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Application of EPR for the detection of irradiated cinnamon

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Abstract

The treatment of foodstuff by gamma-irradiation has been showed to be an adequate technique for improving their hygienic quality and extending their shelf-life. Spices are widely used in the food industry and they are attractive candidates for irradiation. It is important assure an effective means for inactivating microorganism with a minimal chemical alteration and have reliable and sensitive detection methods for identification of radiation processing of the foodstuffs.

The aim of the present work is to study the decomposition of some components of cinnamon (cinnamaldehyde and cinnamic acid) and to study by EPR the behavior of the radiation-induced radicals in ground and bark cinnamon.

Dose-response curves for the decomposition of cinnamaldehyde and cinnamic acid show that these compounds are sensitive to radiation and at 10 kGy there is about 70 % of decomposition.

The EPR spectrum of irradiated cinnamon represented that obtained from foodstuff containing high levels of cellulose. The EPR signals recorded after the exposure to gamma rays is specific enough as compared with those observed with non-irradiated samples.

Kinetic of fading on the intensity on the radiation-induced EPR signal from irradiate ground cinnamon at 7.5 kGy shows that the signal remains after 15 days of irradiation.

Keywords: spice irradiation, irradiation detection, free radicals, electron spin resonance (EPR)

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1. Introduction

The treatment of foodstuff by γ-irradiation has showed to be a reliable and fast method for improving their hygienic quality and extending their shelf life. Spices are widely used in the food industry and in domestic cooking. Since they often suffer high microbiological contamination, they are attractive candidates for irradiation (Farkas, 1996; 2001). However, regulation in several countries limits the use of radiation treatment of food. Also, consumers of many countries have remained skeptical about food preservation by ionizing radiation. It is therefore important to ensure an effective means for inactivating microorganism with a minimal chemical alteration of the components of food and have different reliable and sensitive detection methods for identification of radiation processing of the foodstuffs (Delincée, 1998; Delincée and Soika, 2002; Yordanov and Gancheva, 2000; Stachwicz et al., 1998). Dose of 3 to 10 kGy, sufficient for pasteurization, do not influence the sensory properties of majority of spices.

The techniques for identification of irradiated food are classified in (A) physical, (B) chemical and (C) biological. Among the physical methods EPR is the leading method for identification of irradiated food because of the free radicals that are formed upon irradiation. The radiation induced free radicals are long lived in the solid state and are typically detectable by EPR (Harire et. al., 1997, Yordanov, 2004).

. Dry products, such as species, are less affected chemically by radiation than items of high water contain. Small changes in the chemical composition of spices at radiation decontamination dose levels seem to have no practical significance (Farkas, 2001).

The aim of the present work is to study the decomposition of some components of cinnamon and to study the behavior of the radiation-induced radicals in ground cinnamon using EPR technique.

2. Experimental

2.1 Chemical and Glassware

Cinnamon samples (*Cinnamomum zeylanicum N*) used in this work were purchased from local commercial brands, ground and as bark.
Cinnamaldehyde and cinnamic acid were purchased from Sigma Chemical Co. They were used without any treatment. The compounds were irradiated in methanol-water solutions. For cinnamic acid the concentration was 1.35×10^{-3}M in 30 % methanol-water. Cinnamaldehyde concentration was 2.35×10^{-2} M in 60% methanol-water solution. The preparation of chemicals and the cleaning of the glassware were performing the standard procedures used in Radiation Chemistry. The glassware was cleaned with a sulfo-nitric solution (O´Donnell and Sangster, 1970). The samples were deaerated and irradiated in glass tubes.

2.2 Irradiation

A part of every sample was left non-irradiated. All, non-irradiated and irradiated samples were keep under the same conditions. The storage took place at 22C for 30 days and 40% relative humidity.

The samples were irradiated in a cobalt–60 gamma source (Gammabeam 651 PT). The

absorbed doses varied from 1 to 15 kGy. The dose rate was 82.7 Gy/min. The doses were selected to cover the dose range used in commercial food irradiation.

2.3 Analysis

The cinnamaldehyde was analyzed by UV spectroscopy at 298 nm and also by EPR. Cinnamic acid was analyzed by high-pressure liquid chromatography (HPLC) in a Varian chromatograph model 8055 with a column packed with MCH-10. The detector used was a Varian ultraviolet at 254 nm. The mobile phase was a 50% mixture of two solutions. Solution A: methanol-water mixture (80:20 v/v). Solution B: pH 4 buffer solution of sodium acetate 0.02 M

2.3 EPR analysis

The samples were placed in quartz tubes for measurements using electron paramagnetic resonance (EPR) with an X-band ES-TE300 Jeol spectrometer at "Instituto de Química, UNAM". The measurements were carried at room temperature. The spectrometer used a microwave frequency of 9.43 GHz with 2 G modulation amplitude, 100 kHz modulation frequency, and 1.01 mW microwave power. The standard Mn^{2+}/MgO was used for the correction of the magnetic field. The spectrum was analyzed by the ESPRIT-382 VO1.916 software.

