Food Research International 60 (2014) 38–47

Contents lists available at ScienceDirect

Food Research International

journal homepage: www.elsevier.com/locate/foodres

Monitoring the quality of γ-irradiated macadamia nuts based on lipid profile analysis and Chemometrics. Traceability models of irradiated samples

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ARTICLE INFO

Article history:
Received 31 August 2013
Received in revised form 23 December 2013
Accepted 7 January 2014
Available online 17 January 2014

Keywords:
Macadamia nuts
γ-Irradiation
Packaging
Storage
Lipid profile
Traceability
Foodomics
Chemometrics

ABSTRACT

Macadamia (*Macadamia integrifolia*) is an edible nut species with commercial importance in cosmetic and pharmaceutical industries due to its high concentration in monounsaturated fatty acids and its low cholesterol levels. γ-Irradiation is a food processing procedure that allows the extension of shelf life and is broadly applied to dry nuts. Therefore there is an increasing research interest towards the development of new methods and markers for the detection of irradiated food items. In the present article, ^{60}Co-irradiation was applied to macadamia nuts in increasing doses up to 10 kGy using different packaging and storage conditions in order to monitor changes in their lipid profile. Compositional data showed predominance of triglycerides followed by phytosterols in a much smaller proportion in nuts' lipids. The production of hydrolytic compounds as a result of gamma irradiation was statistically significant but didn't affect the macadamias' fat quality. Classification was achieved in relation to irradiation dose, package and storage conditions, using Chemometrics. More specifically, PCA and OPLS-DA analyses on the GC–FID, TLC–FID and color results managed to differentiate samples according to irradiation doses.
NMR based FoodOmic application is employed for the first time, in order to explore any trends in sample classification according to the irradiation dose and the storage or the packaging effect. Minor lipid components (such as β-sitosterol, C18:2 n − 6, C18:3 and sn1,2 and sn1,3 DGs) have shown high discriminant power over the samples. Results correlated storage and packaging effects with macadamia freshness.

1. Introduction

Macadamia nuts (*Macadamia integrifolia*) belong to the botanical family Proteaceae. Their utility in the composition of hydrating lotions and as a reducer of cholesterol levels has elevated their value in the cosmetic and pharmaceutical industries (Colquhoun, Humphries, Moores, & Somerset, 1996).

Their fatty acid profile and especially the high concentration of oleic acid are beneficial to the decrease of coronary heart disease. Frequent nut consumption is also associated with lower risk of diabetes (Jiang et al., 2006). This cholesterol-lowering and coronary-protective effect may be due to the high percentage of unsaturated fatty acids, as well as other bioactive constituents such as tocopherols, phytosterols, and squalene. In fact, macadamias constitute the edible seeds with the highest content of monounsaturated fats, predominantly oleic (60%) and palmitoleic (20%) acids. Specifically, the macadamia nut oil comprises high content in oleic and in fat and low in protein compared to other common seeds such as almonds and cashews. Moreover, they contain C16:1 (15-30%) from which approximately 22% is palmitoleic (C16:1n-7), myristic (0.6–1.8%), palmitic (7–24%), stearic (2–5%), oleic (40–65%), linoleic (1.4–4.5%), and arachidic (1.2–4.5%) (Wall, 2010). They also contain 9% protein, 9% carbohydrate and 2% dietary fiber, as well as calcium, phosphorus, potassium, sodium, selenium, iron, thiamine, riboflavin and niacin (Kaijser, Dutta, & Savage, 2000; Macfarlane & Harris, 1981).

Abbreviations: M-E, methyl ester; PCA, principal component analysis; OPLS-DA, Orthogonal Partial Least Squares Discriminant Analysis; UV scaling, a variable j is centered and scaled to "Unit Variance". The base weight is computed as 1/sdj, where sdj is the standard deviation of the variable j computed around the mean; Par scaling, a variable j is centered and scaled to Pareto Variance. The base weight is computed as 1/sqrt(sdj), where sdj is the standard deviation of the variable j computed around the mean; A, number of model dimensions; Observations (N), number of observations; Variables (K), total number of variables; R^2X, fraction of the total variation of the X block that can be explained by each component; R^2Y, fraction of the total variation of the Y block that can be explained by each component; Q^2, fraction of the total variation of the X block (PCA) or the Y block (PLS) that can be predicted by each component; Q^2(cum), cumulative Q^2 for the extracted components; VIP, Variable Influence on the Projection. It provides the influence of every term in the matrix X on all the Y's. Terms with VIP > 1 have an above average influence on Y. This vector is cumulative over all components up to the selected one.

