INVESTIGATING THE EFFECT OF THERMAL PROCESSING ON BIOCHEMICAL COMPOSITION AND KERNEL SHELF-LIFE OF MACADAMIA (*MACADAMIA INTEGRIFOLIA*)

By

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DECLARATION

I, Nana Millicent Duduzile Buthelezi (Student No. 216053657), declare that the research reported in this thesis, except where otherwise indicated, is my original work. This thesis has not been submitted for any degree or examination at any other university.

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SUMMARY

The aim of this study was to evaluate and compare quality parameters of raw and roasted macadamia kernels and the impact of different roasting temperatures and cultivars on biochemical composition and shelf life of macadamia nuts. Another objective was to develop visible to near infrared (Vis/NIR) spectroscopy (Vis/NIRS) calibration models that could be used by the macadamia industry to predict rancidity. A critical review of literature identified biochemical markers associated with quality loss in macadamia nuts and the importance of thermal processing on macadamia kernel quality and shelf life. The prospects for the use of Vis/NIRS as a non-destructive technology to predict rancidity on macadamia kernels was also reviewed. Initial studies were conducted to determine the effect of roasting, roasting temperatures and cultivar on chemical and sensory quality of macadamia nuts. It was found that roasted kernels of 'A4' and 'Beaumont' cultivars had good quality during the accelerated storage of 70 days, indicated by lower peroxide value (PV), high concentration of flavonoids, phenols and antioxidants, confirming the vital role of antioxidant activity in delaying lipid oxidation or rancidity. According to sensory panelists, roasted kernels had enhanced crispy texture, aroma, flavour, appearance and good marketability during storage compared to raw kernels. The study suggested that roasting enhanced quality and shelf life of macadamia nuts. The study on the effect of drying temperatures on postharvest quality of macadamia nuts showed that 'A4' and 'Beaumont' kernels roasted at 125 °C had lower PV, higher concentration of phenols and antioxidants and enhanced sensory quality; crispy texture, brown colour and nutty taste compared to the quality of kernels roasted at 50 °C, 75 °C, 100 °C and 150 °C. Kernels roasted at 50 °C, 75 °C and 100 °C were more prone to deterioration as indicated by high PV and poor sensory quality; hard texture, light colour and slightly nutty taste whereas kernels roasted at 150 °C had high levels of rancidity, lower concentration of flavonoids, phenols, antioxidants, excessive crispy texture, dark brown colour and bitter taste. The study on the effect of cultivar on kernel quality and shelf life of roasted macadamia nuts showed that the 'Beaumont' cultivar had lower PV, acid value (AV), high phenols and antioxidants and good sensory quality; nutty taste with no noticeable rancid taste during the accelerated storage of 18 weeks compared to 'A4' cultivar which had poor quality during storage due to higher PV and AV, lower concentration of phenols and antioxidants and poor sensory quality; poor nutty taste and rancid taste. The studies in this thesis suggested that roasting macadamia nuts at 125 °C significantly enhanced kernel quality and storability of macadamia nuts by inactivating

oxidative enzyme system such as lipoxygenic and lipolytic enzymes associated with deteriorative reactions such as oxidative and hydrolytic rancidity. Roasting also leads to denaturation of several enzymes such as peroxidase and polyphenol oxidase, which are responsible for the development of off-flavours and darkening reactions through the development of browning pigments. The inactivation of these enzymes led to low levels of rancidity indicated by lower PV and AV in roasted kernels which in turn might have contributed to high concentration of flavonoids, phenols and antioxidants observed in roasted kernels during storage. This could be due to the release of some bound antioxidant phenolic compounds acting as free radical scavengers from the cell matrix and increase phenolic extractability upon roasting. According to the panelists, kernels roasted at 125 °C had crispy texture, good flavour, taste, aroma, overall appearance and were marketable during storage. Another study in this thesis showed that the 'Beaumont' cultivar had good quality, indicated by lower PV, AV, high concentration of phenols and antioxidants and good sensory quality during the accelerated storage of 18 weeks compared to 'A4' cultivar which had poor quality, indicated by higher PV and AV, lower concentration of phenols and antioxidants and poor sensory quality during storage. These findings suggested that 'Beaumont' cultivar could be preferable for long term storage. The partial least square (PLS) regression models developed in this study to predict peroxide value demonstrated the potential of Vis/NIRS as a non-destructive tool for prediction of rancidity on intact kernels of 'A4', 'Beaumont', roasted and raw macadamia nuts. The high prediction accuracy recorded when models developed to predict rancidity on macadamia kernels demonstrated robustness of PLS models. Where speed and accuracy are required for evaluating the degree of rancidity on individual intact macadamia kernels, Vis/NIRS and models developed in this study are recommended.

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PUBLICATIONS AND CONFERENCE PRESENTATIONS

All chapters of this work, except chapter 1 and 7, were intended for publication, and as a result, are written in the form of manuscripts. Due to the time limit, only chapter 2 is currently accepted for publication and other chapters are currently under review while others are or will be submitted to relevant journals.

Published papers

Buthelezi, N. M. D., Tesfay, S. Z., Ncama, K., and Magwaza, L. S. (2019). Destructive and non-destructive techniques used for quality evaluation of nuts: A review. *Scientia Horticulturae* 247, 138-146.

Conferences

Buthelezi, N.M.D., Magwaza, L.S., Tesfay, S.Z., 2018. The effect of processing conditions on the quality attributes of 'A4' and 'Beaumont' macadamia (*Macadamia intergrifolia*). College of Agriculture, Engineering and Science Postgraduate Research and Innovation Symposium, University of KwaZulu-Natal, Westville Campus, Durban, 25 October, 2018. (Oral).

PREFACE

This thesis is a compilation of manuscripts where individual chapter is an independent article introduced disjointedly. Hence, some repetition between individual chapters has been inevitable.

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CHAPTER 1: GENERAL INTRODUCTION

1.   Introduction

Macadamia F. Muell. is native to coastal rainforests of the east coast of Australia and is a genus of nine species; seven occurring in Australia and two in Indonesia Sulawesi (Walton, 2005). Only *M. integrifolia* Maiden and Betche and *M. tetraphylla* L.A.S. Johnson species and their hybrids are commercially cultivated and comprises of the edible kernel (Monaghan, 2008). *Macadamia integrifolia* is characterized by round nuts with a smooth shell while *Macadamia tetraphylla* has spindle shaped, rough shelled nuts (Walton, 2005). Mature macadamia consist of a cream to white seed, which is the kernel, enclosed in a hard, dry pericarp (shell), which is then enclosed in a green or grayish green or brown pericarp (husk) (Delprete et al., 2015; du Preez, 2015) (Fig. 1).

Husk

Shell/Nut-in-shell

Kernel/Shelled nut
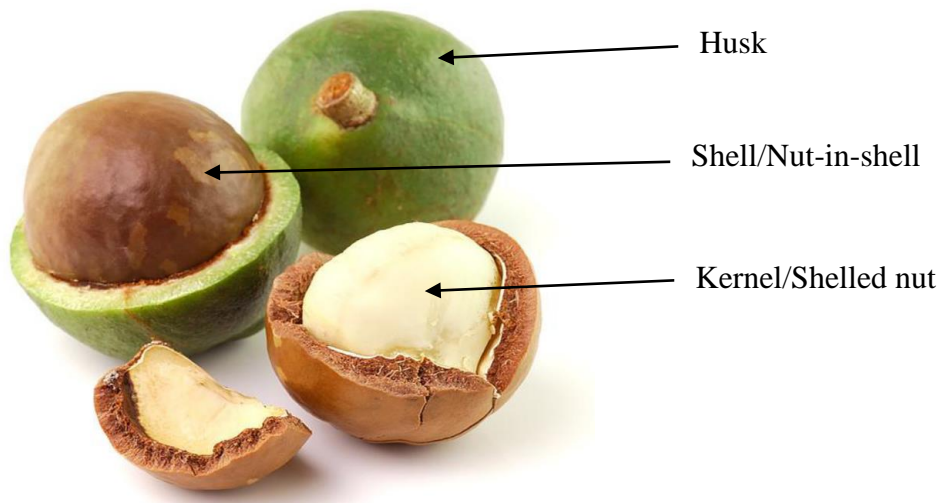
Fig. 1: Illustration of macadamia nut (DAFF, 2015a).

Macadamia is mainly cultivated in Australia, South Africa and Kenya. There are also expanding industries in the USA (Hawaii and California industry), Malawi, Guatemala and China (Jaskiewicz, 2015). The world annual production is currently estimated to be 100 000 tons (Rengel et al., 2015); 86 % of which comes from the five main producing countries, namely, Australia (32 %), South Africa (30 %), Kenya (12 %), United States (8 %), and Malawi (4 %) (Jaskiewicz, 2015; Navarro and Rodrigues, 2016). South Africa is the world's largest

exporter of macadamia nuts (36.37 %) followed by Australia (14.6 %), Kenya (12.1 %), Hong Kong (9.7 %), the Netherlands (4.5 %) and China (3.8 %) (DAFF, 2016).