Extraction: Some samples of cinnamon were extracted in a soxhlet with a polar solvent (methanol) and with a non-polar solvent (hexane) in order to detect the fraction that gives signal. Fading kinetics

3. Results and discussion

3.1 Cinnamaldehyde and cinnamic acid

The decomposition of cinnamaldehyde in solution as a function of the absorbed dose is presented in Fig. 1. The decomposition follows a linear behavior for the dose range studied. With a dose of 10 kGy only 34% of the target compound remains unchanged. The EPR spectrum does not present any signal.

Cinnamic acid in aqueous solution was also very labile and the decomposition formed two unstable products that disappeared with higher radiation doses.

3.2 Bark and ground cinnamon

Non-irradiated samples

Bark cinnamon was ground and was analyzed by EPR before irradiation. This sample presents a signal with one line at g=2.0146. Non-irradiated ground cinnamon presents two signals. One of them is a weak singlet spectral signal and the other is a signal corresponding to Fe^{3+}, these signals probably are contaminations from the grounding machine.

Irradiated samples

X-band EPR signals of irradiated cinnamon show satellite lines that are typical for irradiated samples. The broad signal observed was characteristic free radical trapped in a solid matrix. For food samples containing cellulose, this signal is attributed to cellulose free radicals generated by irradiation (Raffi, 1989). The change of EPR spectra with dose is showed in Fig. 2.

The extractions of polar and non-polar components of cinnamon were analyzed by EPR. Alcoholic extraction of irradiated cinnamon shows an EPR signal that increases with the radiation dose. Non-polar extracts do not present this signal.

An important characteristic of the irradiated materials is the fading of the EPR signal. It limits the time interval in which identification of radiation processing is unambiguous. The results of the kinetic behavior of radiation-induced cellulosic signal in EPR respect to the storage time from irradiate ground cinnamon irradiated at 7.5 kGy is presented in Fig. 3. After 15 days irradiation the signal remained and it can be recorder.

4. Final remarks

Dose-response curves for the decomposition of cinnamaldehyde and cinnamic acid show that these compounds are sensitive to radiation. Both compounds presented about 70 % of decomposition at 10 kGy.

The EPR spectrum of irradiated cinnamon represented that obtained from foodstuff containing high levels of cellulose. The EPR signals recorded after the exposure to gamma rays is specific enough as compared with those observed with non-irradiated samples. The two satellite lines have degraded due to radical recombination and only the central singlet line EPR remains.

Applicability depends on the lifetime of the radiation-induce cellulose free radicals, throughout the commercial shelf life of about 2-3 weeks. The EPR satellite lines observed in the irradiated cinnamon were relatively weak. They gradually decreased in intensity on keeping the sample stock storage conditions. They were present after 15 days of irradiation and remained unchanged. The absence of this signal cannot be always as counter evidence of the radiation treatment.

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References

Farkas J, 1996. Irradiation of dry food ingredients. (Franklin Book Co. Elkings Park, USA) 11-39.

Farkas J., 2001. Radiation Decontamination of Spices, Herbs, Condiments and other dried food ingredients. Food Irradiation: principles and applications. 291-299.

Delincée H., 1998. Detection of food treated with ionizing radiation. Food Science and Technology. 73-82.

Delincée, H., Soika, C., 2002. Improvement of the ESR detection of irradiated food containing cellulose employing a simple extraction method. Radiat. Phys. Chem. 63, 437-441.

Haire D.L., Chen G.., Janzen E., Fraser L., and Lynch J., 1997. Identification of irradiated foodstuff: a review of the recent literature. Food Research International 30, 249-264.

O´Donnell, J.H. and Sangster, D.F., 1970. *Principles of Radiation Chemistry*, American Elsevier Publishing Company, United States.

Raffi, J.J. and Agnel, J.P., 1989. Electron Spin Resonance identification of irradiated fruits. Rad. Phys. Che. 34, 891-894.

Stachwicz W., Burlinska G., and Michalik J., 1998. EPR Detection of foods preserved with ionizing radiation. Radiat. Phys. Chem. 52, 157-160.
Yordanov N. D. and Gancheva V., 2000. A new approach for extension of the identification period of irradiated cellulose-containing foodstuffs by EPR. Applied Radiation and Isotopes. 52, 195-198.
Yordanov N., and Aleksieva K., 2004. X-and Q-band EPR studies on fine powders of irradiated plans. New approach for detection of their radiation history by using Q-band EPR spectrometry. Radiat. Phys. Chem. 69, 59-64.