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0963-9969/$ – see front matter
http://dx.doi.org/10.1016/j.foodres.2014.01.015

On the other hand, macadamias contain the lowest level of antioxidative constituents (polyphenols, tocopherols) compared to walnuts, pistachios, pecans, peanuts with skin, hazelnuts and almonds with skin (Kornsteiner, Wagner, & Elmadfa, 2006).

The fact that macadamia oils have a higher ratio between unsaturated to saturated fatty acids renders them susceptible to oxidation due to increased oxidation potential of unsaturated fatty acids, affecting their quality and shelf life (Frankel, 1998).

Gamma irradiation is a food processing procedure that allows the extension of shelf life. The Food and Drug Administration has specified that food stuffs may be exposed to a maximum dose of 10 kGy, as this irradiation dose does not impart heat to the food and the nutritional quality of the food is generally unaffected (Gecgel, Gumus, Tasan, Daglioglu, & Arici, 2011). In this context, food irradiation and in particular γ-irradiation has been recognized and regulated as an effective food processing technology being able to destroy or reduce ubiquitous pests and pathogens that contaminate various agricultural products and inhibit mycotoxin biosynthesis during storage (Gecgel et al., 2011).

EU Directive 1999/2/EC specifies the provisions including the source of ionizing radiation, controls on the level of radiation permitted and food labeling requirements. Conditions are also specified for the importation of irradiated foods. Greece has been harmonized with these directives as EU member state through the implementation law EEL 66/13-3-1999, 2000. In general lines, EU countries must use validated or standardized analytical methods to detect irradiated foods. Currently, foods & food ingredients authorized for irradiation in the EU include (a) fruit and vegetables including root vegetables; (b) cereals, cereal flakes, and rice flour; (c) spices and condiments; (d) fish and shellfish; (e) fresh meats, poultry, and frog legs; (f) raw milk camembert; (g) gum arabic, casein/caseinates, and egg white; and (h) blood products. Nuts or dry nuts are not included in the list. Nevertheless, the problem arises when irradiated food including nuts (packaged or in bulk) is imported without appropriate labeling. Irradiated food or one containing irradiated ingredients must be labeled.

The impact of gamma irradiation (1, 3, 5, and 7 kGy) on the consistency of various nut types (hazelnut, walnut, almonds, and pistachio nuts) has been investigated. In particular, after irradiation no significant changes in the oil content were traced, while free fatty acid and peroxide value increased proportionally to the dose. Interestingly, the concentration of total saturated fatty acids increased while total monounsaturated and total polyunsaturated fatty acids decreased with the irradiation dose (Gecgel et al., 2011).

Nevertheless, it is well recognized that γ-irradiation produces free radicals that interact with both lipid and protein molecules, leading to the formation of numerous oxidation products, which are responsible for flavor changes in irradiated foods (Diehl, 1981), including aldehydes, esters, ketones, sulphur compounds, etc. (Sajilata & Singhal, 2006). The physicochemical and sensory characteristics of nuts when irradiated are affected by several factors, including specific fruit, irradiation dose, and type. Thus, it is of paramount importance to elucidate the effect of gamma irradiation on the physicochemical and sensory properties of macadamia nuts.

Packaging is also an important factor for food preservation. Nuts are usually stored in vacuum plastic bags although in many countries are sold unpacked in bulk.

