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EPR TESTING OF ORGANIC VERSUS CONVENTIONAL MUSACEAE FRUITS

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ABSTRACT In the present study, the EPR spectroscopy was used to evidence differences in fruits of organically and conventionally grown bananas belonging to musaceae family. If in the investigated samples would be detected specific changes related to paramagnetic resonant centers, these could be regarded as a spectroscopic fingerprint in the differentiation of the organic and conventional fruits and vegetables. The EPR spectra were recorded from freeze-dried shell and pulp samples. The main paramagnetic species (iron, manganese and native semiquinone free radical) delivered for the investigated samples slight different EPR signals. In this stage, the results obtained by EPR testing put in evidence sensible differences between the two classes of samples, and draw the attention on differences in EPR signals recorded from banana pulp and shell.

Keywords: *EPR spectroscopy; organic food; conventional food.*

INTRODUCTION

Organic versus conventional food is a large debate subject especially regarding the food safety [1]. Chemical fertilizers, pesticides, herbicides, and plant hormones are often applied in intensive agricultural areas to maintain high yields [2]. All these are expected to be excluded in the organic farming.

Organic foods are not necessarily better for the body than conventional foods in terms of vitamin and nutrient content, but for sure they are less exposed to pesticides and antibiotic-resistant bacteria.

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According to a comprehensive review on human health implications of organic food and organic agriculture, the organic food may reduce the risk of allergic diseases and of overweight and obesity [3]. The organic foods, despite the higher production costs, are preferable. Consequently, scientific research on food quality and nutritional extracts is considered a high priority by several international organizations [4, 5]. The most analyzed categories of foods are fruits, organic and non-organic vegetables, cereals, meat, eggs and milk [6].

Bananas are the fourth most important food crop in the world after rice, maize and wheat [7]. They belong to the monocotyledonous family of musaceae. Demand and production of organic bananas have been growing in recent years, especially concerning that organic bananas contain no fat or cholesterol and are easy to digest as they are a good source of various nutrients such as vitamin B6, vitamin C, magnesium and potassium. Moreover, the consumption of organic bananas as part of the daily diet helps reduce the chances of stroke and heart attack as the fruit generally helps reduce cholesterol, improve blood sugar control, and enhance digestion. Furthermore, organic bananas contain iron, and thus can stimulate the production of hemoglobin in the blood [8]. But, the requirements of organic production in terms of soil quality, water management, climate change mitigation and biodiversity conservation, make that the organic banana supply to be naturally limited.

The interest in establishing the characteristics of conventionally grown and organically grown bananas is quite high, in the specialized literature there are different case studies. Comparative studies regarding fruit dimensions, color, local differences in surface pigmentation, weight and firmness shown that organically and conventionally grown product had almost identical qualities [8].

Electron Paramagnetic Resonance (EPR) spectroscopy can be used to characterize the changes concerning paramagnetic species present in foods. Depending on the types of biochemical processes involved in fruit or vegetables growth and maturation, these paramagnetic centers may or may not be present, and may have different shapes and intensities of EPR signals [9]. EPR method is often applied for food analysis, particularly in detection of Fe^{3+}, Mn^{2+} and Cu^{2+} metal ions with long relaxation times [10]. Transition metal ions are generally paramagnetic by virtue of their partially filled d orbitals. Using this spectroscopic method for the study of organic and conventional foods, some characteristic features for the studied samples can be established.

The present study aims to evidence by EPR analysis the spectroscopic differences between shell and pulp of banana fruits grown under organic and conventional conditions. Possible characteristic changes could be a spectroscopic fingerprint in the differentiation of organic and conventional fruits and vegetables.

EXPERIMENTAL

Conventionally and organically grown bananas originating in Peru, used in the present study, were purchased from the local market. In order to obtain the samples in powder form, both the shell and the pulp of the fruits were lyophilized by using an Alfa 1-2 LD Christ Freeze dryer, by keeping the samples in a controlled atmosphere (pression 0.04÷0.024 mbar and temperature -50°C ÷ -54°C), for 78 h. EPR measurements were performed on a Bruker EMX spectrometer operating in X-band (~ 9 GHz), with 100 kHz modulation frequency. The EPR spectra were recorded at room temperature, for similar amount of grinded samples.