Fig. 1 Decomposition of cinnamaldehyde as function of irradiated dose. A) UV spectra B) Molar concentration vs absorbed dose.

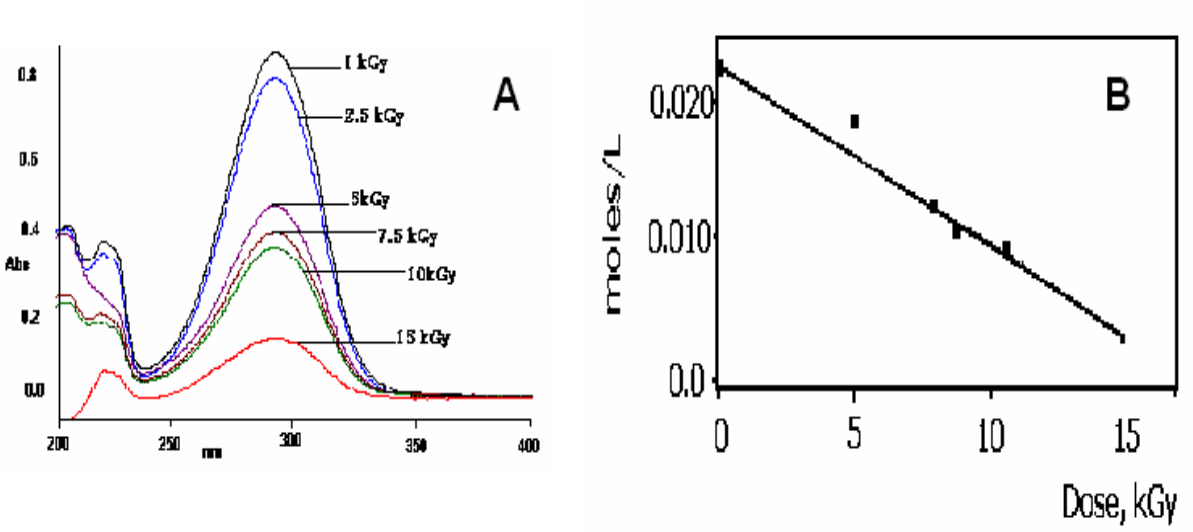


Fig. 2 Recorder EPR spectra for γ irradiated ground cinnamon. The insert presents the increase of free radicals formed as function of absorbed dose.

