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Effect of Gamma Irradiation on Trichromatic Values of Spices*

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The effect of γ-irradiation on trichromatic color values L^*, a^*, and b^* was determined in black pepper, oregano, and allspice samples irradiated at average doses from 5 kGy to 30 kGy. Trichromatic values a^* measured in methanol extracts of treated spices immediately after the irradiation process were significantly changed, but the subsequent storage of allspice and oregano caused much more distinctive alteration of these color values than the irradiation itself. Additionally, the differences in redness between the reference (non-irradiated) allspice and oregano samples and samples treated by γ-radiation gradually disappeared during the storage period. On the contrary, the post-irradiation storage of black pepper samples did not reveal any changes of a^* values.

Keywords: irradiation, trichromatic values, black pepper, oregano, allspice

INTRODUCTION

Irradiation of spices is the treatment with radiant energy aimed at obtaining some beneficial effects, which include disinfestations and improvement of both shelf life (by the inactivation of spoilage organisms) and safety (by inactivation of food-borne pathogens). Gamma irradiation is now internationally accepted as an effective method to maintain the quality of spices for a long time. The Directive 1999/3/EC [1] established a Community List of Food and Food Ingredients that may be treated with ionizing radiation. Maximum overall average absorbed dose was set to 10 kGy for dried aromatic herbs, spices, and vegetable seasonings. Limitations set by the FDA [2] for culinary herbs, seeds, spices, vegetable seasonings, and blends of these aromatic vegetable substances determine that the γ-radiation dose may not exceed 30 kGy.

The primary effect of irradiation on food material is the formation of free radicals from excited molecules. As a consequence, the breakdown of these primary entities by different pathways takes place [3]. Considering that molecular structure common to food colorants is a conjugated diene system, it might be expected that they would be particularly affected by irradiation.

Carotene is for instance, more sensitive to irradiation than vitamin A when present in food with high fat content [4]. In the dry state, carotene did not exhibit any changes when irradiated at doses up to 20 kGy [5]. Moreover, the observed influence of irradiation on carotenoids present in fruit and vegetables is complex and depends on the effects of irradiation on the ripening process within the fruit and not just the direct effect on carotenoids [6]. Many of the reported effects of irradiation on anthocyanin content may also result from the consequences of irradiation on ripening [6]. There are, however, reports of reversible changes in anthocyanins exposed to low radiation doses [7]. According to *Wotton et al.* [8] the browning process in irradiated food has been associated with the occurrence of the Maillard reaction and/or with the oxidation of phenolic compounds and aromatic amino acids.

Among the various food products, spices are the most frequently irradiated. Only little information is available about the effect of irradiation on their trichromatic color values. The influence of irradiation on color and functional properties was recently discussed in several papers, mostly using L^*, a^*, and b^* trichromatic values for the objective evaluation of color changes upon the irradiation. CIE $L^*a^*b^*$ (CIELAB) is the most complete color model used conventionally to describe all the colors perceptible to the human eye. This procedure was developed by the In-

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ternational Commission on Illumination for this specific purpose. The L^* value gives the luminance (essentially the brightness) of the color in a perceptually uniform way. The a^* and b^* values refer to the red-greenness and blue-yellowness of the color, respectively.