The macadamia nut is increasingly consumed due to its dense nutritional value and reported health benefits, including prevention of cardiovascular diseases and type 2 diabetes (Jiang et al., 2005; Lovejoy, 2005; Rengel et al., 2015). These health benefits are linked to low levels of cholesterol, high oil content (69-78 %) which is rich in monounsaturated fatty acid (80 %) predominately oleic, palmitoleic, and palmitic acids (Kaijser et al., 2000; Moreno-Pérez et al., 2011; Sinanoglou et al., 2014). These fatty acids content is the key criterion that indicates the quality of macadamia nuts (Phatanayindee et al., 2012). Macadamia nuts are also a rich source of other bioactive macronutrients such as protein, dietary fiber, essential minerals, vitamin E, and plant sterols (Ros, 2010; Ros et al., 2010). Wall (2010) reported that the presence of phytochemicals such as antioxidants in macadamia nuts are not only beneficial to human health but these compounds may protect the kernels from oxidation reactions during storage and marketing, thereby extending shelf-life. Therefore, most research in recent years has mainly focused on improving the quality of the kernel in response to increasing global production and market competition of macadamia nuts (Walton, 2005). The economic value of macadamia is determined by yield, kernel recovery (percentage of whole kernel after cracking nuts), nut quality and nut style distribution (whole kernel, halves and pieces) (du Preez, 2015). Kernel quality is primarily indicated by appearance (size, shape, colour, freedom from defects), texture, flavour and shelf life (Walton, 2005).

Due to the highest content of unsaturated fatty acids (80 - 81.8 %) present in macadamia nuts (Rengel et al., 2015), kernels are more susceptible to rancidity; related to the occurrence of disagreeable odours and flavours (Borompichaichartkul et al., 2013; du Preez, 2015; Rengel et al., 2015). There are two main pathways resulting in rancidity, oxidation termed oxidative rancidity and lipolysis termed hydrolytic rancidity (Borompichaichartkul et al., 2013). Lipid oxidation is a vital deteriorative reaction with great consequences in the quality and value of edible oils, particularly in relation to the off-flavors that develop as a consequence of autoxidation which is a self-sustaining free radical mechanism that produces hydroperoxides (primary products) and photo-oxidation or enzymic oxidation (Phatanayindee et al., 2012). During the initial stages of the oxidation process, hydroperoxides accumulate as main oxidation

products, subsequently breaking down to form low molecular weight oxygenated constituents, such as alcohols, aldehydes, ketones and free fatty acids, eventually resulting in the development of rancidity (Moigradean et al., 2012; Pannico, 2014). Peroxide value (PV) is the most commonly used technique for determining the onset of oxidation as it is a measure of the hydroperoxides formed in the initial stages of oxidation (Borompichaichartkul et al., 2013; Das et al., 2014). Apart from causing rancidity, lipid oxidation products, mainly hydroperoxides, can react with amino acid residues in the Maillard reaction, causing excessive browning (Walton, 2005).

Hydrolysis results from enzymatic hydrolysis of triacylglycerols and the release of free fatty acids (FFA), leading to hydrolytic rancidity (Das et al., 2014). The hydrolysis reaction or ester bonds in lipids (lipolysis) turns triglycerides into glycerol and free fatty acids, which occurs soon after nut cracking and is caused by the presence of lipase enzymes, heat and moisture as catalyst (Thanonkaew et al., 2012; Walton et al., 2017). The release of short-chain fatty acids by hydrolysis is responsible for the development of disagreeable rancid flavour (hydrolytic rancidity) (Bhosle and Subramanian, 2005). Free fatty acids have a higher oxidative rate than their glycerol esters (Bhosle and Subramanian, 2005; Farhoosh et al., 2009), and are extremely prone to autoxidation than intact triglycerides; once formed they are subject to autoxidation, production of FFA hydroperoxides and then in turn secondary and tertiary products of oxidation (Walton, 2005). Therefore, the content of liberated fatty acid namely; capric, lauric, and myristic negatively affects the oxidative stability of edible oils and are characterized by stronger off-flavours (Bhosle and Subramanian, 2005; Farhoosh et al., 2009; Moscetti et al., 2013; Nayak et al., 2016). In macadamias, even small differences in FFA values are highly correlated with differences in kernel flavour (Walton, 2005). Acid value (AV) is the most commonly used measure of hydrolytic rancidity in edible oils (Phatanayindee et al., 2012). Fig. 2 demonstrates the possible pathways for oxidative and hydrolytic rancidity.

3

Triglycerides

Oxidation
(autoxidation,
photo-oxidation
or enzymic)

I

Hydrolysis
(hydrothermal or enzymic)

II

Triglyceride hydroperoxides
(Mono-, di-, epoxy and cyclic
hydroperoxides)

Free fatty acids + glycerol

Hydrolysis

II

Oxidation

Free fatty acid hydroperoxides

Secondary and tertiary products:
saturated, unsaturated, di- and
epoxyaldehydes
ketones
lactones
furans
monobasic, dibasic, oxo and hydroxy acids
saturated and unsaturated hydrocarbons etc.

Fig. 2: Illustration of overall reaction scheme for (I) oxidative and (II) hydrolytic rancidity (Walton, 2005).

Macadamia can be stored as nut-in shell or shelled nuts (kernels) for about 3 months at room temperature, 12 months at 2 °C and 18 months at -18 °C (Fourie and Basson, 1989; Kaijser et al., 2000; Wall and Gentry, 2007). The kernel is consumed raw, roasted, fried, salted, caramelized or as an ingredient into various confectionary products (Eagappan and Sasikumar,

2014; Navarro and Rodrigues, 2016). In nuts, flavour and variety of aromatic volatile compounds such benzaldehyde, methylphenol, benzyl alcohol and alkylbenzenes (Xiao et al., 2014), largely depends on whether the nuts are raw or roasted. In raw kernels, volatiles result from natural processes such as enzymatic browning which includes the transformation of phenolic compounds to a brown to black polymer because of the influence of polyphenols oxidase enzyme that accelerates the polyphenols oxidation reaction (Wan Daud et al., 2007). During the roasting process, many flavour compounds can be generated from precursor compounds that are formed during drying process (Schlörmann et al., 2015; Taş and Gökmen, 2017).

The brown colour of roasted nuts is a result of pyrazines and pyridines compounds, which are characteristic products resulting from (a) the reaction of carbonyl groups (reducing sugar, aldehydes, ketones, lipid oxidation products) and amino compound (lysine, glysine, peptide, amine, ammonia proteins) (Özdemir et al., 2001; Phatanayindee et al., 2012; Walton et al., 2013), (b) caramelization or pyrolysis of carbohydrate due to heat treatment above the melting point of the sugar under alkaline or acidic conditions (Burdurlu and Karadeniz, 2003; McDaniel et al., 2012), (c) ascorbic acid degradation (Burdurlu and Karadeniz, 2003), (d) lipid browning, which is probably oxidative of unsaturated deterioration of glyceride components followed by polymerization which is accelerated by the presence of ammonia, amines or proteins and (e) Maillard reaction (Srichamnong and Srzednicki, 2015), which requires reducing sugars for reaction with amino acids to form Maillard browning products (Burdurlu and Karadeniz, 2003; Walton et al., 2013).

Raw nuts were reported to have more than 100 volatile compounds, mainly terpenes (Pino et al., 2009). However, research on volatiles in macadamia nut predominantly during processing of kernels is still limited. Furthermore, lipid degradation is one of the main sources of off-flavours in food products that can occur during processing, classified mainly into autooxidation and enzymatically induced degradation (Phatanayindee et al., 2012). Therefore, selection of suitable drying and roasting process and monitoring the changes in lipids and fatty acids at different stages of processing is important.

High quality of macadamia nuts is characterized by low rancidity or peroxide value of less than 1 meq O_2/kg which is considered acceptable for a fresh nuts and is classified at low oxidation state; that between 5 and 10 meq O_2/kg at moderate oxidation and above 10 meq O_2/kg is classified at high oxidation state (Walton, 2005; Borompichaichartkul et al., 2013). Moisture content needed for microbial growth, enzyme activity, and chemical reactions is decreased in dried nuts (Wall and Gentry, 2007; Wang et al., 2014). Consequently, drying is an utmost crucial step during macadamia processing for maximizing kernel quality and storage (Borompichaichartkul et al., 2009).

Nevertheless, internal browning may occur after roasting if drying conditions are not well controlled (Phatanayindee et al., 2012). Browning of nuts may be evident as surface discolouration, or hidden internally as 'concealed damage' of nuts (Wakeling et al., 2003). Browning often cause the formation of off-odour and off-flavour (Le Lagadec, 2009). Browning might be triggered by enzymatic and non-enzymatic reactions forming brown pigment as their end product (Srichamnong and Srzednicki, 2015). Enzymatic browning results when monophonic compounds in the presence of atmospheric oxygen and polyphenol oxidase (PPO), are hydroxylated to o-diphenols, and the latter are oxidized to o-quinones. The quinones condense and react nonenzymatically with other phenolic compounds, amines, amino acids, peptides, and proteins with reducing sugars to produce dark brown, black or red pigments of indeterminate structure (Bittner, 2006).

