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Effects of gamma irradiation on chemical composition and antioxidant potential of processed samples of the wild mushroom *Macrolepiota procera*

Ângela Fernandes [a,b], João C.M. Barreira [a,b], Amilcar L. Antonio [a,c,d], M. Beatriz P.P. Oliveira [b], Anabela Martins [a], Isabel C.F.R. Ferreira [a,*]

[a] CIMO-ESA, Instituto Politécnico de Bragança, Campus de Santa Apolónia, Ap. 1172, 5301-855 Bragança, Portugal
[b] REQUIMTE/Departamento de Ciências Químicas, Faculdade de Farmácia, Universidade do Porto, Rua Jorge Viterbo Ferreira no. 228, 4050-313 Porto, Portugal
[c] IST/ITN, Instituto Superior Técnico, Estrada Nacional 10, 2686-953 Sacavém, Portugal
[d] Departamento de Física Fundamental, Universidade de Salamanca, Plaza de la Merced, 37008 Salamanca, Spain

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ABSTRACT

It was previously demonstrated that gamma irradiation was the processing technology with the highest capacity to maintain the chemical profile of fresh *Macrolepiota procera* wild mushroom, when compared to freeze-dried or oven-dried samples. Herein, it was aimed to evaluate gamma irradiation effects on processed samples. Chemical composition and antioxidant potential of irradiated (0.5 and 1 kGy) fresh, frozen and dried samples were determined by chromatographic techniques and *in vitro* assays, respectively. *M. procera* irradiation attenuated the effects caused by oven-drying or freezing; combining freeze treatment with 0.5 kGy dose preserved total tocopherols. Rather than a conservation methodology, gamma irradiation might act as a useful adjuvant to other conservation techniques (*e.g.*, freezing or oven-drying).

1. Introduction

Mushrooms perish rapidly and they start deteriorating within a day of harvest. In view of their highly perishable nature, fresh mushrooms have to be processed to extend their shelf life for off-season use (Walde, Velu, Jyothirmayi, & Math, 2006). Among the various methods employed for preservation, freezing and drying are the most used technologies. Blast freezing is the most common method used in mushroom freezing although, recently, cryogenic methods have gained in popularity. Cryogenic freezing provides a higher quality product; however, its application in the food industry is rather limited, due to its high cost (Jaworska & Bernás, 2009). Freezing allows a better retention of nutritional attributes, as well as sensory characteristics, such as colour, aroma, flavour and texture; during freezing most of the liquid water changes into ice, which reduces the microbial and enzymatic activities (Haiying, Shaozhi, & Guangming, 2007).

Dried mushrooms packed in airtight containers can have a shelf life of above one year (Bano, Rajarathnam, & Rekha, 1992; Walde et al., 2006). Different drying methods have been developed to preserve food, including mushrooms, such as drying by sun, hot air and oven-drying method (Ma, Haixia, Wenchai, & Zhaoshuai, 2013).

Food irradiation is a processing technique applied for decontamination and increasing shelf life of food, exposing food to ionising radiation in order to enhance its shelf-life as well as its safety. The aim is to destroy microorganisms or insects that could be present in the food, and sometimes to improve the functional properties of food or to eliminate toxins, with the least compromise on sensory and nutritive quality (Akram & Kwon, 2010; Fernandes, Antonio, Oliveira, Martins, & Ferreira, 2012). According to several authors, irradiation decreases the normal changes associated with maturation, germination and ageing; it destroys insects and microorganisms that cause food spoilage (Beaulieu, D'Aprano, & Lacroix, 2002; Jiang, Luo, Chen, Shen, & Ying, 2010) with minimum changes in nutritional and sensory quality (Akram & Kwon, 2010; Fernandes et al., 2012).

Gamma irradiation has been applied in extending the postharvest shelf-life of fresh mushrooms (Sommer, Schwartz, Solar, & Sontag, 2010). The recommended dose for extending the shelf-life of fresh mushroom in different countries (such as Argentina, China,

* Corresponding author. Tel.: +351 273 303219; fax: +351 273 325405.
E-mail address: iferreira@ipb.pt (I.C.F.R. Ferreira).

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Croatia, Hungary, Israel, Korea, Mexico, Poland and United Kingdom) is 1–3 kGy, while the recommended dose regarding the decontamination of dried mushrooms, used as seasonings, is 10–50 kGy (Akram & Kwon, 2010; ICGFI, 1999).

In a previous study, our research group reported the effects of gamma irradiation on chemical composition and antioxidant activity of *Lactarius deliciosus* fresh samples (Fernandes, Antonio, et al., 2013). The obtained data showed that, at or below 1 kGy, gamma irradiation might provide a useful alternative to ensure quality and extend shelf life, since its effects on the assayed parameters were less significant than the changes caused by storage time. In another study, the effects of different processing technologies (freezing, drying and gamma irradiation) on chemical and antioxidant parameters of the wild mushroom *Macrolepiota procera* were accessed, and irradiation was the processing technology with the highest ability to maintain the chemical profile characteristics of fresh samples (Fernandes, Barros, et al., 2013). *M. procera* is one of the most popular mushrooms, being considered an excellent edible species, highly appreciated for its culinary value (Polese, 2005) but so perishable that it is mostly used for self-consumption after harvest.

Therefore, in the present work, the study of gamma irradiation, already evaluated in fresh samples of *M. procera*, was extended to processed samples, comparing the chemical composition and antioxidant potential of irradiated fresh, frozen and dried mushrooms.

2. Materials and methods

2.1. Samples and samples irradiation

M. procera fruiting bodies were obtained from the region of Trás-os-Montes, in the north-east of Portugal, in November 2011.