Irradiation effect on color and functional properties of persimmon (*Diospyros kaki* L. *folium*) leaf extract and liquorice (*Glycyrrhiza uralensis* Fischer) root extract was studied by *Cheorun et al.* [9]. Samples were either non-treated or irradiated using a ^{60}Co source at a dose of 20 kGy. Both groups of samples were subsequently stored at 4 ℃ or −20 ℃ for two weeks. As a result of irradiation, Hunter color values L^*, a^*, and b^* were changed, resulting in a desirable brighter color of the treated samples. During the storage, the bright yellow color of the irradiated sample changed to brown gradually. The changes in the samples stored in the refrigerator (4 ℃) were faster compared to those stored in the freezer (−20 ℃). According to *Cheorun et al.* [10] dried green tea leaves extracted with a 70 % ethanol solution and irradiated at doses of 0 kGy, 5 kGy, 10 kGy, and 20 kGy revealed an increase of the L^* value, while both a^* and b^* values decreased resulting in color change from dark brown to bright yellow. Color changes of dry turmeric and three varieties of dry red chili irradiated with doses of 0 kGy, 1 kGy, 5 kGy, and 10 kGy were periodically estimated during storage up to one year at ambient conditions by *Chatterjee et al.* [11]. γ-Irradiation did not cause any significant changes in the color coordinates of both turmeric and red chili varieties. However, during storage a significant ($p \leq 0.05$) reduction in trichromatic values was observed for all the chili varieties, while the L^*, a^*, and b^* values in turmeric remained unchanged. Changes in aroma and coloring properties of saffron (*Crocus sativus*) after γ-irradiation at doses of 2.5 kGy and 5 kGy were investigated by *Zareena et al.* [12]. Fractionation of the saffron pigments into aglycon and glucosides was achieved using ethyl acetate and butanol, respectively. Analysis of individual pigment fractions by HPLC revealed a decrease in glucosides and an increase in aglycon content in irradiated samples.

The effect of irradiation on color changes was investigated also in other (non-spice) food matrices. The effect of low radiation doses (^{60}Co source) on the species *Robinia pseudoacacia* (false acacia seedlings) has been studied by *Creanga et al.* [13]. The authors found that chlorophyll a^* value was significantly affected already at a short exposure time. *Warchalewski et al.* [14] monitored wheat grain exposed to γ-radiation at selected doses between 0.05—10 kGy. Trichromatic measurements showed that irradiation did not cause any changes of the sample color. *Terzić-Vidojević et al.* [15] studied the color changes of breadcrumbs after sterilization by ionizing radiation. The results showed that the dose of 5 kGy was efficient to achieve suitable microbiological quality of the product and that the color changes determined by photoelectrical tristimulus colorimetry were negligible.

The aim of this contribution is to evaluate the changes of tristimulus color values of black pepper, oregano, and allspice methanol/water extracts resulting both from the γ-radiation treatment using different irradiation doses and the post-irradiation storage during four months.

EXPERIMENTAL

Ground black pepper (density 550 g dm^{-3}, dry matter content 87.9 mass %) from Vietnam, ground oregano leaves originating from Cambidi, Izmir, Turkey (dry matter content 90.1 mass %), and ground allspice from Mexico (dry matter content 86.9 mass %) were used. The spice samples were irradiated according to commercial practices of Artim, Prague, Czech Republic, using ^{60}Co source at average doses of 5 kGy, 7.5 kGy, 10 kGy, 15 kGy, 20 kGy, and 30 kGy (black pepper and oregano) and at average doses of 5 kGy, 10 kGy, 15 kGy, 20 kGy, and 30 kGy (allspice), respectively, using a doses rate of 2 kGy h^{-1}. Irradiation doses were chosen according to the above-mentioned Directive 1999/3/EC [1] as well as FDA [2] limits for spices irradiation. The properties of radiation-processed samples were compared to those of the respective reference (non-irradiated, 0 kGy) samples.

All samples of spices were stored in polyethylene bags under laboratory environmental conditions (25 ℃, relative humidity 40 %). Extracts from individual spices were prepared by mixing 2 g of spices with 50 mL of 80 vol. % water—methanol solution. The mixture was shaken for 1 h using a laboratory shaker (Innova 2000, USA) at 200 min^{-1} and subsequently the solid phase was removed by filtration. Dry matter content in methanol extracts of black pepper, oregano, and allspice was (5.22 ± 0.05) g dm^{-3}, (9.77 ± 0.165) g dm^{-3}, and (5.79 ± 0.138) g dm^{-3}, respectively.

