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EPR study of gamma – irradiated cereal foods

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The results from the EPR studies on wheat and oat bran, rolled oats, buckwheat and different kind of rice – white, brown and parboiled rice before and after gamma-irradiation are reported. Before irradiation all samples exhibit one weak singlet EPR line characterized with common g-factor of 2.0048±0.0005 and six lines due to Mn^{2+} naturally available in the plants. Only parboiled rice did not show any EPR spectrum before irradiation. After irradiation, in addition of the Mn^{2+} signal a typical "cellulose-like" triplet EPR spectrum appears, attributed to cellulose free radicals, generated by gamma-irradiation. This EPR spectrum is superimposed by a partly resolved "carbohydrate" spectrum, which however is the main spectrum for parboiled rice samples. The fading kinetics of radiation-induced EPR signals were studied for a period of 90 days after irradiation. The reported results unambiguously show that the presence of characteristic EPR spectra of cereal samples can be used for identification of previous radiation processing.

Keywords. Cereals, irradiation, EPR

INTRODUCTION

Irradiation of various food products with high energy radiation have been used as effective tool for their disinfestations and microbial decontamination, suitable also for their long-term preservation [1]. Gamma-irradiation has established itself as a safe, secure and clean procedure for sterilization of foodstuffs including in the final packing. The results show that the quantity of irradiated foods in the world in 2005 was 405,000 ton [2]. However, this manipulation should be under control, which is the reason for many recent studies creating suitable analytical methods [3]. As a result, ten protocols were adopted by the European Committee of Normalization, from which six primary and the remaining for screening purpose. Three of the main protocols use EPR (also known as ESR) since high energy radiation yields free radicals in foods, which are stable for a given period of time and therefore easily detected by EPR. One of them (EN 1787) treats cellulose containing foodstuffs, in which "cellulose-like" EPR spectrum appears after irradiation [4].

Cereals, especially wheat is an important nutritive for mankind because of its unique quality characteristics and the fact that large quantities can be produced, harvested, stored and transported in an efficient way. EPR spectroscopy was applied to the studies on laser induced free radicals in wheat grains [5] and in oat grains [6]. Free radicals in irradiated wheat flour were investigated by EPR [7]. The possible use of oat, wheat and corn kernels as dosimeters for high-energy radiation were discussed [8]. Basmati rice were studied by EPR and Thermoluminescence methods. EPR investigation of 0.5-2.0 kGy irradiated basmati rice samples showed short lived free radicals. In view of this the possibility to identify irradiated rice by the relaxation characteristics and thermal behaviour of the free radicals were examined [9] in accordance with our previous research [10]. Rice noodles could be confirmed for irradiation treatment using ESR spectroscopy [11].

In the present communication we report the EPR spectra obtained before and after gamma-irradiation of some widely spread non investigated cereal foodstuffs in order to prove radiation treatment.

EXPERIMENTAL

Samples

Wheat and oat bran, rolled oats, buckwheat and different kind of rice – white, brown and parboiled rice were purchased from local market, and were divided in two portions. The first batch were passed for irradiation, the second was separated as a control samples.

Irradiation

All samples were simultaneously gamma-irradiated by "Gamma 1300" irradiator with a single dose of 10 kGy. The irradiation was performed at room temperature and in the air. All further manipulations of the irradiated cereals were performed at least 72 h after irradiation in order to avoid any interference by the radiation induced short living paramagnetic species.

Instrumentation

EPR measurements were performed at room temperature on Bruker ER 200 D SRC spectrometer operated in X-band. Standard rectangular cavity

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(ER4102ST) operating in TE102 mode and 100 kHz magnetic field modulation were used. All samples were accommodated in quartz EPR sample tubes (i.d./o.d. 4/5 mm). The g-values of all samples were estimated using "EPR marker" available in the F-F Lock module (ER 033) – in our spectrometer g- mark is 2.0050.

RESULTS AND DISCUSSION

EPR spectra before irradiation

Before irradiation EPR spectra of all samples exhibit one weak singlet line (Figure 1a) characterized with common g = 2.0048±0005, which is equal to that observed in all plant origin foodstuffs. It is attributed to free radicals of semi-quinones [12] or to oxidation products of fatty acids present in some fruits and vegetables [13]. In addition to the weak singlet another spectrum can be detected (Figure 1b). It consists of six lines (marked with asterisks in Figure 1b) due to Mn^{2+} naturally available in the plants (nuclear spin of ^{55}Mn, which is 100% in the natural abundance, is 5/2). The spectrum of Mn^{2+} is characterized with g = 2.0014±0.0005 and A_o = 75±1G. Only parboiled rice did not show EPR spectrum before irradiation.

EPR spectra after irradiation

As for non-irradiated samples a spectrum due to Mn^{2+} ions (Figure 2a) can be detected for the samples after radiation treatment. Manganese spectrum is radiation independent. More precise analysis of the EPR spectra after irradiation of wheat and oat bran, rolled oats, buckwheat, white and brown rice (Figure 2b) show that they are similar, consisting of central intense line with g=2.0048±0.0005 and two weak satellite peaks separated *ca*. 3 mT left and right to it. The central line of the triplet is buried by the natural singlet. The presence of two satellite lines is considered in the Protocol EN 1787 as unambiguous evidence for previous radiation treatment of plant origin foodstuffs. Radiation induced triplet, called "cellulose-like", is attributed to cellulose free radicals [14]. On the other hand, additional doublet of lines (marked with asterisks in Figure 2b) are recorded in the EPR spectra of studied samples overlapped with the "cellulose-like" (marked with arrows in Figure 2b) spectrum. This doublet may be attributed to free radicals of starch [15] (Chabane et al., 2001) known as "carbohydrate" spectrum [16].