Walton (2005) and Borompichaichartkul et al. (2013) reported that low initial drying temperature of less than 40 °C is essential to prevent internal browning. Therefore, the potential of drying and roasting to prevent changes in peroxides, PPO activity, fatty acids and other quality attributes of macadamia nuts will be investigated. The study outcome might be useful in setting of guidelines for selecting the suitable processing approach for macadamia nuts to possibly enhance kernel quality which might result in maximized shelf life of nuts. However, the above mentioned quality traits are currently not used by the macadamia industry because they are slow, difficult, time-consuming, use chemicals and expensive to be used for monitoring nut quality at industry scale (Burdurlu and Karadeniz, 2003; Canneddu et al., 2016). Also, scientific laboratory methods of measuring these parameters require specialized sample preparation and are not representative of entire samples (Canneddu et al., 2016). Furthermore,

the symptoms of browning may be internal and rancidity defect manifest during the postharvest shelf life of macadamias, therefore, development of methods for predicting kernel susceptibility to these quality defects during processing and storage is of great significance.

Visible to near infrared spectroscopy (Vis/NIRS) studies the internal characteristics of biological samples by irradiating the product with near infrared (NIR) radiation, measuring the reflected or transmitted radiation. The radiation changes its spectral characteristics when it penetrates the product depending on its chemical composition and microstructures. The spectral change is dependent on wavelength and causes scattering or absorption at certain spectral regions, which can be correlated with the chemical composition of the sample (Nicolai et al., 2007). Vis/NIRS with suitable chemometric software, has been used and shown to be a precise, rapid, and non-destructive method for prediction of different parameters of various nut species (Pannico, 2014). It provides non-visible information about comparative proportions of C–H, O–H, and N–H bonds (Magwaza and Tesfay, 2015). For oil content and quality of various nuts, including macadamia (Pannico, 2014), strong electromagnetic absorption is reported about 2200 to 2400 nm (CH_2 stretch bend and combinations), with weaker absorption about 1750, 1200 and 900 nm (first, second and third overtones of CH_2 stretching). Shorter wavelengths allow better penetration of biological samples and such shorter wavelengths should be useful in assessment of whole macadamia kernels (Guthrie et al., 2004). Therefore, there is a need to develop faster and nondestructive methods for predicting kernel quality.

2. Research hypothesis

It is hypothesized that thermal processing and roasting temperatures will have a positive impact on kernel quality and shelf life of macadamia nuts by preventing changes in rancidity and fatty acids and other quality attributes. Furthermore, it is hypothesized that NIRS is a potential tool for non-destructive prediction of rancidity in macadamia kernels.

3. Research aim

This research aims to evaluate the effect of thermal processing and roasting temperatures on nutritional quality and kernel shelf life of macadamia nuts and to develop Vis/NIRS calibration models that could be used by the macadamia industry to predict rancidity in macadamia nuts.

4. Research objectives

4.1. To investigate the effect of thermal processing on biochemical composition of macadamia nuts during accelerated storage.

4.2. To evaluate the effect of roasting temperatures on biochemical composition of macadamia nuts.

4.3. To evaluate the impact of cultivar on biochemical composition of macadamia nuts during accelerated storage.

4.4. To investigate the reliability of Vis/NIRS and to develop calibration models to predict rancidity in macadamia nuts.

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CHAPTER 2a: LITERATURE REVIEW: THE EFFECT OF THERMAL PROCESSING ON NUTRITIONAL QUALITY AND KERNEL SHELF LIFE OF MACADAMIA NUTS

Abstract

Rancidity is a major limiting factor affecting the postharvest quality and consequently, the storability and market value of macadamia nuts. Initial high moisture content accelerates the primary stages of rancidity where hydroperoxides accumulate as main oxidation products, eventually breaking down to form low molecular weight oxygenated constituents such as alcohols, aldehydes, ketones and free fatty acids, eventually resulting in the development of off-odours and off-flavours. Hydroperoxides can also react with amino acid residues in the Maillard reaction, thereby initiating excessive browning. Kernel browning may be evident as surface discolouration or internal as 'concealed damage' of nuts. Internal browning may be accompanied by off-odours and off-flavours and is impossible to detect during processing, often with no visible signs. Such kernels are unacceptable to both the export and local market. The aim of this chapter was to review the potential of thermal processing on delaying the onset of rancidity and therefore, improving kernel shelf life and nutritional quality of macadamia nuts; and to review the reliability of visible to near infrared spectroscopy (Vis/NIRS) to non-invasively predict kernel rancidity.

Keywords: Rancidity, browning, free fatty acids, near infrared spectroscopy

1. Introduction

Australia is the world's biggest macadamia nuts producing country (32 %), followed by South Africa (30 %), Kenya (12 %), United States (8 %), and Malawi (4 %). These five countries supply about 86 % of the world's market (du Preez, 2015; Jaskiewicz, 2015; Navarro and Rodrigues, 2016). Macadamia was introduced to South Africa approximately in 1935 (du Preez, 2015) and has become the most important and fastest growing tree crop industry in the country (DAFF, 2016). Macadamia is amongst the four widely grown subtropical tree crops in South Africa next to avocados, mangoes and litchis. Between these tree crops, macadamia cover about 44 % of land used followed by avocado (34 %) (du Preez, 2015).

Most of the South African macadamia production is mainly centered in the subtropical regions of Mpumalanga (40 %), Limpopo (29 %) and KwaZulu-Natal (19 %) (DAFF, 2016; du Preez, 2015). Orchards are dominated by Hawaiian-bred cultivars of *M integrifolia* such as '246', '344', '660', '741', '788', '791', '800', '814' and '816' and Australian-bred cultivars of *M integrifolia* such as 'Daddow' and hybrids such as 'A4', 'A16' and 'Beaumont' (Hardner et al., 2009). *Macadamia integrifolia* accounts for the majority of the world output and is preferred due to its higher oil content and superior roasting quality. It has higher sugar content and is therefore sweeter (Moodley et al., 2007). *Macadamia tetraphylla* nuts dominate the worldwide industry, as they are more resistant to water stress and have lower sugar content (Monaghan, 2008). Therefore, selection of higher quality cultivars is very critical for kernel quality and shelf life of macadamia.

South Africa is the world's largest exporter of macadamia nuts (36.37 %) followed by Australia (14.6 %), Kenya (12.1 %), Hong Kong (9.7 %), the Netherlands (4.5 %) and China (3.8 %) (DAFF, 2015b; Manenzhe, 2015). More than 95 % of South African annual production is shipped to international markets, mainly in the US, Europe and Asia (DAFF, 2016). In 2017, macadamia nuts worth R3.2 billion were exported with 30 204 tonnes produced, an increase of 20 % compared to the previous year (https://samac.org.za/industry-statistics-southern-african-macadamia-industry/). According to the South African Macadamia Growers' Association (SAMAC), the average export

price for macadamia kernels (shelled nuts) is currently R224.15/kg and R75,58/kg for nut-in-shell (NIS) (https://www.businessinsider.co.za/sas-most-profitable-crop-2018-3).

Macadamia is increasingly consumed raw, roasted and as an ingredient into various confectionary products (Eagappan and Sasikumar, 2014; Navarro and Rodrigues, 2016). The increase in the global production may be due to its high nutritional content and reported health benefits, including prevention of cardiovascular diseases and type 2 diabetes (Jiang et al., 2005; Lovejoy, 2005; Rengel et al., 2015). These health benefits are associated with low levels of cholesterol, high oil content (69-78 %) which is rich in monounsaturated fatty acid (80 %) predominately oleic and palmitoleic (Kaijser et al., 2000; Moreno-Pérez et al., 2011; Sinanoglou et al., 2014) and antioxidants due to several phytochemicals and polyphenols found in kernels (Leja et al., 2001; Oboh, 2005; Rengel et al., 2015). Macadamia is also, rich in other bioactive macronutrients such as protein, dietary fiber, essential minerals, vitamin E, and plant sterols (Ros, 2010; Ros et al., 2010) (Table 1). Fatty acids are the main standard that indicates the quality of macadamia nuts (Phatanayindee et al., 2012). Wall (2010) reported that phytochemicals such as antioxidants present in macadamia nuts are not only beneficial to human health, but these compounds could protect the kernels from oxidation reactions during postharvest storage, thus prolonging shelf-life. Therefore, most recent research studies have mainly focused on improving the kernel quality due to increasing global production and market competition of macadamia nuts (Walton, 2005).

Since the South African macadamia industry is export oriented, international markets have very strict requirements which include consistent and reliable supply of required volumes of high quality standards of nuts (du Preez, 2015). The economic profit of macadamia depends on the yield, kernel recovery (percentage of whole kernel after cracking nuts), nut quality and nut style distribution (whole kernel, halves and pieces) (du Preez, 2015). Kernel quality is primarily indicated by appearance (size, shape, colour, freedom from defects), texture, flavour and shelf life (Walton, 2005).

