Effect of nut-in-shell storage conditions on volatile profile in macadamia nuts

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Abstract

In order to study the effect of storage conditions on the volatile profile of macadamia nuts, both temperature and the presence of oxygen were controlled. Nuts-in-shell of variety 246 were stored at -18, 10 and 15°C. At each temperature, samples were stored in net bags and vacuum packed in EVOH (ethylene vinyl alcohol) for a period of 2 months. Prior to testing, samples were cracked and roasted. Analytical tests included peroxide value, p-anisidine and TBA (thiobarbituric acid number). Volatile compounds were isolated using Head-Space-Solid-Phase-Micro Extraction (DVB/PDMS/CAR). Volatiles were analysed by chromatography/mass spectrometry (GC/MS). The results show that at –18°C peroxide, p-Anisidine and TBA values were lower compared to the other 2 storage temperatures. This indicates that lipid degradation was lowest at this temperature. The main compounds found in volatile components of both fresh and roasted macadamia nut were hydrocarbons, aldehydes, and ketones. Several compounds deriving from lipid degradation and Maillard reaction were detected such as hexanal, thiazole. This indicates that changes in volatiles of macadamia nuts result from compounds present in macadamia nuts which were the precursors of volatile compounds produced during roasting. Storage materials which were net bag and EVOH showed no significant effect on volatile produced during 2 months storage trial. Volatiles generated depend mainly on processing steps such as roasting. The lipid degradation was minimised at low temperature. Therefore storage conditions for nut-in-shell influence the final macadamia kernel quality, especially shelf-life, as peroxide value and other lipid degradation product were used as criteria of shelf-life changes while volatile produced by Maillard reaction indicated roasting quality.

Keywords: Macadamia, Volatiles, Storage conditions, Head-Space-Micro Extraction, Lipid changes

1. Introduction

Macadamia nuts are among the most nutritious and highest in monounsaturated oil content among edible nuts (AMS, 2009). They are widely grown in Australia, USA, especially in Hawaii, South Africa and Guatemala (USDA, 2008). According to World Horticultural Trade & U.S. Export Opportunities (2002), Australia is the biggest macadamia producer and exporter, accounting for 46% of total macadamia world production. As the industry expands, the importance of maintaining kernel quality is increasing. High quality will increase competitive advantages and increase profits. Usually during harvest season, which is March to October in Australia, macadamia processors receive 10 tonnes or more per week. It is difficult to process all the nuts in the limited time. Therefore, in practice, macadamia nuts are de-husked and dried to 8-10% wet basis moisture content and stored as nut-in-shell until the processor is able to handle the nuts, which might take up to 1-2 months. During that time, kernel deterioration might occur. Due to the large amount of unsaturated fat that they contain, macadamia nuts are susceptible to rancidity. Rancidity is influenced by post-harvest treatments which could contribute to inferior nut quality. As macadamia nut quality is based on oil content and oil is its major component, it is important to investigate the relationship between post-harvest treatment and fatty acid content in macadamia nuts. Other biochemical changes such as changes in enzyme activity may occur. Changes in lipids influence the volatile compounds produced during roasting affect macadamia's unique aroma and flavour. Such changes may also affect consumer preferences. Hence this study focused on how storage conditions influence volatile profile in macadamia nuts. The aim of this study was to:

a. to determine the volatile compounds produced under defined storage conditions,
b. to evaluate the impacts and consequences of nut-in-shell storage conditions on macadamia nut volatile profile.

2. Materials and methods

2.1. Storage conditions

Macadamia nuts-in-shell (NIS) of variety 246 received from Northern New South Wales, (Australia) were stored for 2 months at -18, 10 and 15°C, respectively. Initial moisture content of macadamia was approximately 8-10% wet basis. For each temperature, samples were stored in both net bags and vacuum packed in EVOH. Prior to testing, samples were cracked and roasted at 125°C for 2 hours in an incubator until the kernels became slightly brown.

2.2. Lipid degradation tests

Analytical chemistry tests were performed such as peroxide value, p-anisidine and TBA (thiobarbituric acid test). Samples were analysed by an indirect colorimetric method (Yaacoub et al., 2009*)*.

2.3. Analysis of volatile compounds

Treated macadamias were placed in glass jars (height 10 cm, radius 3.15 cm total volume 117 cm^3). Volatile compounds were isolated by Head-Space-Solid-Phase Micro-Extraction. Sample and fiber (DVB/PDMS/CAR) were left to reach equilibrium for 1.5 hours at 30°C. The absorbed sample was manually injected into a gas chromatograph (Agilent 6890 N and 5975 inert mass selective detector, Agilent Technologies, USA) coupled with a mass spectrometry (GC/MS). The column used was a fused silica capillary with 5% phenylpolysiloxane as the non polar stationary phase (60 m long × 220 µm i.d. × 0.25 µm film thickness, SGE, USA).The injection port was operated in spiltless mode. Colum pressure was 165.5 kPa with average carrier gas velocity of 26 cm/s .The temperature program started at 30°C and temperature was increased 2°C/min until it reached 180°C. At the final stage, temperature was increased at 50°C/min until the oven temperature was 250°C. Data were collected with HP CHEMSTATION software and peak mass spectra were searched in the Wiley registry of mass spectral data to facilitate identification of individual volatile components.

