	0.12 ± 0.03
	74	26.72 ± 1.50	2.09 ± 0.09	0.08 ± 0.01		74	19.36 ± 0.62	2.49 ± 0.10	0.13 ± 0.00
	121	29.23 ± 1.76	2.38 ± 0.43	0.08 ± 0.01		121	17.63 ± 0.01	2.77 ± 0.30	0.16 ± 0.02
	157	29.46 ± 1.30	2.43 ± 0.58	0.08 ± 0.02		157	18.20 ± 1.20	3.18 ± 0.03	0.18 ± 0.03
3	0	15.80 ± 1.05	1.85 ± 0.37	0.12 ± 0.01	10	0	19.63 ± 1.18	2.08 ± 0.40	0.10 ± 0.03
	7	14.92 ± 0.44	3.16 ± 1.98	0.21 ± 0.14		7	20.46 ± 0.28	2.21 ± 0.07	0.11 ± 0.00
	14	14.89 ± 0.50	2.10 ± 0.13	0.14 ± 0.00		14	20.52 ± 0.60	2.18 ± 0.15	0.11 ± 0.01
	21	15.48 ± 0.85	2.21 ± 0.04	0.14 ± 0.01		21	20.35 ± 1.05	1.85 ± 0.08	0.09 ± 0.01
	28	16.16 ± 1.26	2.15 ± 0.12	0.13 ± 0.02		28	19.35 ± 1.08	2.24 ± 0.24	0.12 ± 0.02
	43	16.16 ± 1.40	2.15 ± 0.05	0.13 ± 0.02		43	19.35 ± 0.45	2.24 ± 0.12	0.12 ± 0.01
	58	16.96 ± 0.39	2.20 ± 0.14	0.13 ± 0.01		58	19.29 ± 0.23	2.32 ± 0.20	0.12 ± 0.01
	74	16.41 ± 1.00	2.23 ± 0.13	0.14 ± 0.01		74	16.83 ± 0.05	2.27 ± 0.20	0.13 ± 0.01
	121	16.87 ± 0.35	1.68 ± 0.15	0.10 ± 0.12		121	17.36 ± 0.18	2.37 ± 0.24	0.14 ± 0.01
	157	17.32 ± 0.34	2.43 ± 0.55	0.14 ± 0.03		157	17.52 ± 1.42	2.81 ± 0.25	0.16 ± 0.00
dose		**	ns	**					
storage		ns	ns	ns					
dose × storage		ns	ns	ns					

[a] Statistical differences were analyzed by ANOVA ($p < 0.05$); ns, not significant; **, significance 99%.

In general, a decrease in the oil quality was observed as a consequence of the irradiation treatments applied, sharp differences occurring according to the dose, although levels resulting in an unacceptable quality, according to the classification proposed by Cabada et al. (*31*) for olive oils, were never found.

These results agree with those obtained for the peroxide value, where the lowest dose applied (3 kGy) was the one which, in the short-term, had the greatest effect on the lipid oxidation, and, from the fourth week, the doses of 7 and 10 kGy showed a higher effect on the lipid peroxidation.

Effect of Irradiation on Organoleptic Properties of Almonds. To verify if the irradiation doses had affected organoleptically the almonds, sensory studies were carried out during the whole storage period, with a selected and trained panel of five tasters, who evaluated the sensory attribute "rancid flavor" and its effect on the global appreciation, a correlation between the rancidity found by the taste panel and the lipid peroxidation; no clear sensory differences were found between control samples and those irradiated up to the end of the storage period. Therefore, the results obtained after 157 days are shown here.

Figure 3 shows the numeric assessment given by the panel of tasters. A decrease in the parameter "global quality" exists both in control and in irradiated samples, although sharp differences can be appreciated when the doses of 3 and 7 kGy are compared with that of 10 kGy. A long storage, 4 months at 20 °C, had affected negatively the samples, both control and irradiated.

This situation is verified when rancidity, a sensory attribute indicating the degree of fat oxidation, was analyzed; values for samples treated at doses of 3 or 7 kGy were slightly lower (∼0.4) than for the control samples. The panel of tasters did not find perceptible differences among the three samples regarding the rancid flavor. On the contrary, the dose of 10 kGy showed a completely different profile, with very low values for the global appreciation and rancidity, a fact indicating that at the maximum level of authorized doses there are changes in the lipid composition, implying the formation of hydroperoxides, which favor oxidation and the appearance of the rancid flavors detected by the panel of tasters.

