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Determination of volatiles produced during radiation processing in *Laurus cinnamomum*

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ABSTRACT

In order to protect food from pathogenic microorganisms as well as increase its shelf-life, while keeping sensorial properties (e.g., odor and taste), which are important properties required by spice buyers, it is necessary to analyze volatile formation from irradiation of medicinal and food herbs. Possible changes in the odor of these herbs are evaluated by characterizing different radiation doses and effects on sensorial properties, in order to allow better application of the irradiation technology. The aim of the present study was to analyze volatile formation on cinnamon (*Laurus cinnamomum*) samples after gamma irradiation. These samples were irradiated into plastic packages using a ^{60}Co facility. Radiation doses applied were 0, 5, 10, 15, 20 and 25 kGy. For the analysis of the samples, solid-phase microextraction (SPME) was applied, while for the analysis of volatile compounds, CG/MS. Spice irradiation showed the highest decrease in volatile compounds. For *L. cinnamomum*, the irradiation decreased volatile compounds by nearly 56% and 89.5%, respectively, comparing to volatile from a sample which had not been previously irradiated.

1. Introduction

The interest in irradiation as a food-processing technology has strong economic reasons because of the large losses from the infestation by insects, microorganisms contamination and deterioration. Food and Agriculture Organization of the United Nations (FAO) estimates indicate that about 25% of food world production is lost because of contamination, representing significant financial impact on public health (ICGFI, 1999; Farkas, 2006).

Some chemical changes are induced in food as a result of irradiation. In fact, any treatment a food is subjected to, heating or ionizing radiation, there are changes in some of the food chemical properties. Therefore, we must evaluate the effects caused by chemical and physical interaction of radiation with the irradiated product. Not only to preserve the food, combating pathogenic microorganisms and increasing its shelf-life, but also to preserve the food sensory integrity, since this is one of the main factors required by the consumer, the volatile analysis is necessary. This analysis in food and medicinal herbs irradiation and, the possible sensory changes, such as in spice after radiation and storage treatment, will characterize the various doses used and their effects on the spices sensory value, seeking the best application of this technology (Aquino et al., 2007).

The scientific knowledge of chemical compounds is responsible for the characteristic odor and flavor of spices, which justify the food quality. Considerable efforts have been made to determine the irradiation effects on food components (Diehl, 2002).

2. Objectives

The aims of this work were to analyze the volatile compounds formed by the cinnamon (*Laurus cinnamomum*) irradiation; characterize the profile of volatile compounds in this spice and determine the main volatile compounds profile after processing by radiation from ^{60}Co.

3. Material

Samples of cinnamon-powdered bark (*L. cinnamomum*) were provided by Hikari Industry and Commerce from Brazil. These samples were not previously submitted to any kind of food conservation treatment. Samples were weighed (1 g), packed and sealed into labeled polypropylene plastic packages with its respective radiation doses.

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4. Methods

4.1. Irradiation

Irradiation was performed in a ^{60}Co source (Gammacell 220, A.E.C.L) installed at IPEN-CNEN/SP (São Paulo, Brazil); applied doses were 0, 5, 10, 15, 20 and 25 kGy (dose rate 2.63 kGy/h). Packages, without cinnamon, were irradiated in the same way. Spices samples were analyzed within 1 week after irradiation. Harwell Amber 3042 dosimeters were used for the measurement of radiation dose.

4.2. Solid-phase microextraction (SPME)

SPME employed a polydimethilsiloxane fiber (100 μm thickness—Supelco). One gram of control and irradiated samples were placed into 25 mL Erlenmeyer flasks and sealed with a rubber septum. Each flask was heated to 50 °C in a stove for 5 min, for the release of spice volatiles in the headspace of the flasks. Afterwards, the SPME fiber was introduced throughout the rubber septum and exposed to volatiles of the headspace for 15 min. After that, the fiber was introduced to the GC–MS injector to allow the desorption for 2 min. For each injection, fiber was pre-conditioned within the GC–MS injector settled up to 200 °C for 4 min.