Tristimulus color values of individual extracts were estimated using the UV-VIS spectrometer Specord M40 (Carl Zeiss Jena, Germany) adapted for the determination of L^*, a^*, and b^* color values according to the procedure described in [16]. Measurement of extracts prepared from black pepper and oregano samples was performed using Illuminant A, while in the case of allspice Illuminant C was used. All measurements were carried out using a 2° standard colorimetric observer. A square cell (path length 1 cm) was used for the absorbance spectra measurements in the spectral range from 380 nm to 780 nm, using a step of 10 nm.

For statistical analysis, one-factor ANOVA was used at the significance level of 0.05. Three independent replications of measurements were done including the weighting, extraction, and tristimulus color mea-

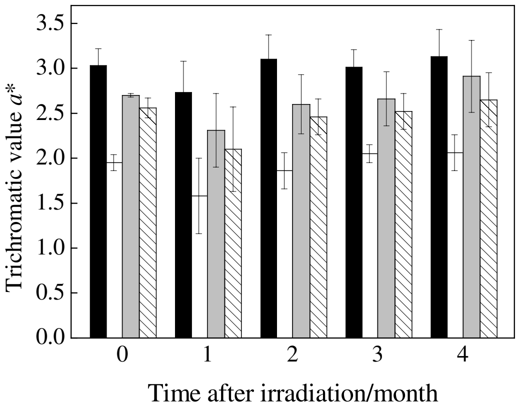

Fig. 1. Time dependence of trichromatic a^* values of methanol/water extracts of reference (non-irradiated) black pepper sample (■) and extracts prepared from samples irradiated at doses: 5 kGy (□); 10 kGy (▥), and 30 kGy (▧).

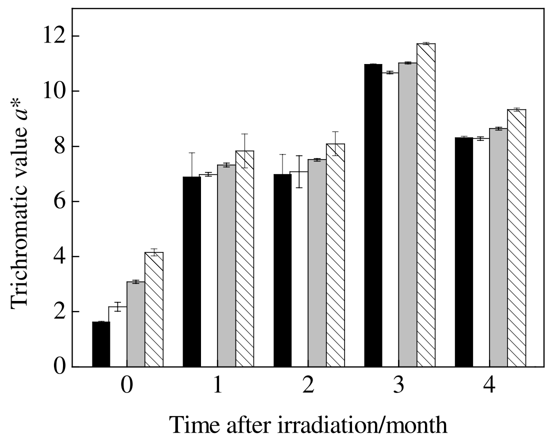

Fig. 2. Time dependence of trichromatic a^* values of methanol/water extracts of reference (non-irradiated) oregano sample (■) and extracts prepared from samples irradiated at doses: 5 kGy (□); 10 kGy (▥), and 30 kGy (▧).

surements for each sample under study.

RESULTS AND DISCUSSION

The trichromatic values of extracts prepared from irradiated spices were compared to those obtained for the corresponding reference (non-irradiated) spice extracts. From the trichromatic values (L^*, a^*, and b^*), measured immediately after the irradiation, the value a^*, characterizing the redness of spices, underwent the most significant changes upon the radiation treatment. As the effect of irradiation on L^* and b^* values was statistically insignificant and practically negligible, the main attention was focused on the influence of absorbed dose of γ-radiation and time of subsequent storing on the a^* value.

The effect of radiation treatment and storage of spices at laboratory conditions on the color value a^* of all investigated spices is shown in Figs. 1—3. In order to improve legibility of these diagrams, only the a^* values obtained for the samples irradiated at 0 kGy, 5 kGy, 10 kGy, and 30 kGy are presented.

Influence of Irradiation Dose on a^* Value

It was found that the increasing irradiation dose caused a decrease of the redness of the black pepper methanol extracts. However, the change of the a^* value was not monotonous, as the most intensive decrease of this color value was observed not at 30 kGy, as one would expect, but at the irradiation dose of 5 kGy. The redness reduction as a result of irradiation is relatively rare, but it was noticed *e.g.* in the apple juice irradiated at doses of *ca.* 9 kGy [17]. On the other hand, our results are in good agreement with the previously published data arguing that lower doses of γ-radiation (below 10 kGy) do not cause destructive changes, but contrarily to higher absorbed doses, in a positive way stimulate some biochemical processes causing the color changes [6].