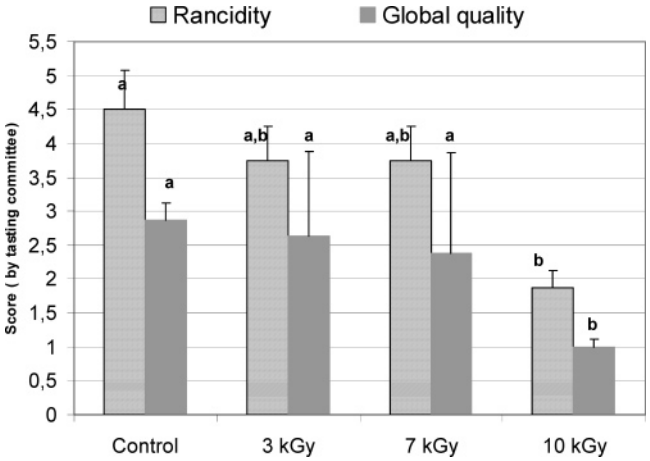

Figure 3. Tasting committee scores for rancidity and global quality attributes.

DISCUSSION

The effects of radiation on food depend, among other factors, on the kind of food irradiated, the dose applied, and the conditions of application of the treatment (*32*). One of the main effects of the irradiation is the formation of free radicals, which are responsible for the lipid degradation and oxidation, resulting in volatile compounds generating off-odor. This limits the shelf life of the product, even for those products with fat levels under 1% of lipids (*33*).

The lipid fraction of the almond seed ranges from 50 to 60% and, within this fraction, ∼80−90% are mono- or polyunsaturated fatty acids (*20*, *23*, *24*, *26*, *34*). The degree of unstauration of the fatty acids is a very significant factor in the oxidation speed because, although saturated fatty acids oxidize only at temperatures >60 °C, polyunsaturated fatty acids oxidize during the storage period, even at freezing points (*35*, *36*). Thus, the

lipid fractions of plants, as in this case for almond, can be easily oxidized when ionized, due to their high degree of unstauration (*37*).

There is disagreement in the literature about the optimum conditions for the irradiation of dried fruits without producing changes in their organoleptic quality. Most authors agree that doses between 0.3 and 0.9 kGy result in a correct hygienization without the induction of undesirable changes (*38*, *39*). Rodees et al. (*38*) found that for these doses (0.3−0.9 kGy), no changes were caused in the foodstuff immediately after the treatment, but a sensory quality deterioration was observed during the storage period. On the other hand, Khan et al. (*40*) did not find changes at doses over 1 kGy during the storage period, and Wilson-Kahashita et al. (*41*), when studying walnuts irradiated at doses from 5 to 20 kGy, did not find changes in the lipid composition, the iodine indices, or the levels of TBA after the treatment, but there was a significant increase in the peroxide levels during storage.

Many authors have found changes in the lipid composition caused by irradiation treatments (*9*, *10*, *42*). Todoriki et al. (*27*, *43*), in studies on the irradiation of potatoes, found an increase in the content of linolenic acid and a decrease in the content of linoleic acid, as well as a delay in the desaturation of the saturated fatty acids for doses of 0.5 kGy. Chiou et al. (*44*), in studies of peanuts irradiated at increasing doses of up to 20 kGy, found decreases in the contents of linoleic and linolenic acids, which were higher as the irradiation doses increased but lower when the samples were stored at low temperatures.

In this study, the almond seeds irradiated at 3, 7, or 10 kGy showed changes in the lipid fraction immediately after the treatment, both in the fatty acid composition and in the formation of compounds that absorb UV radiation; on the contrary, no significant differences were observed between the applied doses during the 157 days of storage at 20 °C. On the other hand, the value of the peroxide index increased during the storage period, both in control and in irradiated samples, with significant differences between the dose of 10 kGy and the remaining samples. These results agree with those obtained by other authors for the irradiation of dried fruits (*9*, *11*). Likewise, although it is known that lipids are sensitive to irradiation and that the presence of oxygen accelerates the autoxidation (*45*), some authors have stated that, after long storage periods, the final oxidation products do not differ from those found in the non-irradiated lipids (*46*).