4.3. GC–MS analysis

Volatiles compounds of cinnamon samples were analyzed in a Hewlett-Packard chromatographic system (HP6890) coupled to a selective mass detector (MSD—model HP 5973). Samples were injected in splitless mode (25 m L/min purge flow at 1 min) and separated in a HP5MS capillary column (30 m, 0.25 mm internal diameter, 0.25 μm film thickness). GC temperature program was: 50 °C (initial) for 2 min, rising up to 280 °C at 10 °C/min, and kept at this temperature for 5 min. The carrier gas (helium) flow was 1 mL/min. The ion source of the MSD operated at 70 eV and the data acquisition was done in scan mode (30–550 m/z). The identification of the main compounds of the cinnamon aroma was done with the NIST98 mass spectral database using the NIST Mass Spectral Search Program v. 2.0. Only the compounds with a match qualifier higher than 70 are presented.

4.4. Statistical analysis

Principal components analysis was performed using the Win-Das software (Kemsley, 1998).

5. Results and discussion

The main compounds of non-irradiated samples of cinnamon were identified and are presented in Table 1, with the respective qualifier.

The presence of linalool and cinnamaldehyde were identified by Jirovetz et al. (2001), being considered essential oils of the cinnamon. However, both authors employed different methods from the SPME, so this could explain the identification of some compounds in the samples analyzed, e.g., sativen, eucalyptol and alpha-bergamotene, which had not been described by those authors. However, Jayaprakasha et al. (2002) observed that alpha-bergamotene is one of the major compounds of the *Cinnamomum zeylanicum* buds volatile oil. Lima et al. (2005), examining essential oils from the cinnamon leaves and twigs (*L. cinnamomum zeylanicum* BLUME), identified the presence of benzaldehyde, borneol, terpineol, cinnamaldehyde, beta-caryophillene e copaene, with the predominance of caryophyllene oxide, caryophyllene and cinnamaldehyde in twigs.

Table 1
Volatile compounds in the aroma of the cinnamon non-irradiated samples.

Compounds	Qual
Benzaldehyde	76
Eucalyptol	98
Beta-Linalool	83
Benzenepropanal	89
Borneol	83
4-Terpineol	97
(+)−.alpha.−Terpineol	91
Cinnamaldehyde	96
Cumaldehyde	97
Bornyl acetate	91
(+)−4−Carene	95
Alpha.−Cubebene	98
(+)−Cyclosativene	97
Copaene	99
Cedrene	90
Beta-Elemene	99
(+)−Sativen	89
Alpha-Bergamotene	97
Caryophyllene	94
(Z,E)−alpha-Farnesene	93
Alpha-Guaiene	91
Beta-Patchoulene	86
Epsilon-Muurolene	99
Alpha-Guaiene	98
Alpha-Amorphene	99
Beta-Bisabolene	93
Epsilon-Cadinene	98
(−)−Calamenene	95
Naphthalene, 1,2,3,4,6,8a-hexahydro−1-isopropyl−4,7-dimethyl-	98
1,1,6-Trimethyl−1,2-dihydronaphthalene	72
Cadalene	95
2-Methyl−1H-imidazo(1,2−a)pyrrolo(3,2−E)pyridine	83

Table 2
Peak areas of the main volatile compounds, area and relative percentages of 0, 5, 10, 15, 20 and 25 kGy-irradiated samples.

Compounds	Area	Relative percentage					
	0 kGy	0 kGy	5 kGy	10 kGy	15 kGy	20 kGy	25 kGy
Bornyl acetate	33,829,599	100	98.48	43.80	41.52	31.89	19.39
Copaene	84,478,339	100	87.70	36.35	26.68	20.48	7.34
α-Bergamotene	13,688,072	100	89.87	37.23	23.95	14.81	7.42
Caryophyllene	44,663,952	100	117.63	50.60	21.71	18.09	9.18
Calamenene	20,178,877	100	101.36	49.67	42.62	24.63	9.45

A comparison among the main chromatographic peaks areas found in cinnamon control samples, 10- and 20 kGy-irradiated samples are shown in Table 2. The relative percentage among them, considering the non-irradiated as 100%, indicates a drastic decrease in the main volatiles, suggesting, as a consequence a decrease in the sensorial quality of these irradiated samples.

