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Dedicated to Professor Dr. Cozar Onuc on His 70th Anniversary

EPR STUDY OF ORGANICALLY-GROWN VERSUS GREENHAOUSE STRAWBERRIES

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ABSTRACT. EPR spectroscopy was used to characterize changes in main paramagnetic components (Fe^{3+}, free radical, Mn^{2+}) and antioxidant capacity of two types of strawberries (grown in the greenhouse and in natural conditions). The results of studied samples show the interpretable differences between the analyzed samples, which may be consequences of different types of biochemical processes involved in the growth and maturation of fruits depending on the environmental conditions in which they are grown.

Keywords: *strawberry, EPR spectroscopy, antioxidant capacity*

INTRODUCTION

Scientific research on food quality and nutritional extracts are targets of major importance, both in commercial terms and on their impact on human health [1,2] One of the most common questions about fruits and vegetables in the market, is to detect in those grown in the greenhouse or organically [3].

Most organic greenhouse fruits and vegetables are grown in soil amended with compost and organic fertilizers. But these amended soils do not contain the full range of elements and substances essential [4]. This can have a significant impact on nutritional quality of fruits and vegetables used in the human diet. Growers in of natural organic matter can enhance soil structure, improve the water-holding capacity of the soil, and as a source of high quality nutrients. Therefore, organic foods are much preferred in worldwide because they are free of diseases pure and possess good physiochemical features [5].

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What are the differences can be measured spectroscopically? Different research methods follow some characteristic features and allow qualitative and quantitative evaluation of specific parameters [6, 7]

In our work we try to find an answer of this question, by using EPR spectroscopy for two types of strawberries, namely grown in the greenhouse and in natural conditions (organically). Strawberries with remarkable content of antioxidants and phytonutrients with anti-inflammatory role, protect the heart and reduce oxidative stress, preventing damage blood vessels in the body [8,9,10]. Among all healthy fruits, strawberries have the highest level of vitamin C. After raspberries and grapes, these fruits are known as one of the best sources of manganese. As we know, manganese is an important antioxidant mineral, because of its key role as a trace element that is part of composition of the enzyme superoxide dismutase, powerful free radical scavenger that prevents cell damage and helps cell regeneration. In addition, strawberries is a rich source of B vitamins, especially folic acid and vitamin B6 and several essential minerals (such as iron, calcium, magnesium) [11]. EPR spectroscopy has been able to characterize changes in main paramagnetic components, which may be consequences of different types of biochemical processes involved in the growth and maturation of fruits.

EXPERIMENTAL

Freeze-dried two types of strawberries fruits (grown in the greenhouse and organically) and their fresh juice we have analyzed in terms of EPR structure and antioxidant activity. EPR measurements were performed on a Bruker EMX spectrometer operating in X band (~ 9 GHz) with 100 kHz modulation frequency, at room temperature. Antioxidant activity was measured according to their ability to scavenge 2,2′-azinobis(3-ethylbenzothiazoline-6-sulfonic acid) radical cation ($ABTS^+$) in the reaction mixture. 100 μl $ABTS^+$ solution was added in 20 μl strawberry juice.

The homogenized solution was injected with a Hamilton microsyringe into a quartz capillary of about 10 cm length and an interior diameter about 1 mm. The rate of reaction between antioxidant compounds and $ABTS^+$ was monitorised by using normalized double integrated residual EPR signal which is correlated with number of paramagnetic species in time [14]. The integral intensities of EPR spectra were obtained by evaluating their double integrals using Origin8 software.

RESULTS AND DISCUSSION

EPR spectra of lyophilized strawberries are shown in Figure 1.

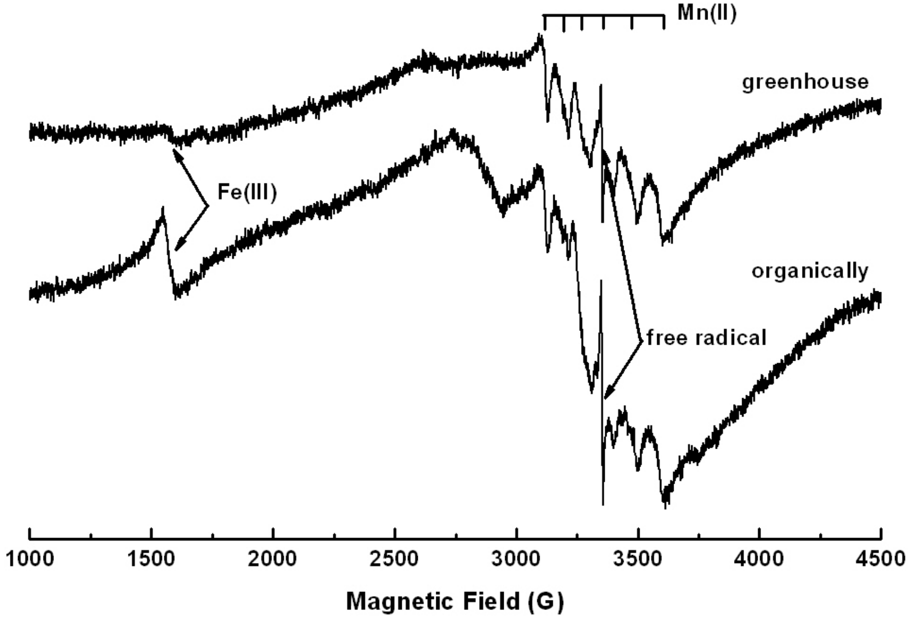

Figure 1. EPR spectra of freeze-drying of strawberries

Main features of the EPR spectra are given by the signal of organic free radicals in addition to traces of Mn^{2+} and Fe^{3+} with various signal intensities and degree of resolution for Mn^{2+} sextet lines (I=5/2) due to hyperfine interaction.