Thus, in this study, it has been verified that irradiation treatments affect the processes of lipid degradation in almond at lower levels than could be expected when their high fat content and fatty acid composition are taken into consideration. Although a significant increase in the peroxide value was observed during the storage period, this increase was only appreciated at the maximum dose of 10 kGy and, when the changes in the fatty acid composition and the formation of products absorbing in the UV range were studied, there were no differences among the doses applied, whereas the index *R* did not change during the storage period.

On the one hand, the temperature of the product in the irradiation treatment can rise between 2 and 5 °C, causing an increase of the oxygen solubility in the almond fat, which increases the quantity of oxygen disolved in it and thus the oxidative reactions of the fatty acids (*47*). On the other hand, for foods with low moisture contents, elimination of the products of the radiolysis takes longer (*48*−*50*). Thus, the initial decrease of the oil quality after the treatment, according to the index *R* (K_{232}/K_{270}) and the change in the fatty acid composition, could be explained.

Although an increase in the peroxide value was observed during the storage period, for all irradiation doses, significant differences in the peroxide value were found only for samples irradiated at the maximum dose of 10 kGy. This stability against oxidation by irradiation at lower doses could be due, on the one hand, to the low water content of the almonds, a fact inhibiting the mobility of the radicals and peroxides produced during oxidation (*48*−*51*), and, on the other hand, to the high tocopherols content of almonds.

It has been observed that treatments with doses under 7 kGy do not affect the organoleptic properties of the almonds, although slight changes in the lipid fraction were observed, whereas at 10 kGy, the sensory quality is negatively affected. Therefore, the dose of 3 kGy in almond irradiation can be considered as adequate and enough for their correct hygienization without significant quality losses.

LITERATURE CITED

(1) FAO−UNESCO. *Soil Map of the World*, revised legend; Word Resources Report 60; FAO: Rome, Italy, 1988; p 115.

(2) Hoosmand, H.; Klopsfenstein, C. F. Effects of gamma irradiation on mycotoxin disappearance and amino acid contents of corn, wheat, and soybeans with different moisture contents. *Plant Foods Hum. Nutr.* **1995**, *47*, 227−238.

(3) Alvarez, M.; Prieto, E.; Mesa, J.; Fraga, R.; Fung, V. Desinfestación del frijol de soja por irradiación. *Alimentaria* **1996**, 39−41.

(4) Murano, P. S. Microbiology of irradiated foods. In *Food Irradiation: A Source Book*; Murano, E. A., Ed.; Iowa State University Press: Ames, IA, 1995.

(5) Murano, P. S. Quality of irradiated food. In *Food Irradiation: A Source Book*; Murano, E. A., Ed.; Iowa State University Press: Ames, IA, 1995.

(6) Comunicación de la comisión relativa a los alimentos e ingredientes alimentarios autorizados para el tratamiento con radiación ionizante en la comunidad. *Off. J. Eur. Communities* **2001**, *C*241, 29.08, 6−11.

(7) Kildkast, D. Irradiation and combination treatment. *Food Control* **1991**, *1*, 6−8.

(8) Narvaiz, P.; Lescano, G.; Kairiyama, E. Irradiation of almonds and cashew nuts. *Lebensm. Wiss. -Technol*. **1992**, *25*, 232−235.

(9) Sattar, A.; Mohammad, J.; Saleem, A.; Jan, M.; Ahmad, A. Effect of fluorescent light, gamma radiation and packages on oxidative deterioration of dry nuts. *Sarhad J. Agric.* **1990**, *6* (3), 235−240.

(10) O'Mahony, M.; Wong, S. Y.; Odbert, N. An initial sensoryexaminationof the effect of postharvest irradiation on almonds. *J. Ind. Irradiat. Technol*. **1985**, *3* (2), 135−140.

(11) Uthman, R. S.; Toma, R. B.; Garcia, R.; Medora1, N. P.; Cunningham, S. Lipid analyses of fumigated vs irradiated raw and roasted almonds. *J. Sci. Food Agric*. **1998**, *78*, 261−266.