RESULTS AND DISCUSSION

The EPR spectra of conventionally and organically grown bananas (liophilized shell and pulp) are shown in Figure 1. The six-line multiplet spectrum centered at g = 2.0 is a fingerprint of paramagnetic Mn^{2+} ions subjected to tetragonal crystal field and hyperfine magnetic interaction between unpaired electrons and nuclear spin (I = 5/2). The average hyperfine splitting between neighboring peaks of the Mn^{2+} sextet reflects, approximately, the degree of ionicity of the bonds involving the manganese ions, and, for an average hyperfine splitting of 80−90 G, is considered the ionicity degree of 80−90% and the covalency degree of 20−10% [11].

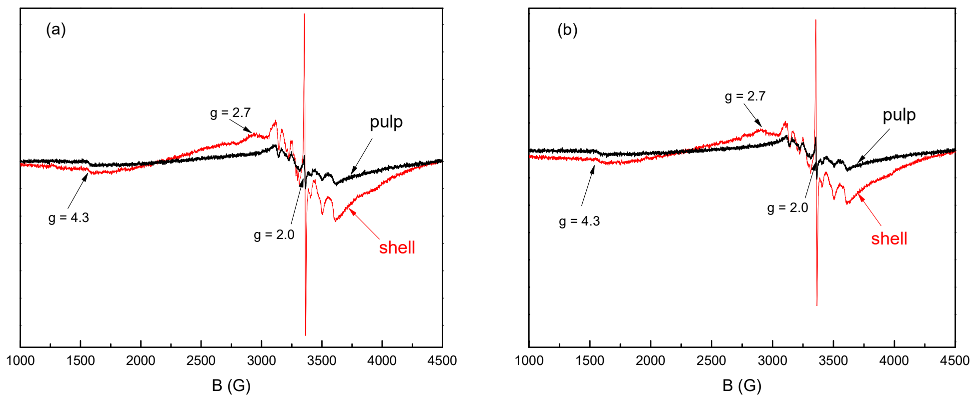

Fig. 1. *EPR spectra of freeze-dried bananas: (a) conventional fruit; (b) organic fruit.*

Manganese is a trace element present in almost all foods of vegetal origin, and manganese ions play an important role in biochemical processes especially in green plants, as cofactors of proteins and enzymes [10-13]. In the studied samples, the EPR intensity of the signals associated with Mn^{2+} ions are much higher in the shell of both conventional and organic fruits. In the hyperfine structure of Mn^{2+} EPR line no changes are observed, the average hyperfine splitting is kept 90 G in all samples.

At the same time, on the six-line multiplet spectrum a narrow signal of organic free radical can be observed at g = 2.0 (Fig. 1). This line is assigned to semiquinone radical [10, 12, 14, 15] and it was shown that Mn^{2+} ions play an important catalytic role in the formation of this organic free radical [12]. Semiquinones may be regarded as a special kind of phenoxyl radicals [16]. They result as free radicals after removal of a hydrogen atom by dehydrogenation of a hydroquinone. Quinones (Q) are used as oxidizing agents in organic synthesis, whereas hydroquinones (H_2Q) are used as reducing agents [17]. The reduction of a quinone can occur in two sequential one-electron transfer reactions (Eqs.1 and 3). The complete reduction of a quinone to a hydroquinone requires two electrons and two protons (Eq. 3). The intermediate semiquinone ($SQ^{\bullet-}$) is a relatively stable free radical, compared to highly reactive free radicals such as the hydroxyl radical; however, semiquinone radicals are relatively unstable species compared to quinones and hydroquinones [17].

$$Q + e^- \rightleftharpoons SQ^{\bullet-} \qquad (1)$$

$$SQ^{\bullet-} + e^- + 2H^+ \rightleftharpoons H_2Q \qquad (2)$$

$$\text{Net} \quad Q + 2e^- + 2H^+ \rightleftharpoons H_2Q \qquad (3)$$

Nevertheless, it was shown that semiquinones can have extremely long half-lives, up to days at 37 °C, and tend to be neither reactive nor toxic [18].