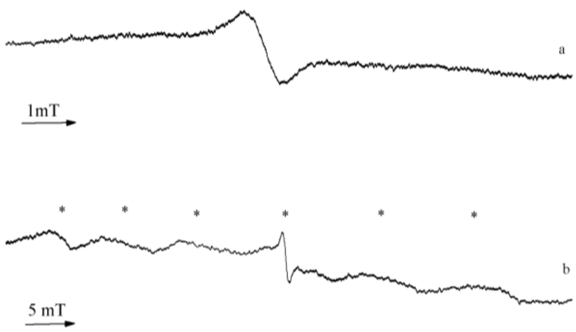

Fig. 1. EPR spectra of non - irradiated samples, recorded at magnetic field sweep 10 mT (a) and 60 mT (b).

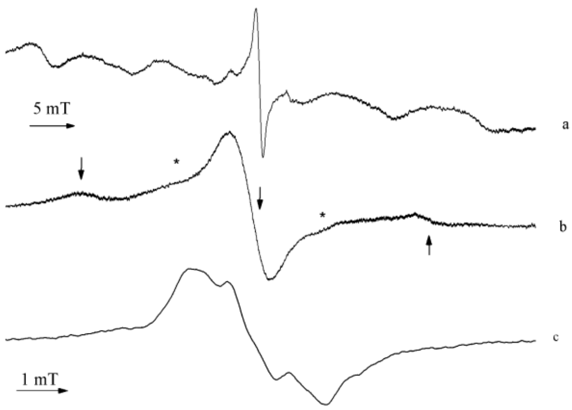

Fig. 2. EPR spectra of irradiated wheat and oat bran, rolled oats, buckwheat, white and brown rice, recorded at magnetic field sweep 60 mT (a) and 10 mT (b); parboiled rice 10 mT (c).

There is no difference between EPR spectra of wheat and oat bran, rolled oats, buckwheat, as well as white and brown rice except intensity. EPR spectrum of irradiated parboiled rice (Figure 2c) differs from the spectra of all other samples. For this sample "carbohydrate" spectrum is better pronounced and "cellulose-like" spectrum is not registered.

Study of the EPR fading kinetics

In order to find the time stability of radiation-induced EPR signals of cereal food samples, their decay kinetics was studied for a period of 90 days after irradiation. It follows from Figure 3 that the intensity of the radiation induced signals of the food samples gradually decrease in identical way with the storage time. Nevertheless the following order of stability is recorded: parboiled rice > white, brown rice > buckwheat > rolled oats > wheat and oat bran.

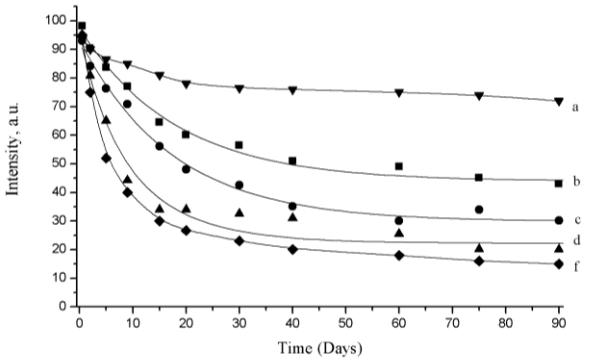

Fig. 3. Kinetics of fading of the radiation induced signals in parboiled rice (a); white, brown rice (b); buckwheat (c) rolled oats (d); wheat and oat bran (f).

CONCLUSION

The obtained EPR spectra of some gamma-irradiated cereal foodstuffs are complex because of the overlapping signals of different free radicals due to carbohydrates. Nevertheless, the individual components of each spectrum lead to the specific EPR spectra. Identification of radiation treatment can be proved by these characteristic EPR spectra, thus enriching European protocols concerning irradiated foodstuffs.

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ЕПР ИЗСЛЕДВАНЕ НА ГАМА-ОБЛЪЧЕНИ ЗЪРНЕНИ ХРАНИ

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(Резюме)

Представени са резултати от ЕПР изследване на пшеничени и овесени трици, овесени ядки, елда и различни видове ориз - бял, кафяв и бланширан ориз преди и след гама-облъчване. Преди облъчване при всички проби се регистрира слаба синглетна ЕПР линия, характеризираща се с g-фактор 2.0048±0,0005 и шест линии, които се дължат на Mn^{2+} йони природно съдържащи се в растенията. Единствено бланширания ориз не показва ЕПР спектър преди облъчване. След облъчване заедно със сигнала от Mn^{2+} йони, се детектира типичен „целулозоподобен“ триплетен ЕПР спектър, който се приписва на свободни радикали от целулозата, генерирани в следствие на гама-облъчване. В допълнение на този ЕПР спектър е насложен и частично разрешен „въглехидратен“ спектър, който е основен спектър за пробите от бланширан ориз. Кинетиката на затихване на радиационно-индуцираните ЕПР сигнали е проследена за период от 90 дни след облъчване. Докладваните резултати показват недвусмислено, че присъствието на характерни ЕПР спектри на проби от житни растения може да се използва за идентифициране на предходна радиационна обработка.