3 Results and discussion

3.1. Lipid degradation

Measurement of lipid degradation by-products was performed by a colorimetric method (Yaacoub et al., 2009*)*. The change of colour varied in proportion to the amount of compounds in the sample. Figure 1 shows that overall, lipid oxidation was minimised if the sample was stored at 18°C especially with the absence of oxygen (Fig.1a) and (b). However, lipid oxidation rate as indicated by the amounts of lipid oxidation compounds including peroxide, TBA and p-anisidine value were not significantly different between samples with presence (net bags) and absence of oxygen (EVOH vacuum packing). Therefore macadamia processors may not need to invest in oxygen control system to maintain nut quality. However, this study was conducted for only 2 months, and different outcomes may result for longer storage time, as oxygen plays an important role in lipid degradation processes. Peroxide value of after-roasted samples was higher compared to before-roasting (Figure 1). This was because the high roasting temperature accelerated lipid oxidation and decomposition of hydroperoxides was lower than production of hydroperoxide compounds. In contrast to other samples, peroxide value of vacuum pack stored at -18°C was reduced after roasting, which can be seen from Figures 2b and 2c. This indicated there might be a correlation between the peroxide value and TBA at -18°C. TBA, which measures the amount of malondialdehyde, was the only value that increased as storage temperature (net bag) became lower. This explanation could be that peroxide compound underwent secondary oxidative reaction, resulting in the increasing of TBA values at the lower temperatures.

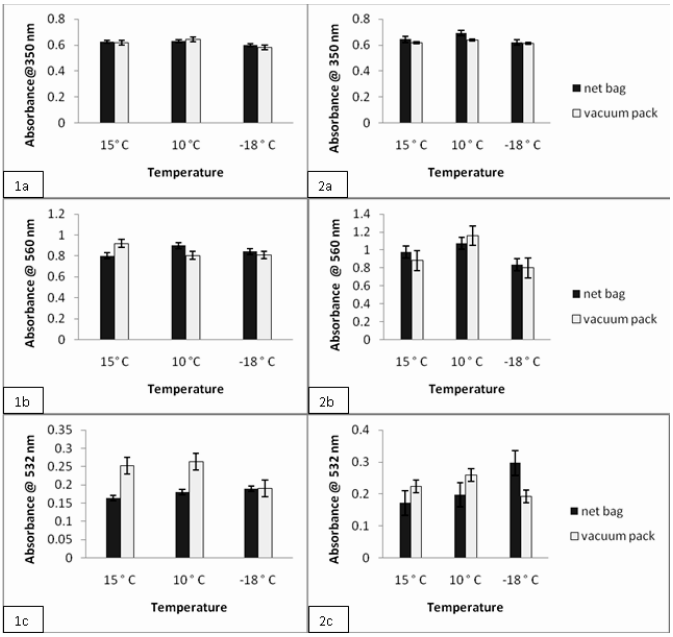

Figure 1 Accumulation of lipid degradation by products of macadamia nut expressed as absorbance against storage temperatures; (a) p-anisidine value before (1a) and after roasting (2a), (b) Peroxide value before (1b) and after roasting (2b), (c) TBA value before (1c) and after roasting (2c).

3.2. Volatile profile

Regardless of packaging material and storage temperature, the concentrations of volatile compounds found in the stored unroasted nuts were not significantly different. From Table 1, hexanal was found in all vacuum packed unroasted nut samples in storage, irrespective of storage temperature. Other volatiles detected were octanal, heptanal and hydrocarbons while in roasted nuts, compounds detected were pyrazine, furan, thiazole, pyranose and pyran. Compounds present in macadamia nuts before and after roasting were qualitatively and quantitatively different. Volatile compounds generated during roasting can occur through Maillard reaction and lipid oxidation pathways. More compounds arose from Maillard reaction than from lipid degradation.

Macadamia is mainly composed of lipids, proteins and sugars. These chemical elements can participate in chemical reactions to form new compounds. Macadamia has high contents of oleic and linoleic acids which oxidize and decompose into hexanal or octanal (Shahidi, 2001) which is supported by the results shown in Table 1.

Table 1 Classification of compound presence in before and after roasting (oven at 125°C) of macadamia nut-in-shell stored for 2 months.