Table 1: Nutrient composition of macadamia kernels per 100 g (Monaghan, 2008; Eagappan and Sasikumar, 2014)

Nutrients	Units	Amount per 100 g	Minerals (continued)	Units	Amount per 100 g
Energy	kJ	3004.00	Copper (Cu)	mg	0.76
Fat	g	75.80	Sodium (Na)	mg	5.00
Saturated fatty acids (SFA)	g	12.06	Manganese (Mn)	mg	4.13
Monounsaturated fatty acids (MUFA)	g	58.87	Selenium (Se)	µg	3.60
Polyunsaturated fatty acids (PUFA)	g	1.50	**Vitamins**		
Protein	g	7.91	Vitamin C	mg	1.20
Fiber	g	6.00	Thiamin	mg	1.20
Arginine	g	1.40	Riboflavin	mg	0.16
Minerals			Niacin	mg	2.47
Magnesium (Penter)	mg	130.00	Pantothenic acid	mg	0.76
Phosphorus (P)	mg	188.00	Vitamin B-6	mg	0.28
Potassium (K)	mg	368.00	Folate	µg	11.00
Calcium (Ca)	mg	85.00	Tocopherol, α	mg	0.54
Iron (Fe)	mg	3.69			
Zinc (Yahia and Hernandez)	mg	1.30			

Some of the highest monounsaturated fatty acids present in macadamia oil include oleic (60 %), palmitoleic (20 %) and gadoleic acid (2.48 %); polyunsaturated fatty acids include linoleic acid (2.03 %), α-linolenic acid (2.4 %) and saturated fatty acids include palmitic (9.38 %), stearic (3.40 %) and arachidic (2.56 %) (Kaijser et al., 2000; Rengel et al., 2015)

However, because of the high content of unsaturated fatty acids (80 - 81.8 %) and high moisture content present in macadamia nuts (Rengel et al., 2015), kernels are more susceptible to rancidity; related to the occurrence of disagreeable odours and flavours (Borompichaichartkul et al., 2013; du Preez, 2015; Rengel et al., 2015). Also, chemical changes can occur due to storage period and conditions, affecting flavour and palatability of kernels (Walton, 2005), therefore, the macadamia industry has developed postharvest handling methods such as thermal processing, grading and packaging to improve sensory, nutritional quality and shelf life of kernels (du Preez, 2015; Srichamnong and Srzednicki, 2015). Little is known about the potential of thermal processing to delay the onset of rancidity during the storage on macadamia nuts therefore, this chapter will examine the available literature on these subjects.

2. Thermal processing

Freshly harvested macadamia nut has a moisture content of about 81.8 % on dry basis (d.b.) in husk and 33.3 % (d.b.) in nut-in-shell (NIS) and is prone to deterioration (Borompichaichartkul et al., 2009). Such high moisture content promotes the development of micro-fungi, that produce particular enzymes that break down carbohydrates; and promotes the hydrolysis of lipids into free fatty acids, resulting in rancidity (Borompichaichartkul et al., 2009; Pannico, 2014; Wang et al., 2014). Also, high-moisture kernels have softer texture and browns faster during roasting (Phatanayindee et al., 2012). Therefore, drying is an utmost crucial step during macadamia processing for maximizing kernel quality and storage (Borompichaichartkul et al., 2009). Moisture content essential for microbial growth, enzyme activity, and chemical reactions is reduced in dried nuts (Wall and Gentry, 2007; Wang et al., 2014). However, during thermal processing, nuts can undergo deteriorative reactions such as rancidity which result in quality degradation, due to the odd colours and off-flavours (Kashani et al., 2003). Furthermore, lipid deterioration is the main

source of off-flavours in food products that can occur during processing, classified mainly into autooxidation and enzymatically induced degradation (Phatanayindee et al., 2012).

Internal browning can occur after roasting if drying conditions are not well controlled (Phatanayindee et al., 2012). Kernel browning could be evident as surface discolouration, or internal as 'concealed damage' of nuts (Wakeling et al., 2003). Browning often cause the formation of off-odours and off-flavours (Le Lagadec, 2009). Browning might be caused by enzymatic and non-enzymatic reactions forming brown pigment as their end product (Srichamnong and Srzednicki, 2015). Enzymatic browning results when monophonic compounds in the presence of atmospheric oxygen and polyphenol oxidase (PPO), are hydroxylated to o-diphenols, and the latter are oxidized to o-quinones. The quinones condense and react nonenzymatically with other phenolic compounds, amines, amino acids, peptides, and proteins with reducing sugars to form brown, black or red pigments of indeterminate structure (Bittner, 2006).

Therefore, it is commercially recommended that macadamia nuts be dried at low initial temperatures below 40 °C when the moisture content is above 10 % on wet basis (wb) to avoid a high concentration of reducing sugars in the centre of the kernel, which might lead to kernel center-browning after drying (Phatanayindee et al., 2012; Borompichaichartkul et al., 2013). Phatanayindee et al. (2012) recommended that the moisture in raw kernels be decreased to about 1.5 % (wb) before roasting in order to achieve a moisture content of 1 % (wb) after roasting for maintaining kernel quality, maximizing sensory and chemical quality and for a good shelf life (Borompichaichartkul et al., 2009; DAFF, 2016). Previous studies also report that macadamia nuts within this commercial range of moisture content have an increased kernel recovery during cracking and higher stability against oxidation during storage (Walton, 2005; Borompichaichartkul et al., 2009). Common industrial drying methods includes oven drying (Silva et al., 2006; Wall and Gentry, 2007), hot pump (Borompichaichartkul et al., 2013), bin drying, vertical continuous and cylindrical drying (Kashani et al., 2003), microwave or radio frequency (Zhang et al., 2006), vacuum drying (Clary et al., 2005) and freeze-drying (Wang et al., 2005).

Roasting is one of the most popular methods of macadamia thermal processing (Navarro and Rodrigues, 2016). It enhances flavour, aroma, colour and texture of the nuts through non-enzymatic (Maillard browning) reactions, resulting from the reaction between sugars and amino acids (McDaniel et al., 2012; Schlörmann et al., 2015; Taş and Gökmen, 2017). It also inactivates oxidative enzyme system (lipoxygenic enzymes), reduces moisture content therefore, eliminates microorganisms and minimizes deteriorative reactions such as lipid oxidation which exhibit antioxidant activity (Belviso et al., 2017; Taş and Gökmen, 2017).

During the roasting process, variety of flavour and aromatic compounds such benzaldehyde, methylphenol, benzyl alcohol and alkylbenzenes (Xiao et al., 2014), can be generated from precursor compounds that are formed during drying process (Schlörmann et al., 2015; Taş and Gökmen, 2017). Also, the browning of roasted nuts is due to pyrazines and pyridines compounds, pyrolysis of carbohydrate, loss of ascorbic acid, lipid browning and Maillard reaction (Burdurlu and Karadeniz, 2003; Phatanayindee et al., 2012; Walton et al., 2013).

However, although favorable for many aspects, roasting may cause reactions leading to the loss of nutritional quality or development of disagreeable compounds such as 5-hydroxymethylfurfural (Taş and Gökmen, 2017). Several physical and chemical changes such as microstructural and lipid modifications may enhance the susceptibility of roasted nuts to oxidation thus, reducing its shelf life (Belviso et al., 2017). Therefore, it is essential to establish the best roasting temperatures to avoid quality loss. Industrial roasting is conducted at temperatures ranging from 30 to 180 °C for 5 to 60 minutes (Srichamnong and Srzednicki, 2015; Belviso et al., 2017; Taş and Gökmen, 2017). Furthermore, roasting can be accomplished by several methods such as commercial electrical ovens, infrared heating and dielectric processes of radiofrequency and microwave (Belviso et al., 2017).

3. Rancidity

Macadamias are seasonal nuts and nonorthodox seeds, meaning they do not become dormant and thus, can be stored for limited periods before deteriorating (Walton, 2005). They can be stored as

nut-in shell or shelled nuts (kernels) for about 3 months at room temperature, 12 months at 2 °C and 18 months at -18 °C (Fourie and Basson, 1989; Kaijser et al., 2000; Wall and Gentry, 2007). Because of high oil content and unsaturated fatty acids, rancidity is the most important problem during storage, causing flavour deterioration (Borompichaichartkul et al., 2013; du Preez, 2015; Rengel et al., 2015). High-moisture kernels rapidly develop rancidity when stored at room temperature (McDaniel et al., 2012; Pannico et al., 2015; Taş and Gökmen, 2017; Walton et al., 2017). Also, rancidity is a consequence of prolonged storage or improper storage conditions (Kaijser et al., 2000).

There are two main pathways resulting in rancidity; oxidation termed oxidative rancidity and lipolysis termed hydrolytic rancidity (Borompichaichartkul et al., 2013). Lipid oxidation and hydrolysis are the main reactions resulting in the deterioration of sensory and nutritional quality of nuts (Walton et al., 2017). Lipid oxidation is a vital deteriorative reaction associated with unsaturated fatty acids causing off-flavours that develop as a consequence of autoxidation which is a self-sustaining free radical mechanism that produces primary products such as hydroperoxides (Phatanayindee et al., 2012). It is usually autocatalytic, with oxidation products accelerating the reaction so that the rate increases with time (Kashani et al., 2003; Nahm, 2011; Walton et al., 2017). Micro-organisms or enzyme action, heat, moisture content and the hydrolysis of the triglycerides which produces glycerol and free fatty acids (FFA's) are the main catalysts of hydrolytic rancidity, resulting in a progressive increase of food acidity therefore, causing much stronger off-flavours (Saponaro et al., 2015; Walton et al., 2017). Walton (2005) reported that oxidative stability of macadamias can be influenced by cultivar; however, little is known about the impact of processing conditions to possible delay the onset of rancidity thereby improving the storability of nuts.