A weak broad shoulder around g = 2.7 is recorded only from shell samples (Fig. 1). This resonant signal is assigned to Mn^{2+} ions disposed in sites of distorted tetrahedral symmetry [12]. It was assumed that also the weak signal at g = 4.3 arises from Mn^{2+} ions in distorted tetrahedral symmetry [12, 15], but additional research on Mn^{2+} EPR spectra of vegetal samples [15] proved that this signal arises from Fe^{3+} ions. Fe^{3+} experiencing a rhombic ligand/crystal field / in a fully rhombic ligand field configuration. [11].The low intensity of g = 4.3 signal arising from Fe^{3+} ions denotes a low amount of iron as trace element. Nevertheless, the iron concentration could be due several causes like iron concentration in the soil, specific absorption by the plant, or environmental conditions [19].

Resuming, the EPR spectra evidence Mn^{2+} and Fe^{3+} ions and semiquinone free radical. A significant difference between the intensity of organic free radical can be observed (Fig.1) for shell and pulp samples. Both for conventional and organic banana shell, the intensity of the semiquinone radical is higher than for pulp sample, probably because the shell is much more exposed to atmospheric oxygen than the pulp.

Considering as reference the same amplitude for Fe^{3+} EPR signal, one observes for conventionally grown sample that the amplitude of free radical line is about 10 times higher in shell than in pulp, while in organically grown sample this ratio is lower, namely about 7. As a result, according to this reference, for the samples investigated in this study, the shell appears to concentrate a relative larger number of free radicals than in pulp, in conventional and organic bananas. Total antioxidant capacity of organics is reported to exceed by 80% that of conventionally grown products [20]. For the samples investigated in this study, the shell appears to concentrate a relative larger number of free radicals in conventional than in organic bananas, while in pulp a higher number of free radicals is observed for organic bananas.

A careful examination of pulp (Fig. 2) and shell (Fig. 3) spectra highlights differences in the two classes of fruits regarding the amount of free radicals. Referencing the amplitude of the free radical signal to that of the Mn^{2+} hyperfine structured envelope line (Fig. 2), one obtain for conventional pulp sample the ratio 0.85 and for organic pulp sample this ratio is increased to 1.2.