In general, food processors prefer that food be prepackaged in the final packaging form before irradiation to prevent recontamination and to facilitate prompt shipment to market after irradiation. Food could potentially become contaminated with radiolytic products formed in the packaging materials when irradiated in contact with food which may lead to a safety concern. The radiolytic products formed upon irradiation could migrate into food and affect odor, taste, and safety of the irradiated food. These undesirable products may be formed in the presence (polymer degradation) or absence (polymerization) of oxygen. Vacuum or inert atmospheres belong to the last category of polymer cross-linking (polymerization). Both reactions are random, and depend on dose rate and the oxygen content of the atmosphere in which the polymer is irradiated. Presently authorized packaging material by FDA for irradiation in contact with food under non-oxygen atmospheres is included under 21 CFR 170.39 (Komolprasert, 2007).

The listed materials include films and homogeneous structures at doses up to 10 kGy incidental to the use of any radiation source in the treatment of packaged food.

To our best knowledge, no published results are currently available regarding optimum preservation using different storage and packaging conditions for macadamia nuts and there is a complete lack of research results related to macadamia nuts and gamma irradiation.

The present work focuses on the effects of γ-irradiation and packaging and storage periods on the lipid profile of macadamia nuts (*M. integrifolia*). In particular, γ-irradiation was applied to doses of 0.5, 1.5, 3.0, 5.0 and 10.0 kGy, while packaging conditions included atmospheric air, vacuum and modified atmosphere (41% CO_2–59% N_2).

The main objectives of the article focus on (a) proximate composition, lipid classes and fatty acid profile and content of macadamia nuts since they constitute a rich source of nutritionally important lipids and unsaturated fatty acids; (b) effect of gamma irradiation on lipid profile of macadamia nuts; (c) nutritional value of nuts in relation to different doses of irradiation treatment; and (d) packaging effect versus irradiation doses and storage time at 4 ± 1 °C in order to elucidate the packaging tolerance/endurance/to secure the consistency of the macadamias' intrinsic quality when irradiated.

Our approach is based on combined analytical techniques including GC–FID, Iatroscan TLC–FID and NMR spectroscopy, complemented with Chemometrics (principal component analysis, PCA; Orthogonal Partial Least Squares Discriminant Analysis, OPLS-DA). Chemometric techniques have been recently introduced to food science towards discrimination of several products (Cruz et al., 2013; Granato, Branco, Faria, & Cruz, 2011).

NMR spectroscopy can be also used as a screening tool for detection of gamma irradiated food items (Zoumpoulakis et al., 2012). This holistic "FoodOmic" application may provide evidence for irradiated samples.

2. Materials and methods

2.1. Reagents and standards

Analytical-grade solvents were obtained from Merck (Darmstadt, Germany). All reagents used were of analytical grade and they were purchased from Mallinckrodt Chemical Works (St. Louis, MO) and from Sigma Chemical Co. (Sigma-Aldrich Company, UK).

The lipid standards used for TLC–FID and NMR spectroscopy were: cholesteryloleate, cholesterol, tristearoyl-glycerol, lauric acid, oleic acid, linoleic acid, 1,2-distearoyl-glycerol, 1-monostearoyl-rac-glycerol, phosphatidic acid, phosphatidylcholine, phosphatidylethanolamine, lyso-phosphatidylcholine, phosphatidylinositol and phosphatidylserine standards of the Sigma Chemical Co, (Sigma-Aldrich Company, Dorset, Great Britain and St. Louis, MO).

Fatty acid methyl esters used as GC standards were: lauric acid M-E, *cis*-5,8,11,14,17-eicosapentaenoic acid M-E, and *cis*-4,7,10,13,16,19-docosahexaenoic acid M-E (purity ≥98%) purchased from Sigma Chemical Co. (Sigma-Aldrich Company, UK); Matreya Bacterial Acid Methyl Esters CP™ Mix; Supelco™ 37 Component FAME Mix C4–C24; Supelco PUFA No. 1, Marine Source.

2.2. Radiation process

Samples were purchased from a local supermarket (all samples selected were of the same lot number). Macadamia nuts (*M. integrifolia*) were packed in 50 g sachets, in atmospheric air, vacuum and modified atmosphere (41% CO_2–59% N_2). Irradiation was carried out in the Institute of Pharmaceutical Research and Technology — IPRT S.A (Mandra