3.1. Oxidation

Lipid oxidation is the main reason for quality loss in foods and is caused by the reaction of fats and oils with molecular oxygen resulting in the development of off-flavours (Márquez-Ruiz et al., 2007). Lipid oxidation constitutes a complex chain of reactions that firstly produces primary

products such as peroxides that cause secondary oxidation products such as aldehydes, ketones, epoxides, hydroxy compounds, oligomers and polymers (Kanner, 2007). These compounds result in off-odours and off-flavours and are potentially toxic, which can be threatening to the health of the consumer (Moure et al., 2001). Lipid oxidation occurs through a chain reaction (Fig. 1) that includes initiation, propagation and termination stage (Schaich, 2005).

Primary oxidation products are caused by the reaction of an alkyl radical, which is caused by reaction to metals, light, heat, high energy-radiation, etc. with oxygen to produce a peroxy free radical (initiation) (Gülçin, 2012). In the propagation stage, a free radical produced during initiation first reacts with oxygen to form a peroxyl radical, which then abstracts a hydrogen atom from a nearby lipid molecule to produce a hydroperoxide and a new acyl radical (Schaich, 2005). This radical repeats peroxyl radical formation and hydrogen abstraction to produce another new free radical and continue the chain, potentially producing very high levels of hydroperoxides (Peng, 2010). However, hydroperoxides themselves are decomposed by ultraviolet light, heat, and metals to produce alkoxyl radicals, which are even more reactive than peroxyl radicals. This produce is tasteless and odourless (Schaich, 2005). The reaction progresses until there is a reduction of oxygen or when a fatty radical reacts with a stable antioxidant radical (termination) (Fig. 1). During the termination stage, radicals react with themselves to form a variety of non-radical monomer, dimers, and polymer products, and alkoxyl radicals undergo scission to generate aldehydes, alkanes, and other oxidation ordours, which are responsible for the development of rancidity (Choe and Min, 2006; Gülçin, 2012). Initiation, propagation and termination oxidative chemical reactions are all together called autoxidation (Choe and Min, 2006; Figure1).

Initiation *(formation of ab initio lipid free radical)*

$$L_1H \xrightarrow{\;k_i\;} L_1^{\bullet}$$
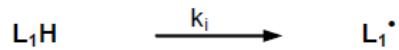
Propagation

Free radical chain reaction established

$$L_1^{\bullet} + O_2 \;\underset{k_{\beta}}{\overset{k_o}{\rightleftharpoons}}\; L_1OO^{\bullet}$$

$$L_1OO^{\bullet} + L_2H \xrightarrow{\;k_{p1}\;} L_1OOH + L_2^{\bullet}$$

$$L_2OO^{\bullet} + L_3H \xrightarrow{\;k_{p1}\;} L_2OOH + L_3^{\bullet} \quad etc. \dashrightarrow L_nOOH$$
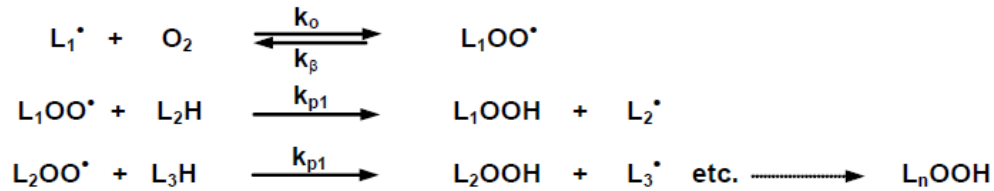
Free radical chain branching (initiation of new chains)

$$L_nOOH \xrightarrow{\;k_{d1}\;} L_nO^{\bullet} + OH^{-} \quad (reducing\ metals)$$

$$L_nOOH \xrightarrow{\;k_{d2}\;} L_nOO^{\bullet} + H^{+} \quad (oxidizing\ metals)$$

$$L_nOOH \xrightarrow{\;k_{d3}\;} L_nO^{\bullet} + {}^{\bullet}OH \quad (heat\ and\ uv)$$

$$\left.\begin{matrix} L_nO^{\bullet} \\ L_nOO^{\bullet} \\ HO^{\bullet} \end{matrix}\right\} + L_4H \xrightarrow[\substack{k_{p1} \\ k_{p3}}]{\;k_{p2}\;} \left.\begin{matrix} L_nOH \\ L_nOOH \\ HOH \end{matrix}\right\} + L_4^{\bullet}$$

$$L_1OO^{\bullet} + L_nOOH \xrightarrow{\;k_{p4}\;} L_1OOH + L_nOO^{\bullet}$$

$$L_1O^{\bullet} + L_nOOH \xrightarrow{\;k_{p5}\;} L_1OH + L_nOO^{\bullet}$$
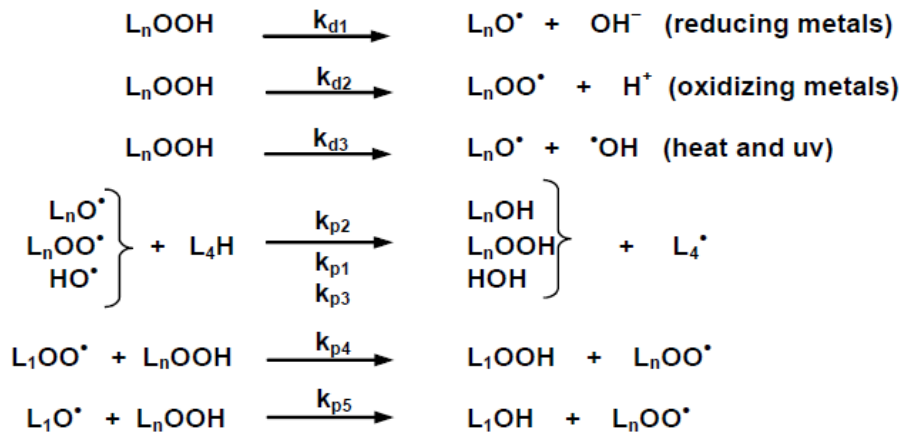
Termination *(formation of non-radical products)*

Radical recombinations

$$\left.\begin{matrix} L_n^{\bullet} \\ L_nO^{\bullet} \\ L_nOO^{\bullet} \end{matrix}\right\} + \left.\begin{matrix} L_n^{\bullet} \\ L_nO^{\bullet} \\ L_nOO^{\bullet} \end{matrix}\right\} \xrightarrow[\substack{k_{t2} \\ k_{t3}}]{\;k_{t1}\;} \text{polymers, non-radical monomer products (ketones, ethers, alkanes, aldehydes, etc.)}$$

Radical scissions

$$\left.\begin{matrix} LOO^{\bullet} \\ LO^{\bullet} \end{matrix}\right\} \xrightarrow[k_{ts2}]{\;k_{ts1}\;} \text{non-radical products (aldehydes, ketones, alcohols, alkanes, etc.)}$$
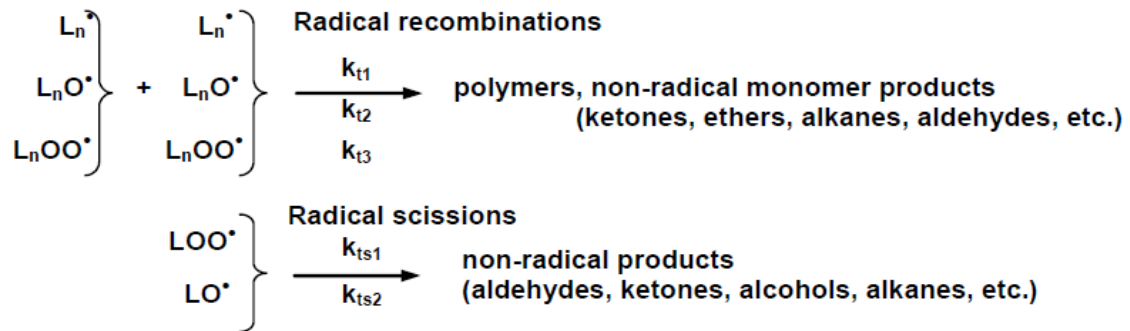
i - initiation; o-oxygenation; β- O_2 scission; p-propagation; d-dissociation; t-termination; ts–termination/scission

Fig. 1: Mechanisms of autoxidation, including initiation, propagation and termination steps in edible oils, according to Schaich (2005).

High temperatures, irradiation, light, ionizing radiation, peroxides, organic metal catalysts, low levels of natural antioxidants such as tocopherol, high oxygen partial pressure, monolayer dispersion, polyunsaturation, and conjugation, free fatty acids and water, etc. are all the factors affecting and accelerating the rate and course of oxidation in food (Peng, 2010).

3.1.1. Fatty acid composition

Unsaturated fatty acids such as oleic, linoleic, linolenic and arachidonic acids present as phosphoglyceride esters in lipid membranes, are specifically prone to autoxidation (Repetto et al., 2012). Linoleic acid is more prone to oxidation and it produces hydroperoxides, which decomposes to secondary oxidation products mainly, aldehydes, ketones, hydrocarbons and alcohols (Gülçin, 2012). Aldehydes are predominantly responsible for off-flavours, either directly or indirectly through their enol or tautomer forms (Macfarlane et al., 2001). Moodley et al. (2007) reported that polyunsaturated fatty acids are more prone to oxidative deterioration; therefore, low concentration is recommended for long term storage of macadamia nuts. Canola oil with low linolenic acid (polyunsaturated fatty acid) of 2.5 % was reported to have a longer shelf-life (Shen et al., 1999). Macadamia oil is reported to contain about 0.7 - 2 % linolenic acid (Himstedt, 2002; Rengel et al., 2015), which might have a positive impact on the quality and storability of nuts. However, Rengel et al. (2015) reported that fatty acid composition may vary significantly among different cultivars. There are currently few published studies reporting on fatty acid composition of different cultivars of macadamia and its impact on the quality and storability of kernels.