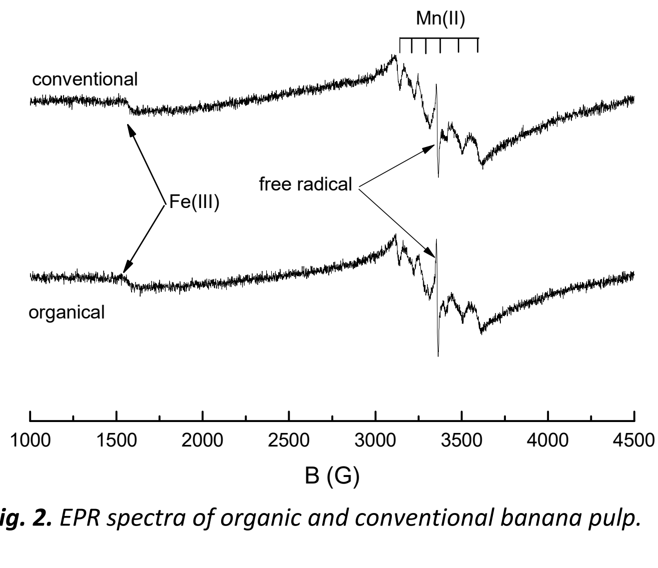

Fig. 2. *EPR spectra of organic and conventional banana pulp.*

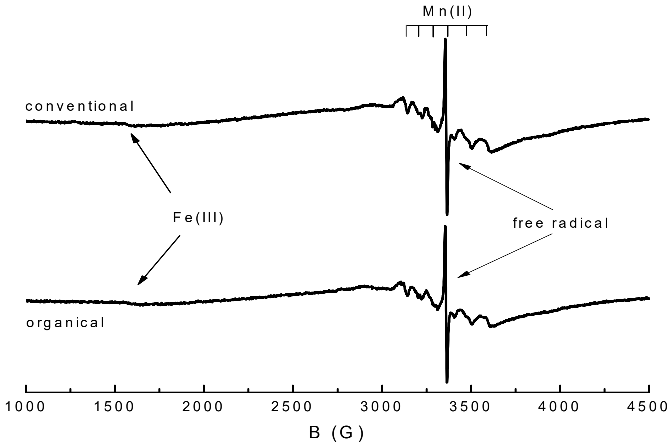

Fig. 3. *EPR spectra of organic and conventional banana shell.*

This is not the case in shells (Fig. 3) wherein a similar value about 3.4 is obtained for both organic and conventional samples as ratio between the amplitude of the free radical signal to that of the Mn^{2+} hyperfine structured envelope resonance line.

Concerning the free radical resonance line, it appears worth to analyze beside the relative line intensity also the peak-to-peak width in the organic and conventional samples (Fig. 4).

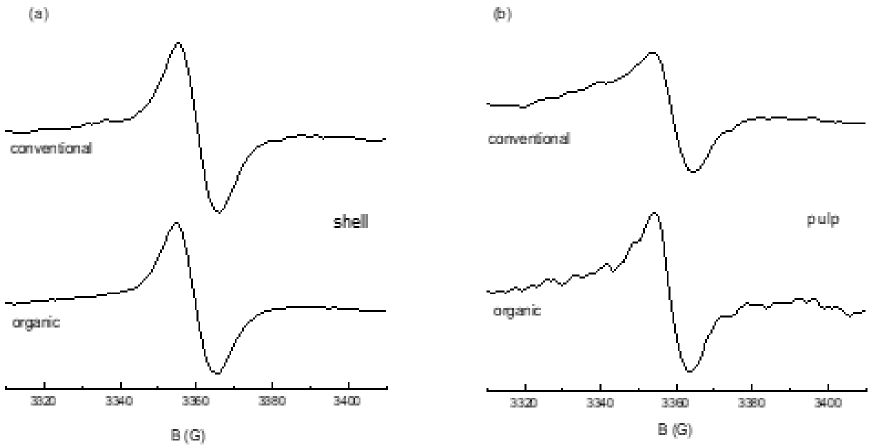

Fig. 4. *EPR signal of semiquinone radicals in organic and conventional samples: (a) shell and (b) pulp.*

The free radical line width in shells is the same, 11.2 G, both in organic and conventional samples, and the same value is also in pulp of conventional sample, but it is evidently lower, 9.1 G, in pulp of the organic sample. On the other hand, the line intensity is proportional to the number of semiquinone free radicals. Assuming the line intensity as the product between line height and square of peak-to-peak line width [21], one can conclude that the number of semiquinone free radicals is higher in pulps of organic then in pulps of conventional samples (Fig. 4b).

CONCLUSIONS

The present EPR study attempted to characterize EPR spectroscopic differences detectable in freeze-dried banana fruits grown under natural and conventional conditions, of same geographic origin. The analysis of room temperature EPR spectra points out some changes delivered by the resonant paramagnetic species Fe^{3+}, Mn^{2+} and semiquinone free radical, both in pulp and in shell of the fruits. Regardless of growth conditions, the Fe^{3+} ions occur in sites of rhombic crystal field; Mn^{2+} ions in pulp are subjected only to tetragonal crystal field and the line is split into sextet due to hyperfine interaction experienced by unpaired electrons with the nuclear spins, while in shell a low number of Mn^{2+} ions are detected also in sites of distorted tetrahedral symmetry; semiquinone free radicals occur in much higher number in shell than in pulp.

Specific differences between organic and conventional fruits refer to the ratio between the amplitude of the signals arising from free radicals in shell and pulp that is about 10 for conventionally grown and about 7 for organically grown fruits. The peak-to-peak width of free radical line width in pulp of conventional sample is 11.2 G, but this is diminished to 9.1 G in pulp of the organic sample. According to the intensity of EPR signal delivered by semiquinone free radicals, the number of these radicals is lower for shell and higher for pulp, in organically, than in conventionally grown samples. These results could promote further investigations concerning an EPR spectroscopic fingerprint in the differentiation of the organic and conventional musaceae fruits.

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