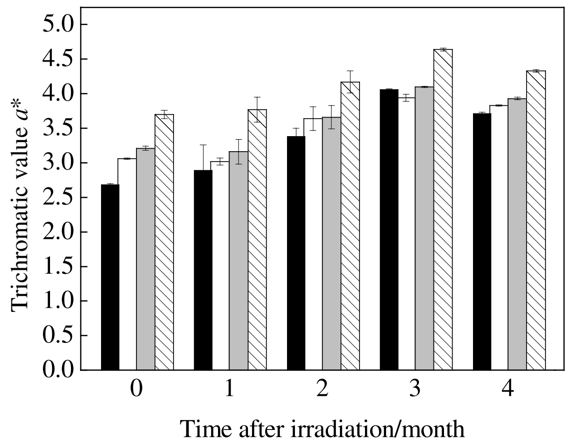

Fig. 3. Time dependence of trichromatic a^* values of methanol/water extracts of reference (non-irradiated) allspice sample (■) and extracts prepared from samples irradiated at doses: 5 kGy (□); 10 kGy (▥), and 30 kGy (▧).

In contrary to black pepper, γ-irradiation caused a significant increase of a^* values of both oregano and allspice extracts (Table 1). An important increase of this value, by about 150 % for oregano, and 40 % for allspice samples irradiated at a dose of 30 kGy, was noticed immediately after irradiation.

These findings correlate well with the data presented by some other authors reporting on the color changes of irradiated food, *e.g.* the color of irradiated beef meat becomes a deeper red, while that of pork and poultry becomes pinker. On the other hand, irradiation causes distinguishable color changes of beef meat from a bright red to a green/brown [9, 18—20]. The observed increase of the red color values in irradiated food was previously associated with the creation of colored compounds by the Maillard reaction [21], other non-enzymatic browning reactions [22], or with enzymatic oxidation of some phenolic compounds present in food matrix [8].

Influence of Storage on a^* Value

The data summarized in Table 1 reveal that the storage of black pepper caused practically no changes in redness during the time. The a^* values determined in regular time intervals after irradiation remained constant or their change was negligible for both reference and irradiated samples extracts. On the contrary, the significant effect of storage on a^* values determined for allspice and oregano was noticed. In the case of oregano, the a^* value increased 4—5 times compared to the values obtained immediately after the radiation treatment. It should be noted that although the changes of the a^* values in these spice samples during storage were statistically significant, they could be detected only by color spectrometry, as they are hardly noticeable by eye. Four months of post-irradiation storage period of allspice caused 25—30 % increase of redness values (Table 1).

Recently, *Sádecká et al.* [23, 24] examined microbiological activity of the same samples as those investigated in this study. The authors found that the total amount of microorganisms in samples exposed to a dose of 5 kGy decreased considerably, in the case of black pepper from 10^6 colony-forming units per gram of sample (CFU g^{-1}) to less than 1 CFU g^{-1} and in the case of allspice from 1.2×10^4 CFU g^{-1} to less than 1 CFU g^{-1}. The same effect was achieved irradiating oregano sample with a dose of 7.5 kGy (from 1.4×10^6 CFU g^{-1} to less than 1 CFU g^{-1}). Additionally, it was shown that the total count of microorganisms in samples γ-irradiated at doses 7.5 kGy, 10 kGy, and 30 kGy remained unchanged during four months and even eight months of storage.

Therefore, it can be concluded that the optimal dose of irradiation ensuring microbiological safety of investigated spice commodities is 5—7.5 kGy, almost completely suppressing the contamination with microorganisms.

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