Macadamia nuts consist of the highest amounts of monounsaturated fatty acids, mainly oleic (60%) and palmitoleic (20 %) acids than any known natural food (Hardner et al., 2009; Rengel et al., 2015). However, high amount of these unsaturated fatty acids makes macadamia kernels prone to oxidative rancidity (Hardner et al., 2009; Moreno-Pérez et al., 2011; Rengel et al., 2015). Very few research studies report on the effect of these unsaturated fatty acids on storability of macadamia nuts, which is a critical issue because the development of rancidity is generalized to increase with increasing storage, without thoroughly evaluating fatty acid profile and cultivar selection.

In addition, except from causing rancidity, lipid oxidation products can react with sugars and amino acid residues in the Maillard reaction, generating excessive browning (Burdurlu and Karadeniz, 2003; Walton et al., 2013). Such kernels with browning are classified as second grade and are of lower market value and completely undermine customer confidence at retail level, hence reducing repeat sales leading to postharvest and economic loss (Hardner et al., 2009; Le Lagadec, 2009). Therefore, lipid oxidation is major threat affecting the postharvest quality of macadamia nuts.

3.2. Hydrolysis

Hydrolysis is the result of lipolysis or hydrothermal activity and hydrolysis of triglycerides in the presence of micro-organisms or enzyme action, moisture and heat and is the initial step in the deteriorative rancidity pathway (Fig. 2), leading to the liberation of free fatty acids (FFAs) which then leads to hydrolytic rancidity (Walton, 2005; Walton et al., 2017). The liberated FFAs such as capric, lauric, and myristic acid have stronger off-flavour or distinctly soapy flavour, which is the main reason hydrolytic rancidity is often referred to as soapy rancidity (Peng, 2010; Saponaro et al., 2015). Once FFAs are formed they are subject to autoxidation, production of FFA hydroperoxides and sequentially secondary and tertiary products of oxidation (Buransompob et al., 2003; Walton, 2005; Walton et al., 2017). They oxidize to different small products such as aldehydes, methyl ketones, and lactones that are distinctive flavour and aroma compounds. They also polymerize to dimers, trimers, and higher polymers, with and without oxygen bridges that increase viscosity of oils and react with any soft metals present to form soaps that contribute to foaming and formation of off-flavours (Peng, 2010; Figure 2). Lipid browning may be a consequence of these reactions, where oxidation of unsaturated deterioration of glyceride components and polymerization which is promoted by the presence of ammonia, amines or proteins react together to form brown pigments (Burdurlu and Karadeniz, 2003; Walton et al., 2013).
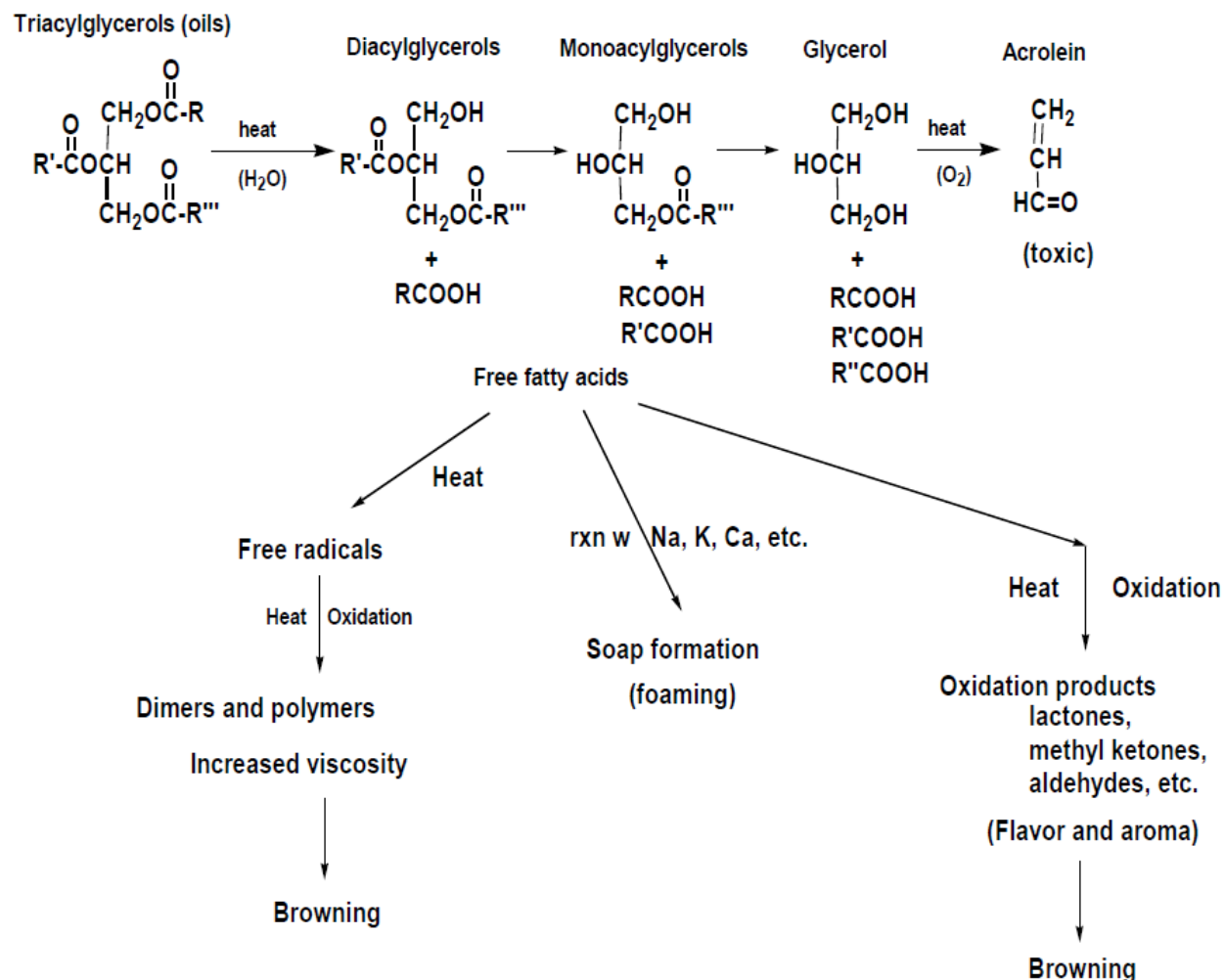
Fig. 2: Comprehensive scheme for oil degradation as a consequence of triacylglycerols, free fatty acids, free radicals and oxidation products resulting in hydrolytic rancidity and eventually in lipid browning (Peng, 2010).

In addition, lipases hydrolyze only emulsified acyl lipids and are active on water or lipid interface, therefore, low moisture content is essential for effective storage of macadamia nuts (Belitz et al., 2004). Therefore, drying macadamia nuts to a commercial recommended moisture content of 1.5 % is significantly effective for the removal of excessive moisture or water needed for microbial growth (Wall and Gentry, 2007; Walton et al., 2013; DAFF, 2015). In macadamia nuts even small differences in FFA values are considered as measurement of hydrolytic activity or rancidity and are highly linked with differences in flavour scores (Walton, 2005). Moscetti et al. (2013) reported

that FFAs concentration exceeding 1 % decreases the shelf life of hazelnuts. Therefore, FFAs can be used to access postharvest quality and storability of nuts. Future studies should consider fatty acid composition of macadamia nuts as a determinant of kernel quality.

3.3. Measurements of rancidity

Different chemical and instrumental techniques are available for evaluating rancidity in foods (Table 2). Free fatty acids are a measure of hydrolytic activity in edible oils and indicate the amount of fatty acids hydrolyzed from triacylglycerols, expressed as a percentage by weight of an identified fatty acid such as oleic acid (Walton, 2005). Acid value (AV), also referred to as acid index (AI), is another measure of hydrolytic rancidity (Farhoosh et al., 2009). It is linked to the acidification of fats because of enzymatic reactions producing FFA, which might have disagreeable taste (Canneddu et al., 2016). Peroxide value (PV) is a frequently used technique for determining the onset of oxidation or oxidative rancidity (Borompichaichartkul et al., 2013; Das et al., 2014) as it is a measure of peroxides or hydroperoxides originating from the break of the double bounds, which produces short chain volatile products responsible for the rancid flavour (Canneddu et al., 2016). Other measurements of rancidity include thiobarbituric acid (TBA) test which measures malonaldehyde, a secondary product of lipid oxidation and anisidine value which measures the content of aldehydes, mostly 2-alkenals and 2,4-dienals in edible oils (Walton, 2005; Table 2).

