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Effect of gamma radiation on some saccharides: an EPR study

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In the present work an Electron Paramagnetic Resonance (EPR) spectroscopic study of γ irradiated mannitol and stevia is reported. It is found that the EPR spectra of irradiated samples strongly depend on the applied microwave power and modulation amplitude. On the basis of microwave saturation is found that both mannitol and stevia EPR spectra are complex, containing at least two individual and overlapping signals. The produced free radicals are stable at room temperature at least six months. This is the fundament to distinguish irradiated products containing mannitol or stevia from non-irradiated ones even six months after irradiation.

Keywords: *EPR spectroscopy, γ radiation, mannitol, stevia*.

INTRODUCTION

In the last three decades EPR or ESR (Electron Spin Resonance) spectroscopy has expanded significantly in the field of practical applications. This is mainly due to its selectivity (only paramagnetic substances), high sensitivity (10^{-11} – 10^{-12} M) and non-destructive analysis. One direction in this field is detection of radiation induced defect in the matter. On the other hand gamma radiation is considered as a clean, not too expensive and effective method for sterilization of foodstuffs [1], medical and pharmaceutical products [2], etc. The irradiation procedure must be controlled because generated paramagnetic defects or free radicals in the mater and especially their recombination products in the food form new, unknown substances with unknown effects in regard to human health. This fact justifies the necessity of control of the radiation processing. A lot of works described the application of EPR method for identification of irradiated foodstuffs [3-7] as well as for dosimetric control [8,9] were published. In the literature there is only one publication about EPR investigations of gamma irradiated stevia [10] who study it as a material for accidental dosimetry. This study demonstrated the potential use of sweeteners for retrospective dosimetry. No data about EPR investigation of gamma-irradiated mannitol are reported up to now.

In the present work for the first time EPR spectra of gamma irradiated mannitol and stevia in respect to their structure and time stability in order to their potential application for identification of irradiated foodstuffs containing them, as well as for dosimetric purposes are reported.

EXPERIMENTAL

Materials. Mannitol ($C_6H_8(OH)_6$) was purchased from Aldrich whereas stevia (made from the leaves of the plant species Stevia rebaudiana with sweet taste coming from steviol glycoside ($C_{20}H_{30}O_3$)) was purchased from local market. The substances were used as obtained.

Irradiation. The samples were irradiated with single dose of 10 kGy γ-rays on "Gamma-1300" irradiator (^{137}Cs) in air and at room temperature.

Instrumentation. The EPR spectra were recorded at room temperature on a JEOL JES-FA 100 EPR spectrometer operating in the X–band, equipped with a standard TE_{011} cylindrical resonator.

RESULTS AND DISCUSSION

Features of the EPR spectrum of mannitol and stevia

In non-irradiated samples of mannitol and stevia no EPR spectra were recorded. After irradiation the samples exhibit an unresolved and a complex signal containing several overlapped and not well resolved EPR patterns. The nature of these radicals is not clear up to now. Figure 1a shows the EPR spectrum of gamma irradiated mannitol which is characterized with g factor 2.0170 ± 0.0002 of the most intense peak. The first step after irradiation was to study the influence of the instrumental settings microwave power and modulation amplitude on the EPR signal in order to find more deep information about their possible structure. It is seen from Figure 1a that the radiation induced EPR spectrum of mannitol is consists of four peaks (noted as P1, P2, P3 and P4) all sensitive to the magnitude of the applied microwave power (Figure 1b).

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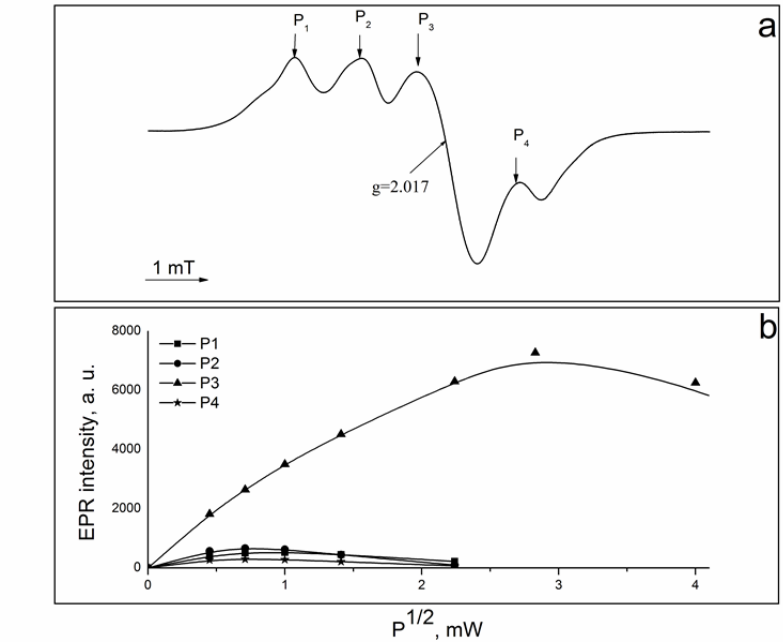

Fig. 1. (a) EPR spectrum of irradiated mannitol; (b) EPR signal intensity of irradiated mannitol as a function of square root of microwave power.