Thus, in the case of strawberries grown in the greenhouse, the signal characteristic of Fe^{3+} is very weak, which shows a small presence of iron in the paramagnetic state. This may be due to iron deficiency which is related with Fe uptake by plant and the level of available Fe concentration in soil and environmental conditions (high pH, low organic matter content, low soil temperature) [12,13]. In addition, manganese signal is well resolved sextet, reflecting the presence of partial unbounded Mn^{2+}. On the other hand, EPR spectrum of strawberries grown in natural conditions, presents some spectral features. First an intense signal of narrow band at g =4.3 indicating that there is isolated high spin Fe^{3+} (S=5/2) with a rhombic symmetry in the complexes and second, an increase of the line broadening of the Mn^{2+} signal, probably due to the fact that manganese ion is bound to other nutritional macromolecules (Carbohydrates, Lipids, Proteins, and Nucleic Acids). It can be also noticed a difference between the signal intensities centered on g ≈ 2.0 due to the free radical (possibly semiquinones) overlapped with the signal of low-spin Fe^{3+} (S=1/2) and can be correlated with the antioxidant activity of the studied samples. Antioxidant activity was measured according to their ability to scavenge $ABTS^{+}$ in the reaction mixture.

The rate of reaction between antioxidant compounds (fresh juice) and $ABTS^{+}$ was monitorised by using normalized double integrated residual EPR signal which is correlated with number of paramagnetic species in time (Fig.2).

The best fit was obtained using the first order exponential decay:

$$I(t) = I_0 + I_1 e^{-kt}$$

were I_0, and I_1 are the fitation constants, and k is the kinetic constants of reaction corresponding to each type of extracts. The k constant is specific to each type of sample and processing way. It represents the oxido-reduction rate of the ABTS+ radical cation in time. The EPR spectra of studied samples show the interpretable differences between the analyzed samples.

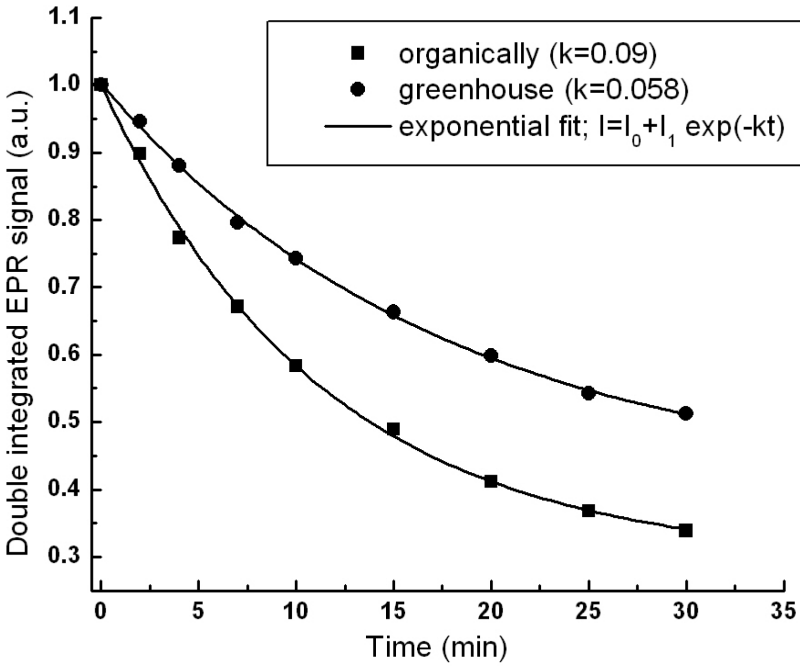

Figure 2. Antioxidant activity of fresh strawberries juices

The analysis of the antioxidant activity of extracts of strawberry shows that antioxidant capacity of strawberries grown naturally (organically) is significantly higher than those grown in the greenhouse.

CONCLUSIONS

In the present study, we tried applying the EPR spectroscopy to evaluate the possibility to characterize strawberry fruits grown in the greenhouse and in the natural conditions (organically). The result shows that ESR spectroscopy has been able to characterize changes in main paramagnetic components, i.e. iron, manganese and native semiquinone-like free radicals. The differences between the EPR spectra of the studied samples may be consequences of different types of biochemical processes involved in the metabolic process of growth. Detection and characterization of these paramagnetic species can be an important indicator (a spectroscopic fingerprint) in the detection of the fruits grown in the greenhouse and grown in natural conditions.

In addition, the study of the antioxidant activity of fresh strawberry juice showed that antioxidant capacity of strawberries grown naturally (organically) is significantly higher than those grown in the greenhouse.

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