Table 2: Units and representative values for rancidity evaluation according to Walton (2005) and Borompichaichartkul et al. (2009)

Characteristic	Units	Representative values
Free fatty acids (FFAs)	Free fatty acids % m/m, expressed as oleic acid	0.2 % of free acid, mainly lauric and capric acid generates off-flavour
Peroxide value (PV)	meq O_2/kg	> 1, freshly refined oils; > 10, moderate oxidation, potential lack of product stability; < 10, high oxidation, adequate breakdown to aldehydes to produce rancid flavour in produce
Kreis	Red units on the Lovibond scale	3, initial development of rancidity; 3-8, rancid, near end of initiation period; > 8, definite rancidity
Anisidine value	NS	< 10 generally represents an acceptable oil

Not specified, NS

Among numerous instrumental methods available for evaluating rancidity are gas chromatography-mass spectrometry (GC-MS), high-performance liquid chromatography (HPLC) and fourier transform infrared spectroscopy or mass spectrometry (FTICR-MS) which gives an extensive analysis for a clearer profile of rancidity and allow a correlation of sensory assessment with instrumental analysis (Walton, 2005). These instrumental methods are able to identify and quantify volatiles therefore, determining the extent of oxidation in almonds, hazelnuts, macadamia, pecans and walnuts (Fard et al., 2003; Walton, 2005). Other analytical methods of analyzing rancidity include titrating using burette (Walton et al., 2017). Furthermore, evaluation of rancidity using these analytical and instrumental methods during long term storage would help estimate macadamia cultivars that are less prone to develop rancidity during storage.

Even though these techniques are commercially effective, they are currently not used by the macadamia industry because they are slow, difficult, time-consuming, use chemicals and costly to be used for evaluating nut quality at an industrial scale (Burdurlu and Karadeniz, 2003; Canneddu et al., 2016). Also, these methods require specialized sample preparation and are not representative of entire samples (Canneddu et al., 2016). These methods are also limited to laboratories due to specific instrument required and growers are likely to deliver nuts with inferior quality to the market because of quality variation within a consignment (Pannico, 2014; Canneddu et al., 2016). Furthermore, there are no known visible symptoms of early development of rancidity other than end results of rancidity observed by off-odours and off-flavours during the postharvest shelf life of macadamias, therefore, it is necessary to develop a rapid, accurate and non-invasive technique that can be used to precisely evaluate nut quality.

4. Non-destructive methods

Recently, non-invasive methods and instruments for quality evaluation in various dry fruit, including hazelnut, chestnut, macadamia, shea nut, walnut and peanuts have become popular and researchers have made a considerable attempt to develop them (Jensen et al., 2001; Pannico et al., 2015). The online non-invasive grading and sorting system for the evaluation of internal fruit quality attributes includes those based on electrical properties such as visible to near infrared (Vis/NIR) spectroscopy (Jensen et al., 2001; Saranwong et al., 2011), vibrating energy (Magwaza and Tesfay, 2015), ultrasound, nuclear magnetic resonance (NMR) (Zhang and McCarthy, 2013), X-ray (Donis-González et al., 2012), volatile emission and others (Butz et al., 2005). For the purpose of this review, the discussion will be limited to Vis/NIRS.

4.1. Application of visible to near infrared spectroscopy

The use of near infrared (NIR) spectroscopy (NIRS) has provided fast, non-invasive and precise control in agriculture, pharmaceuticals and food industry (Cao, 2013). Near infrared spectroscopy was first used in agricultural products in 1964 to quantify moisture in grain. From then, it has been effectively used for fast analysis of mostly moisture, protein and fat content of different

agricultural products (Nicolai et al., 2007). In the nut industry, it has been used for predicting moisture content, oil content, internal mold, lipid oxidation and fatty acid composition (Jensen et al., 2001; Guthrie et al., 2004; Moscetti et al., 2014; Pannico et al., 2015). Cassells et al. (2007) reported that NIRS was able to predict changes occurring in the grain seed during storage according to the spectral difference, thereby, providing a more cost effective and fast method for assessing quality conditions to adjust the storage management in advance to maintain grain quality and market value.

4.1.1. Basic concepts

Visible and near infrared radiation covers the wavelength range between 780 and 2500 nm (Magwaza and Opara, 2015). This technique studies internal composition of biological samples by irradiating the product with NIR radiation and quantifying its reflection, absorption or transmission (Jha and Matsuoka, 2000; Ruiz-Altisent et al., 2010). The radiation changes its spectral characteristics while penetrating the product because of wavelength dependent absorption and scattering processes. This change depends on the chemical and physical properties of the product (Ruiz-Altisent et al., 2010). Specular reflection is due to gloss, while external diffuse reflection is influenced by external characteristics of a sample such as uneven surfaces. Reflection only provide information about the samples surface (Nicolai et al., 2007).

The main scattering elements in produce are the cell wall interfaces since they cause abrupt changes in refractive index. The scattering may also be caused by the shape, size and microstructure of the particles; and heterogeneities such as pores and capillaries that are randomly distributed through the produce (Nicolai et al., 2007). Absorption bands in the NIR region are overtone or combination bands of fundamental absorption because of vibrational and rotational transitions (Pannico, 2014). Visible to near infrared spectroscopy with suitable chemometric analysis gives non-visible information about relative proportions of C–H, O–H, and N–H bonds (Magwaza and Tesfay, 2015). Nut quality attributes such as moisture content, oil content, lipid oxidation, fatty acid composition and internal disorders are based on organic molecules which

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comprise C–H, O–H, C–O, and C–C bonds; thus, it is possible to use NIRS techniques to measure these attributes (Guthrie et al., 2004; Pannico et al., 2015).

Pannico et al. (2015) stated that lipid degradation and kernel defect in hazelnuts were possibly the major factor for the detected differences in the NIR spectra shown in Figure 3. Peaks at 1729 and 1761 nm correspond to the C-H bond of the -CH$_2$ group first overtone stretching band, and the peaks at 2307 and 2347 nm correspond to the -CH$_2$ group stretching and deformation combination band precise for lipids (Pannico et al., 2015). These authors further predicted lipid oxidation in the range from 2100 to 2200 nm, corresponding to the C (C=C) double bond stretching and deformation band of lipids. Therefore, NIR proves to be able to detect changes in products during storage according to the spectral difference (Cao, 2013).
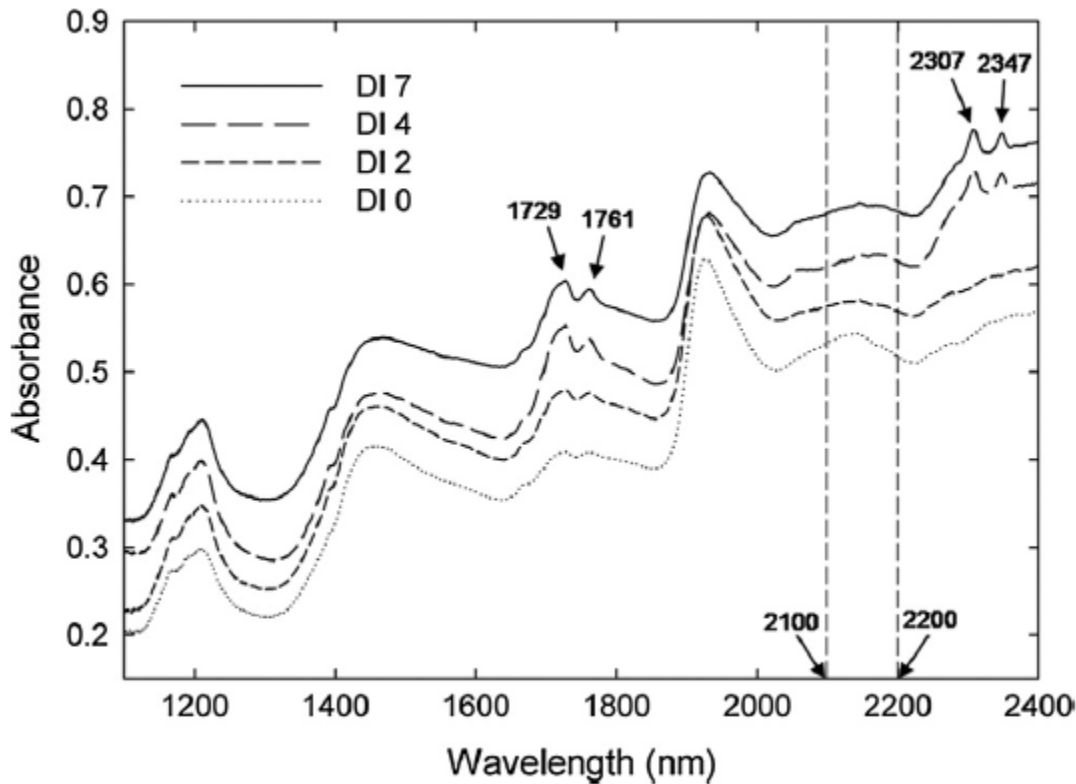
Fig. 3: Raw spectra of hazelnuts categorized by different defect index (DI), where 0 = no defect and 7 = severely flawed. Arrows specify four peaks at corresponding wavelengths (1729, 1761,

2307 and 2347). Vertical dashed lines specify the wavelength range from 2100 to 2200 nm (Pannico et al., 2015).