Compounds	
Before roasting	After roasting
Hexanal	Pyridinamine
Octanal	Pentanamine
Butenal	Pyrazine
Ester	Thiazole
Indole	Oxazine
Nonyl aldehyde	Hexanol
Heptanal	Cyclobutanone
Butanone	Pyrrolidine
Propenal	Propenal

Compounds	
Octyldodecan-1-ol	Butanone
Propenal	Pyran
	Furan
	Pyranose
	Pyrrolepyran
	Aziridine
	Amine

Predominant volatile compounds produced during storage of macadamia vary between different nuts. Hexanal was the major volatile compound formed in almond, Brazil nut, hazelnut, pecan, pine nut and pistachio by lipid oxidation while propanal was highest in walnut (Miraliakbari and Shahidi, 2008). Crain and Tang (1975) reported that methyl sulphide, methylpropanal, 2-methylbutanal, 3-methylbutanal were present in high concentrations in roasted macadamia nut. The major volatiles such as pyrazine, furan, thiazole, pyranose, and pyran are formed through Maillard reactions as the nut is subjected to thermal processing steps. In addition to Maillard reaction compounds, Figure 2 shows that there were several other compounds in roasted macadamia. These included pyran, propenal, pyrazine, furan, pyranose, amine, thiazole, pyrrolidine, pyridinamine, pentanamine and oxazine. These findings agreed with the results of others including Pino et al. (2009) and Alasalvar et al. (2003). Studies on other nuts showed similar trends. Morini and Maga (1995) studied volatile compounds in roasted and boiled Chinese chestnut and also concluded that heating processes induce Maillard reactions based on amino acids and sugars as substrates. This process is accompanied by colour development. These results show that volatile compounds produced after roasting were not dependent on storage conditions but rather on how the roasting process was controlled.

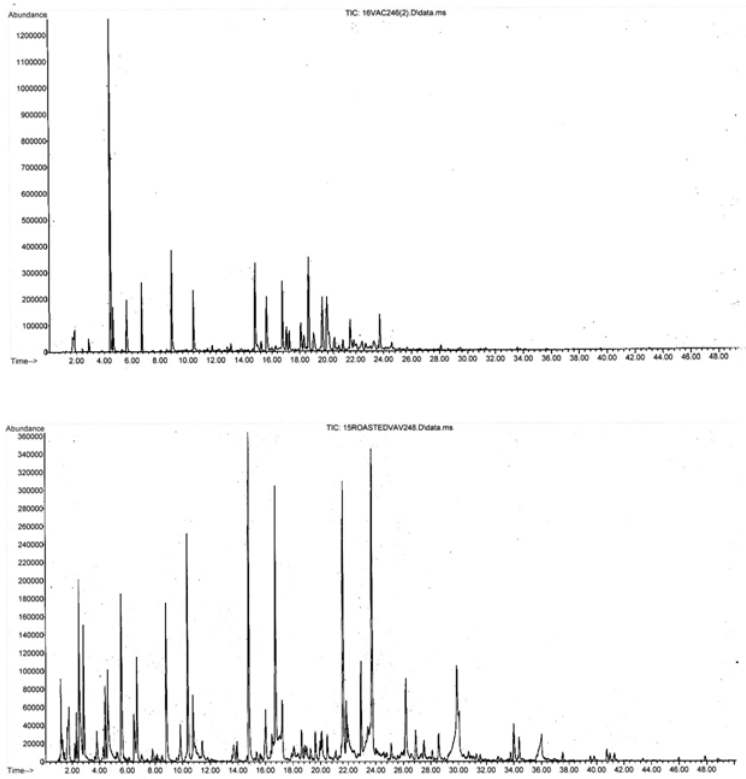

Figure 2 Comparison of volatiles produced in macadamia nut stored at 15°C in vacuum pack before (above) and after roasted (below) at 125°C.

4. Conclusions

This study investigated the effect of storage conditions and temperature on the volatile compounds in macadamia nuts. The results indicated that the changes to lipids were reduced under low temperature storage conditions regardless of packaging material. Therefore storage conditions for nut-in-shell can influence final macadamia kernel quality. Close control of storage and roasting treatments could minimize degradation of fatty acids in macadamia kernels. Volatile compounds produced before and after roasting were mainly due to reactions of precursors in macadamia nut including lipids, sugars and amino acids, which showed no difference between packaging in net bags or vacuum packed in EVOH. However, lipids and others compounds undergo different reactions to produce different end-products, especially volatile compounds which could affect consumer preferences. Volatile compounds generated from Maillard reactions are a good indicator of the effectiveness of roasting, as they play an important role in determining overall flavor while by-products of lipid degradation are good indicators for shelf-life determination of macadamia nut.

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