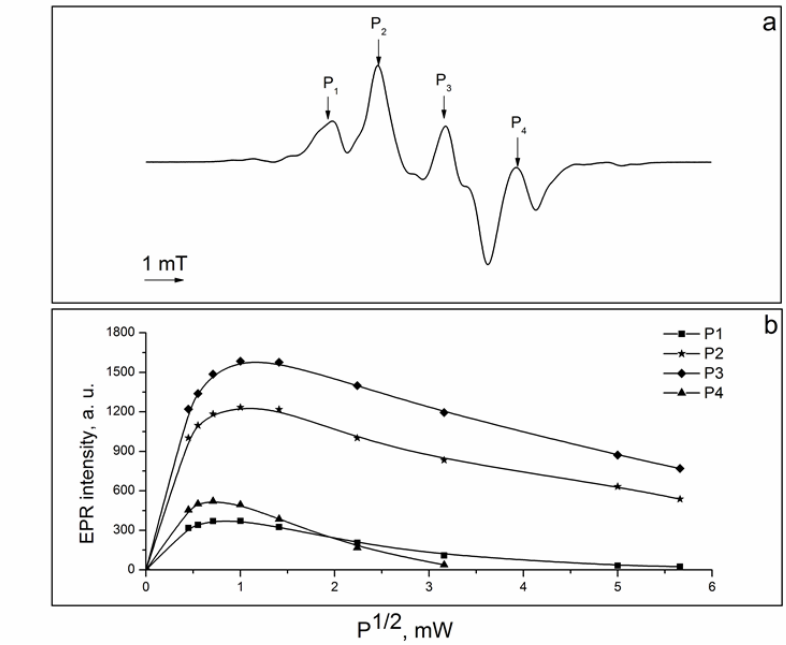

Fig. 2. (a) EPR spectrum of irradiated stevia; (b) EPR signal intensity of irradiated stevia as a function of square root of microwave power.

It was found (Figure 1b) that the peaks P1, P2 and P4 have equal behavior of saturation - they are saturated at microwave power less than 0.2 mW and above 8 mW they disappear. Because of the same behavior of saturation from the applied microwave power it was concluded that the peaks P1, P2 and P4 probably are belonging to one and the same free radical. The peak P3 is slightly broadened at microwave power higher than 1mW, which unambiguously indicate saturation effect but it is well observed at 8 mW and higher power. In respect of the applied modulation amplitude the EPR spectrum of irradiated mannitol linearity depends of it up to 0.16 mT and after that over-modulation of the separate EPR lines appears. In view of this it may be concluded, that in gamma irradiated mannitol at least two free radicals are present.

Figure 2a shows the EPR spectrum of irradiated stevia which is composed of four peaks marked in the figure as P1, P2, P3 and P4. These peaks are characterized with g-values 2.0379, 2.0280, 2.0155

and 2.0045 (± 0.0002) respectively. The behavior of to microwave power saturation and modulation amplitude shows increasing of the EPR signal intensity to about 1 mW but linear dependence is obtained to and down 0.3 mW (Figure 2b). On the other hand the peak P4 disappear over 10 mW. In view of the dependence of the EPR signal intensity from the applied modulation amplitude as a whole there are not changes in the EPR spectrum of stevia up to 0.6 mT modulation amplitude, after that the spectrum become slightly broadening.

Time stability of radiation-induced EPR signals

Previous works [11,12]show that immediately after irradiation, the shape and the intensity of the EPR spectra of saccharides undergo changes during a certain period of time, characteristic for each material. Having this in mind, the EPR spectra of γ -irradiated mannitol and stevia were monitored for six months after the irradiation. It was found that the EPR spectra of both samples undergo small transformations in the first days after irradiation. After that the shape of the spectra of irradiated mannitol and stevia remains unchanged only decreasing of the intensity of the EPR spectra with 250 $g.kg^{-1}$ was recorded. This means that six months after irradiation these substances are suitable for identification of radiation processing. Moreover, mannitol and stevia can be considered as appropriate substances for dosimetric purposes.

The obtained results describe for the first time some features of EPR spectra of manitol and stevia. It is shown that each spectrum consist at least two independent paramagnetic species. Also it may be suggested that using EPR technique is possible to investigate irradiated foodstuffs containing them as well as for their potential as dosimetric materials. The present initial studies about EPR investigation of mannitol and stevia suggest that some additional work must be done though, before it can be taken in regular use.

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ЕФЕКТ НА ГАМА РАДИАЦИЯ ВЪРХУ ЗАХАРИДИ: ЕПР ИЗСЛЕДВАНЕ

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(Резюме)

В настоящата работа са представени резултати от изследване на гама облъчени манитол и стевия с Електрон Парамагнитен Резонанс (ЕПР) спектроскопия. Установено е, че ЕПР спектъра на облъчените проби зависи силно от приложената микровълнова мощност и амплитуда на модулация. Въз основа на насищането на ЕПР сигнала при увеличаване на микровълновата мощност е установено, че ЕПР спектрите на манитол и стевия са сложни и съдържат най-малко две отделни и припокриващи се ЕПР линии. Образуваните свободни радикали са стабилни при стайна температура най-малко шест месеца. Това дава възможност да се разграничат облъчени манитол и стевия съдържащи продукти от необлъчени, дори шест месеца след облъчване.