Increasing radiation doses promoted a decrease in volatiles compounds. Comparing to control samples, the chromatographic profiles of irradiated cinnamon with a dose of 5 kGy showed an average decrease of 47.18% of the total area of the chromatograms and for those samples irradiated with 15 kGy, it was found an average decrease of 89.7%.

The difference of partial chromatographic profiles between non-irradiated samples and those irradiated with 20 kGy, showed a clear decline of chromatographic peaks due to radiation treatment, as can be shown in Fig. 2, where the compounds have a major drop, obtaining an average decrease of 85.4%.

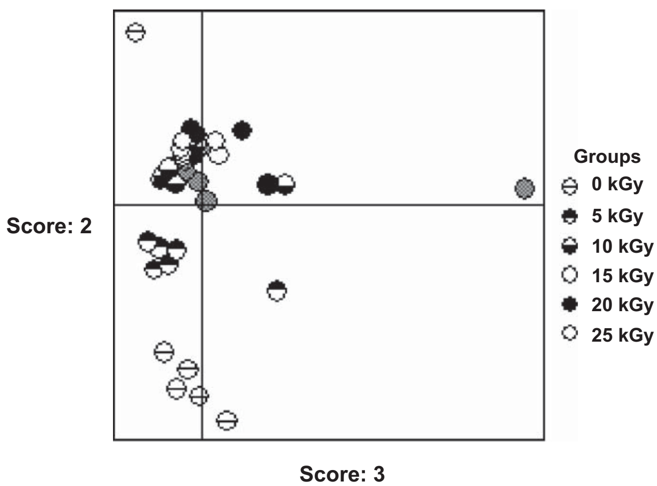

Fig. 1. Analysis of canonical variables of chromatographic volatiles profiles of cinnamon-irradiated at different doses.

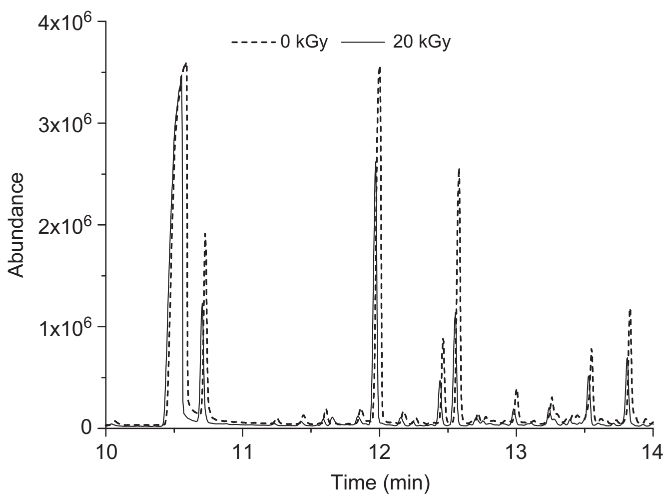

Fig. 2. Partial chromatogram of the volatiles from the irradiated cinnamon samples with a dose of 20 kGy superimposed on a cinnamon control sample (0 kGy).

Irradiated cinnamon with 10 and 25 kGy, showed a similar decrease. These samples showed an expressive reduction on principal volatiles compounds. As an example, comparing to unirradiated samples, for 10 kGy-irradiated samples, borneol acetate showed a decrease of 43.80%, copaene (36.35%), alpha-bergamotene (37.23%), caryophyllene (50.60%) and calamenene (49,67%). In the same way, for 25 kGy-irradiated samples, borneol acetate showed a decrease of 19.39%, as well as copaene (7.34%), alpha-bergamotene (7.42%), caryophyllene (9.18%) and calamenene (9.45%) (Table 2).

The analysis of canonical variables indicated a difference between unirradiated samples and irradiated samples, even though a slight difference was observed between control samples and 5 kGy-irradiated samples. In contrast, irradiated samples with 10, 15, 20 and 25 kGy showed no significant difference among them; however, its difference to control samples were significant (Fig. 1).

6. Conclusions

According to the results obtained, we could conclude that the treatment with gamma irradiation of ^{60}Co caused a general decrease in volatile compounds of cinnamon. Increasing radiation doses also promoted an increase in volatiles loss. Even though cinnamon irradiated with 5 kGy lost almost 50% of its compounds, this dose showed less negative influence.

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