The samples were divided into three groups with nine mushrooms per group with different stages of maturation included in each sample, and further submitted to different processing technologies: freezing (at −20 °C in a freezer) and drying (at 30 °C in an oven); the third group was kept fresh (stored at 4 °C in a refrigerator). Each group was further subdivided into three subgroups: control (non-irradiated, 0 kGy); sample 1 (0.5 kGy) and sample 2 (1.0 kGy).

The estimated dose rate for the irradiation position was obtained with Fricke dosimeter, and the irradiation of the samples was performed in a Co-60 experimental chamber with four sources, total activity 267 TBq (7.216 kCi) in November 2011 (Precisa 22, Graviner Manufacturing Company Ltd., UK), following the procedure previously described by the authors (Fernandes, Antonio, et al., 2013). The estimated doses after irradiation were 0.6 ± 0.1 kGy and 1.1 ± 0.1 kGy for samples 1 and 2, respectively, at a dose rate of 2.3 kGy h^{-1}. For simplicity, in the text, tables and graphs we considered the values 0, 0.5 and 1 kGy, for non-irradiated and irradiated samples, respectively.

After irradiation, all the samples were lyophilised (FreeZone 4.5 Model 7750031; Labconco, Kansas City, MO), reduced to a fine dried powder (20 mesh), mixed to obtain homogenate samples and promptly analysed.

2.2. Standards and reagents

For irradiation: to estimate the dose and dose rate of irradiation it was used a chemical solution sensitive to ionising radiation, Fricke dosimeter, prepared in the lab following the standards (ASTM & Materials., 1992) and Amber Perspex dosimeters (batch V, from Harwell Co., UK). To prepare the acid aqueous Fricke dosimeter solution the following reagents were used: ferrous ammonium sulphate(II) hexahydrate, sodium chloride and sulphuric acid, all purchased from Panreac S.A. (Barcelona, Spain) with purity PA (proanalysis), and water treated in a Milli-Q water purification system (Millipore, Billerica, MA).

For chemical analyses: acetonitrile 99.9%, *n*-hexane 95% and ethyl acetate 99.8% were of HPLC grade from Lab-Scan (Lisbon, Portugal). The fatty acid methyl ester (FAME) reference standard mixture 37 (standard 47,885-U) was purchased from Sigma (St. Louis, MO), as were other individual fatty acid isomers, tocopherol and sugar standards. Racemic tocol, 50 mg/mL, was purchased from Matreya (Pleasant Gap, PA).

For antioxidant potential analysis 2,2-diphenyl-1-picrylhydrazyl radical (DPPH·) was obtained from Alfa Aesar (Ward Hill, MA). Standards Trolox (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid) and gallic acid were purchased from Sigma. Methanol and all other chemicals were of analytical grade and obtained from common sources.

2.3. Chemical composition

2.3.1. Nutritional value

Moisture, protein, fat, carbohydrates and ash were determined following the AOAC procedures (AOAC, 1995). The crude protein content ($N \times 4.38$) of the samples was estimated by the macroKjeldahl method; the crude fat was determined by extracting a known weight of the sample with petroleum ether, using a Soxhlet apparatus; the ash content was determined by incineration at 600 ± 15 °C using a chamber furnace (Lenton Thermal Designs Ltd., Hope Valley, UK; model ECF 12/22); total carbohydrates were calculated by difference: total carbohydrates = 100 − (g moisture + g protein + g fat + g ash). Total energy was calculated according to the following equation: energy (kcal) = 4 × (g protein + g carbohydrate) + 9 × (g fat).

2.3.2. Free sugars

Free sugars were determined by high-performance liquid chromatography coupled to a refractive index detector (HPLC–RI) after the extraction procedure described by Reis, Barros, Martins, and Ferreira (2012), using melezitose as internal standard (IS). The equipment consisted of an integrated system with a pump (Knauer, Smartline system 1000, Berlin, Germany), degasser system (Smartline manager 5000), autosampler (AS-2057; Jasco, Easton, MD) and an RI detector (Knauer Smartline 2300). Data were analysed using Clarity 2.4 Software (DataApex). The chromatographic separation was achieved with a Eurospher 100-5 NH_2 column (4.6 × 250 mm, 5 mm, Knauer) operating at 30 °C (7971 R Grace oven). The mobile phase was acetonitrile/deionised water, 70:30 (v/v) at a flow rate of 1 mL/min. The compounds were identified by chromatographic comparisons with authentic standards. Quantification was performed using the internal standard method and sugar contents were further expressed in g per 100 g of dry weight (dw).

2.3.3. Fatty acids

Fatty acids were determined by gas chromatography with flame ionisation detection (GC–FID), after extraction and derivatisation procedures described previously (Reis, Barros, et al., 2012). The analysis was carried out with a DANI model GC 1000 instrument (Milan, Italy) equipped with a split/splitless injector, an FID at 260 °C and a Macherey–Nagel column 50% cyanopropylmethyl 50% phenylmethylpolysiloxane (30 m × 0.32 mm i.d. × 0.25 μm d*f*). The oven temperature programme was as follows: the initial temperature of the column was 50 °C, held for 2 min, then a 30 °C/min ramp to 125 °C, 5 °C/min ramp to 160 °C, 20 °C/min ramp to 180 °C, 3 °C/min ramp to 200 °C, 20 °C/min ramp to 220 °C and held for 15 min. The carrier gas (hydrogen) flow-rate was 4.0 mL/min (0.61 bar), measured at 50 °C. Split injection