(12) Ahmad, A.; Sattar, A.; Ali, I.; Iqbal, M. Z. Effect of gamma irradiation on thermoluminiscence emissions from dust of Asian plant nuts. *Nahrung* **1999**, *43* (1), 39−41.

(13) Aegerter, A. F.; Folwell, R. J. Selected alternatives to methyl bromide in the postharvest and quarantine treatment of almonds and walnuts: an economic. *J. Food Process. Preserv.* **2001**, *6* (25), 389−410.

(14) Khan, H. M.; Bhatti, I. A.; Delincée, H. Thermoluminiscence of contaminating minerals for the detection of radiation treatment of dried fruits. *Radiat. Phys. Chem*. **2002**, *63*, 403−406.

(15) AOAC. In *Official Methods of Analysis*; Association of Official Analytical Chemists: Washington, DC, 1994; Method 990.31.

(16) *Métodos Oficiales de Análisis*; Ministerio de Agricultura Pesca y Alimentación. Dirección General de Política Alimentaria. Preparación de los ésteres metílicos; Madrid, Spain, 1993; Vol. 41 (2), p 135.

(17) AOAC. Peroxide value 26.024. In *Official Methods of Analysis*; Association of Official Analytical Chemists: Washington, DC, 1985.
(18) UNE 87-004-79. Análisis sensorial. *Guía para la instalación de una sala de cata*; Asociación Española de Normalización y Certificación: Madrid, Spain, 1995.
(19) Tukey, J. W. *Exploratory Data Analysis*, 1st ed.; Addison-Wesley: Reading, MA, 1977.
(20) Al-Bachir, M. Effect of gamma irradiation on fungal load, chemical and sensory characteristics of walnuts (*Juglans regia* L.). *J. Stored Prod. Res.* **2003** [(Artículo en prensa) disponible en línea en: www.sciencedirect.com (consulta 25 de Julio de 2003)].
(21) Chiou, R. Y. Y. Gamma irradiation of peanut kernels to control growth and to diminish aflatoxin contamination. *Acta Aliment.* **1994**, *25*, 311−314.
(22) García-Pascual, P.; Mateos, M.; Carbonell, V.; Salazar, D. M. Influence of storage conditions on the quality of shelled and roasted almonds. *Biosyst. Eng.* **2003**, *84* (2), 201−209.
(23) Kazantzis, I.; Nanos, G. D.; Stavroulakis, G. G. Effect of harvest time and storage conditions on almond kernel oil and sugar composition. *J. Sci. Food Agric.* **2003**, *83*, 354−359.
(24) Zlatanov, M.; Ivanov, S.; Aitzetmüller, K. Phospholipid and fatty acid composition of Bulgarian nut olis. *Fett/Lipid* **1999**, *101* (11), 437−439.
(25) Zacheo, G.; Cappello, M. S.; Gallo, A.; Santino, A.; Cappello, A. R. Changes associated with postharvest aging in almond seeds. *Lebensm. Wiss. -Technol.* **2000**, *33*, 415−423.
(26) Nanos, G. D.; Ioannis, K.; Panagiotis, K.; Christos, P.; Stavroulakis, G. G. Irrigation and harvest time affect almond kernel quality and composition. *Sci. Hortic.* **2002**, *96*, 249−256.
(27) Todoriki, S.; Hayashi, T.; Kouchi, H. Effects of gamma-irradiation on lipid metabolic changes of potato tubers in response to mechanical injury. *Biosci., Biotechnol., Biochem.* **1992**, *56* (12), 1991−1994.
(28) Wills, E. D. Studies of lipids peroxides formation in irradiation of synthetic diets and the effects of storage after irradiation. *Int. J. Radiat.* **1981**, *4*, 383−401.
(29) Carballido, A.; Prestamo, G. Características espectrofotométricas de los aceites extraídos de almendras, avellanas, cacahuetes y piñones. *An. Bromatol.* **1970**, *22*, 80−100.
(30) Borregón, M.; Carballido, A.; Valdehita, M. T. Espectrofotometría en la zona ultravioleta de aceites de oliva, soja, cacahuete, girasol y sus mezclas. *An. Bromatol.* **1965**, *17*, 360−388.