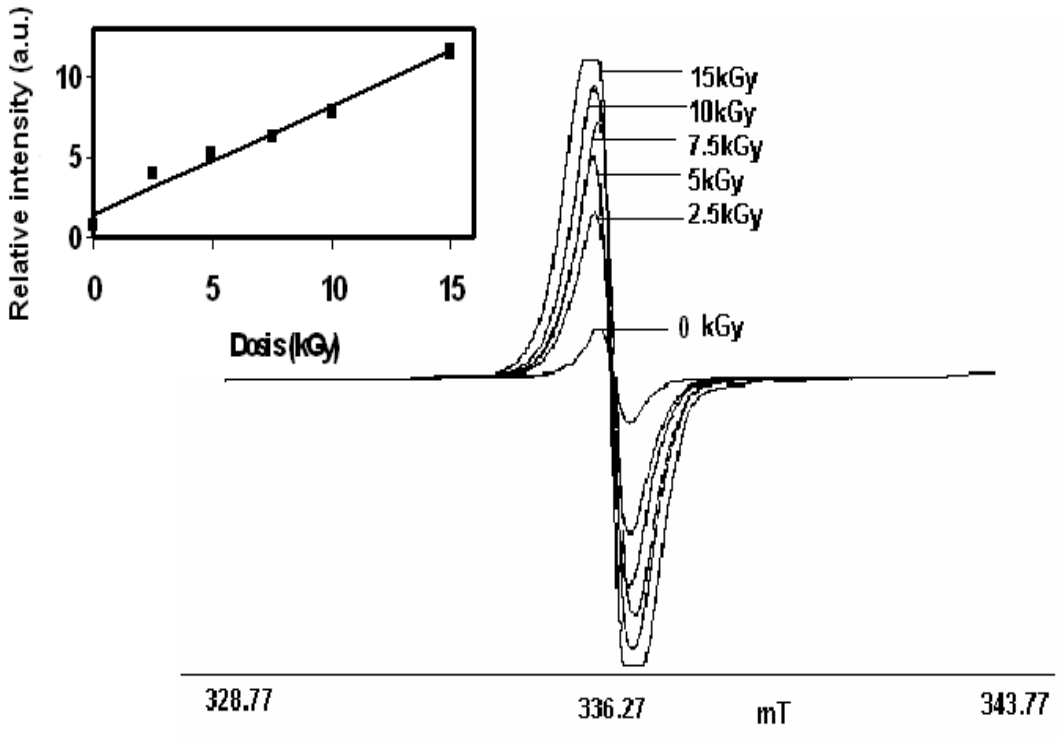
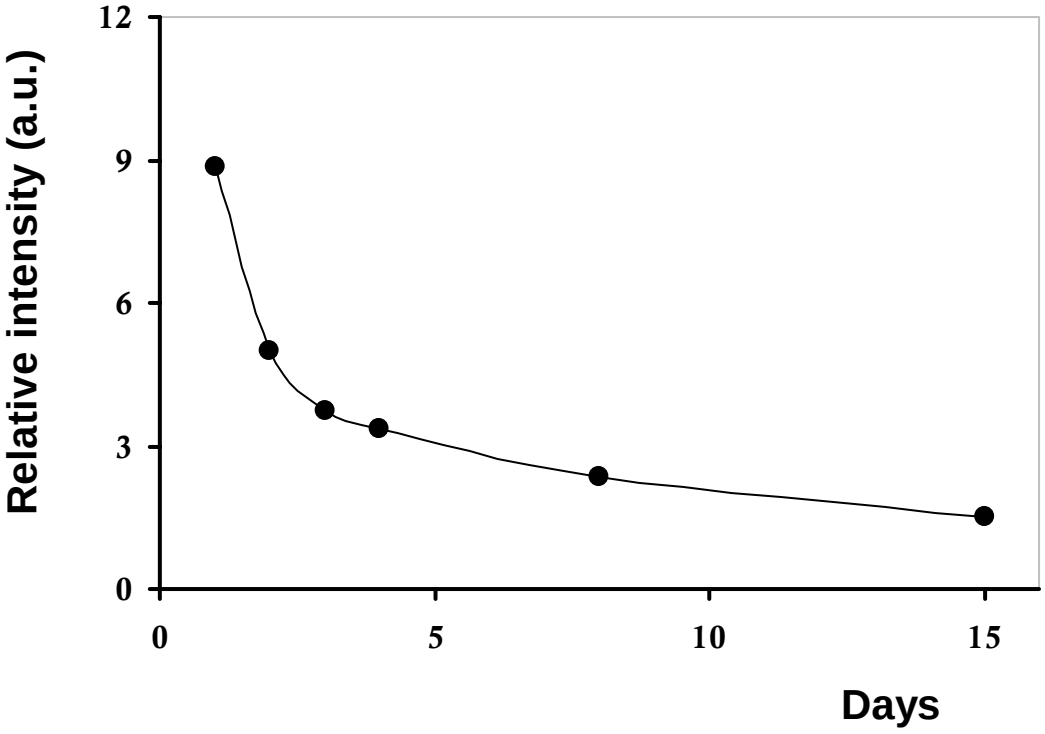


Fig. 3 Kinetic of fading on the intensity on the radiation-induced EPR signal from irradiate ground cinnamon at 7.5 kGy.



The EPR spectra of the irradiated spice samples were characterized by an additional triplet signal at g = 2.006 with a hyperfine coupling constant of 3 mT, associated with the cellulose radical. EPR analysis on various sample pretreatments in the irradiated spice samples demonstrated that the spectral features of the cellulose radical varied based on the pretreatment protocol.Â Electron spin resonance spectroscopy can be used for the detection of irradiation of various groups of foodstuffs. The results of ESR-measurements on irradiated meat and fish and fresh fruit, as well as dried fruit, spices and nuts as performed by the food irradiation laboratory of the German Federal Health Office are summarized in this report. For the detection of irradiated meat and fish, we Applications of EPR method to determine the optimal conditions of photodynamic therapy [24-26], the best conditions of sterilization of drugs [35-48], herbs [22] and cosmetic substances [49, 50], was proposed. 1.1. Aim. The aim of this work is to present usefulness of EPR analysis in ophthalmology. EPR studies of free radicals and their interactions with tissues structures are described.Â Magnetic moments of paramagnetic centers result from their spins, and they are responsible for the orientations in magnetic field during their EPR detection. Paramagnetic centers differ in lifetime [8, 11]. Stability of paramagnetic centers is connected with their chemical building and the external conditions in the environment. free radicals for direct EPR applications [15,16]. Paramagnetic probes are introduced into the sam- ple and they transfer valuable information about the dynamic and structural changes in their envi- ronments without perturbing this environment. This technique has a wide application in biologi- cal systems such as model membranes, blood cells, proteins [17â€“21]. Recently, spin probe technique was applied to the investigation of plant seeds [22]. After this ï¬rst application the technique was utilized to test the viability of seeds [23â€“26].Â The aim of the current study is to develop a more practical way for detection of irradiated seeds using spin probe technique together with simulation methods and to test the ability of the spin probe method for long storage times. 2. Experimental.