(31) Cabada, L.; Carballido, A.; Villanúa, L.; Valdehita, M. T. Aplicación de la espectrofotometría al análisis del aceite de oliva. *An. Bromatol.* **1963**, *15*, 27−52.
(32) Sendra, E.; Capellas, M.; Guamis, B.; Felipe, X.; Mor-Mur, M.; Pla, R. Revisión: Irradiación de alimentos. Aspectos generales. *Food Sci. Technol. Int.* **1996**, *2*, 1−11.
(33) Bello-Gutiérrez, J. Las alteraciones de los lípidos de los alimentos. In *Ciencia Bromatológica. Principios Generales de los Alimentos*; Díaz de Santos: Madrid, Spain, 2000.
(34) Sánchez-Bel, P.; Madrid, R.; Guillén, I.; Romojaro, F. La calidad de la almendra Española. II. Fracción lipídica. *Cuad. Fitopatol.* **2001**, *18*, 49−54.
(35) Nawar, W. W. Reaction mechanisms in the radiolysis of fats: a review. *J. Agric. Food Chem.* **1978**, *26*, 21−25.
(36) Nawar, W. W. *Lipids*. Fennema, O., Ed., Food Chemistry; Marcel Dekker: New York, 1985; pp 125−135.
(37) St-Lèbe, L.; Raffi, J.; Hénon, Y. *Le Traitement Ionisant des Denrées Alimentaries*; Commissariat à l'Energie Atomique; 1982; report R-5182.
(38) Rhodes, A. A. *Irradiation Disinfectation of Dried Fruits and Nuts*; final report to U.S. Department of Agriculture; 1986; p 229.
(39) Wahid, M.; Sattar, A.; Neelofar, A.; Khan, I.; Ehlermann, D. A. E. Radiation disinfestation and quality of dried fruits. *Acta Aliment.* **1987**, *16*, 159−166.
(40) Khan, I.; Sattar, A.; Wahid, M.; Jan, M. Radiation disinfectation of dry fruits. In *Radiation Disinfectation of Food and Agricultural Products*; Moy, J. H., Ed.; University of Hawai Press: Honolulu, HI, 1985; pp 207−221.
(41) Wilson-Kahashita, G.; Gerdes, D. L.; Hall, W. R. The effect of gamma irradiation on the quality of English walnuts (*Junglans regia*). *Lebensm. Wiss. -Technol.* **1995**, *28*, 17−20.
(42) Ajlouni, S.; Hamdy, M. K. Effect of combined gamma-irradiation and storage on biochemical changes in sweet potato. *J. Food Sci.* **1988**, *53*, 477−481.
(43) Todoriki, S.; Kazuhiro, D.; Hayashi, T. Lipid content and fatty acid composition of gamma-irradiated potato tubers. *Nippon Shokuhin Kogyo Gakkaishi* **1994**, *41*, 358−362.
(44) Chiou, R. Y. Y.; Shyu, S. L.; Tsai, C. L. Characterization of gamma irradiated peanut kernels stored under ambient and frozen conditions. *J. Food Sci.* **1991**, *56*, 1375−1377.
(45) Diehl, S. J. *The Safety of Irradiated Foods*; Dekker: New York, 1990.
(46) Urbain, W. N. *Food Irradiation*; Academic Press: London, U.K., 1986.
(47) Maskan, M.; Karatas, S. Storage stability of whole-split pistachio nuts (*Pistachia vera* L.) at various conditions. *Food Chem.* **1992**, *66*, 227−233.
(48) Hayashi, T.; Aoki, S. Effect of irradiation on the carbohydrate metabolism responsible for sucrose accumulation in potatoes. *J. Agric. Food Chem.* **1985**, *33*, 13−17.
(49) Hayashi, T.; Kawashima, K. Activities of enzymes of sugar metabolism in gamma-irradiated potato tubers. *J. Food Sci.* **1983**, *48*, 1242−1245.
(50) Thayer, D. W. Food Irradiation: Benefits and concerns. *J. Food Qual.* **1990**, *13*, 147−169.
(51) Komiya, T.; Nara, S. The effects of moisture content on the formation of radicals in various starches by gamma-irradiation. II. Changes in radical contents of various irradiated starches in relation to adsorption and desorption of moisture. *Food Irradiat.* **1974**, *9*, 62−68.

Received for review April 14, 2004. Revised manuscript received January 6, 2005. Accepted January 7, 2005.

JF040184R