4.2. Potential use of NIRS to predict internal quality of macadamia nuts

A need for non-invasive quality evaluation of nuts has spurred investigations into the potential use of NIRS as a tool to non-destructively grade the quality on-line (Moscetti et al., 2014; Pannico, 2014). Near infrared spectroscopy can be used in postharvest quality control and for real-time quality evaluation during processing and storage (Singh et al., 2006). Near infrared spectroscopy allows qualitative and quantitative evaluation of various types of nuts through spectral information and multivariate calibration models (Cao, 2013; Canneddu et al., 2016). These models are often used to evaluate nut quality attributes such as moisture content, oil content, lipid oxidation and internal mold (Guthrie et al., 2004; Moscetti et al., 2015; Pannico et al., 2015).

The use of NIRS is based on a calibration model, which build a mathematical correlation between the absorption spectra and the parameter of interest. Calibration optimization is an important process for evaluating the optimal chemometric methods (linear or non-linear) for interpreting the spectra and improving the predictive ability on future samples. The analyses of statistical techniques (chemometrics) provides chemical characteristics of product (Nicolai et al., 2007; Cao, 2013). However, extensive literature reviews on NIRS, covering its origin, principles, instrumentation, modes of spectra acquisition and chemometrics have been conducted by Nicolai et al. (2007), Bellon-Maurel et al. (2010), Minasny and McBratney (2013), Magwaza and Tesfay (2015) and Lucà et al. (2017).

The increasing requirement for quality assurance by the export market has caused recent research to focus on the use of NIRS to non-destructively predict nut quality parameters (Jensen et al., 2001; Moscetti et al., 2014; Pannico et al., 2015). Canneddu et al. (2016) developed an NIR calibration model for predicting rancidity in macadamia nuts with coefficient of determination of cross-calibration (R^2) of 0.80 with a root mean square error of prediction (RMSEP) of 0.14 %. Guthrie et al. (2004) tested the use of NIR in estimating the oil content of macadamia nuts and obtained a

good prediction statistics of R^2 = 0.99 and RMSEP = 1.7 %. These research studies show the potential of NIRS as a tool for non-destructive prediction of macadamia nuts.

5. Conclusion

The application of NIRS technique is becoming popular in the nut industry. The NIR system can be based in the laboratory, portal and in/on-line with grading and sorting lines. However, establishing an average application protocol and comparable analytical chemometrics software remains a challenge. Furthermore, although NIRS has been used for decades, it is not yet as advanced with nuts as it is with fruits such as mango and apples where spectrophotometers have been applied in the pack house. Also, information of NIRS application on predicting rancidity in macadamia nuts is very scarce. Future studies would greatly benefit not only the macadamia industry but the entire nut industry by combining quantitative evaluation of both external and internal quality parameters in one system and also by concentrating on developing and establishing models that might be used with grading and sorting on industrial lines to select cultivars with high stability against rancidity during processing and storage or shelf life. This would greatly benefit the South African macadamia industry since it is export oriented, nuts that are susceptible to rancidity would then be exported as processed products thereby extending their shelf life.

It would further benefit the South African macadamia industry if kernels are processed and stored at optimal conditions to further extend the shelf life of kernels since seasonal availability and limited shelf life of kernels are the major challenges facing the macadamia industry. Macadamia nuts quality and storability highly depend on the initial composition of nuts at harvest and the methods by which nuts are processed and stored. Processing such as roasting inactivates enzymes that accelerates nutrient deterioration, removes microorganisms and reduces degradative reactions such as lipid oxidation and rancidity which are the major limiting factors for the shelf life of nuts. Although roasting is a commercial practice of the macadamia industry, little is known about the effect of roasting on kernel nutritional quality and shelf life. Also, information on different roasting temperatures is very limited. Therefore, there is a need for future research to specifically focus on the effect of processing methods on nutritional quality and storability of macadamia kernels.

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CHAPTER 2b: DESTRUCTIVE AND NON-DESTRUCTIVE TECHNIQUES USED FOR QUALITY EVALUATION OF NUTS: A REVIEW

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Abstract

Moisture content (MC), oil content (OC), fatty acid composition and rancidity are considered as major determinants of quality of nuts. These parameters are destructively quantified from a batch of representative samples used to estimate quality of nuts of an entire orchard. Although destructive techniques are helpful, they involve extensive sample preparation and solvent extractions, are slow, expensive and obtained results specifically reflect the properties of the evaluated produce. Recently, non-invasive analytical methods and instruments for evaluating quality of various produce have become popular with researchers putting more effort in developing them. Non-destructive methods are an alternative to traditional methods for inspection of internal quality parameters because they are fast, simple and cost-effective. In this review, invasive and non-invasive analytical methods and instruments for evaluating MC, OC, fatty acid composition and rancidity in different nuts are discussed. This paper also reviews the implementation of visible to near infrared spectroscopy, nuclear magnetic resonance and X-ray computed tomography on nuts for evaluation of quality attributes. Technical challenges and future possibilities for commercial use of these non-invasive methods for quality evaluation of nuts are presented.

Keywords: Near infrared spectroscopy, nuclear magnetic resonance, X-ray tomography, moisture content, oil content, lipid oxidation

1. Introduction

Nuts are extremely rich in nutrients specifically unsaturated fatty acids and other phytochemicals such as proteins and antioxidants (Ros, 2010; Settaluri et al., 2012; Shakerardekani et al., 2013). Their consumption is linked with low incidence of heart disease, diabetes, gallstones and cholesterol (Eagappan and Sasikumar, 2014; Pannico, 2014; Rengel et al., 2015).

Traditionally, nuts are manually inspected by skilled workers who classify nuts by their colour and the incidence of visible deformations (Guthrie et al., 2004; Pannico, 2014). The disadvantage of this method is its inaccuracy and the fact that this sorting system may result in unsound and immature nuts being encompassed in the batch to the processor which decreases the market value of the entire batch (Pannico, 2014; Canneddu et al., 2016). This technique is only suitable for evaluating external quality of in-shell nuts (Pannico, 2014). Internal quality of shelled nuts is often based on moisture content, peroxide value (PV) and acidity index (AI) (Pannico, 2014; Canneddu et al., 2016), which cannot be detected by the manual method (Pannico, 2014).

Visually sorting shelled nuts can be slow and require an expert. Common PV and AI evaluation methods are also time-consuming, use chemicals, and are costly to be used for evaluating nut quality in industrial scale (Canneddu et al., 2016). Furthermore, destructive analysis of PV and AI require precise sample preparation from a batch of representative samples on which quality analysis of nuts from an entire orchard is based on (Guthrie et al., 2004; Canneddu et al., 2016). Aside from their hard-labor and invasive nature, the disadvantage of traditional analytical methods is that growers are likely to deliver nuts of inferior quality to the market because of quality variation within a consignment (Pannico, 2014; Canneddu et al., 2016). Therefore, there is a necessity to develop a rapid, accurate and non-invasive method that can be effectively used to precisely evaluate nut quality. The purpose of this paper was to review current invasive techniques and instruments for evaluating the quality of nuts. This paper also reviews the trends in implementing evolving optical and imaging methods for non-invasive analysis of nut chemical characteristics. Application of visible and near infrared spectroscopy (Vis/NIRS), X-ray tomography and nuclear magnetic resonance (NMR) were particularly reviewed.

2. Terminology

The botanical use of the term "nut" refers to an indehiscent fruit with a hard and dry pericarp that is usually shed as a one seeded unit (Swanevelder, 1998). Tree nuts are defined as dry fruits with a single seed with ovary wall that hardens with maturity. The most prevalent palatable tree nuts are almonds (*Prunus amigdalis*), hazelnuts (*Corylus avellana*), walnuts (*Juglans regia*), and pistachios (*Pistachia vera*). Other common palatable nuts include pine nuts (*Pinus pinea*), cashews (*Anacardium occidentale*), pecans (*Carya illinoiensis*), macadamias (*Macadamia integrifolia*), and Brazil nuts (*Bertholletia excelsa*) (Ros, 2010; Settaluri et al., 2012; Shakerardekani et al., 2013). Mature nuts consist of a cream to white seed, which is the kernel, enclosed in a hard, dry pericarp (shell) which is then enclosed in a green or grayish green or brown pericarp (husk) (Delprete et al., 2015; du Preez, 2015).

The customer interpretation of nuts also comprises peanuts (*Arachis hypogea*), which are botanically belonging to legumes and are extensively acknowledged in the nuts group (de Oliveira Sousa et al., 2011; Settaluri et al., 2012; Shakerardekani et al., 2013). In addition, peanuts are used in a manner comparable to tree nuts and share the same nutrient profile as tree nuts (Ros et al., 2010). In this paper, the term "nuts" refer to all common tree nuts and peanuts. In a similar manner to tree nuts, mature peanuts consist of an edible kernel that is enclosed in a shell (de Oliveira Sousa et al., 2011; Navarro and Rodrigues, 2016). The kernel (Fig. 1) is often referred to as shelled nut. The kernel that is enclosed in a shell is referred to as nut-in-shell (Ros, 2010; Walton and Wallace, 2015). Figure 1 serves as an example of the nut's husk, shell and kernel (DAFF, 2016).

Husk

Shell/Nut-in shell

Kernel/Shelled nut
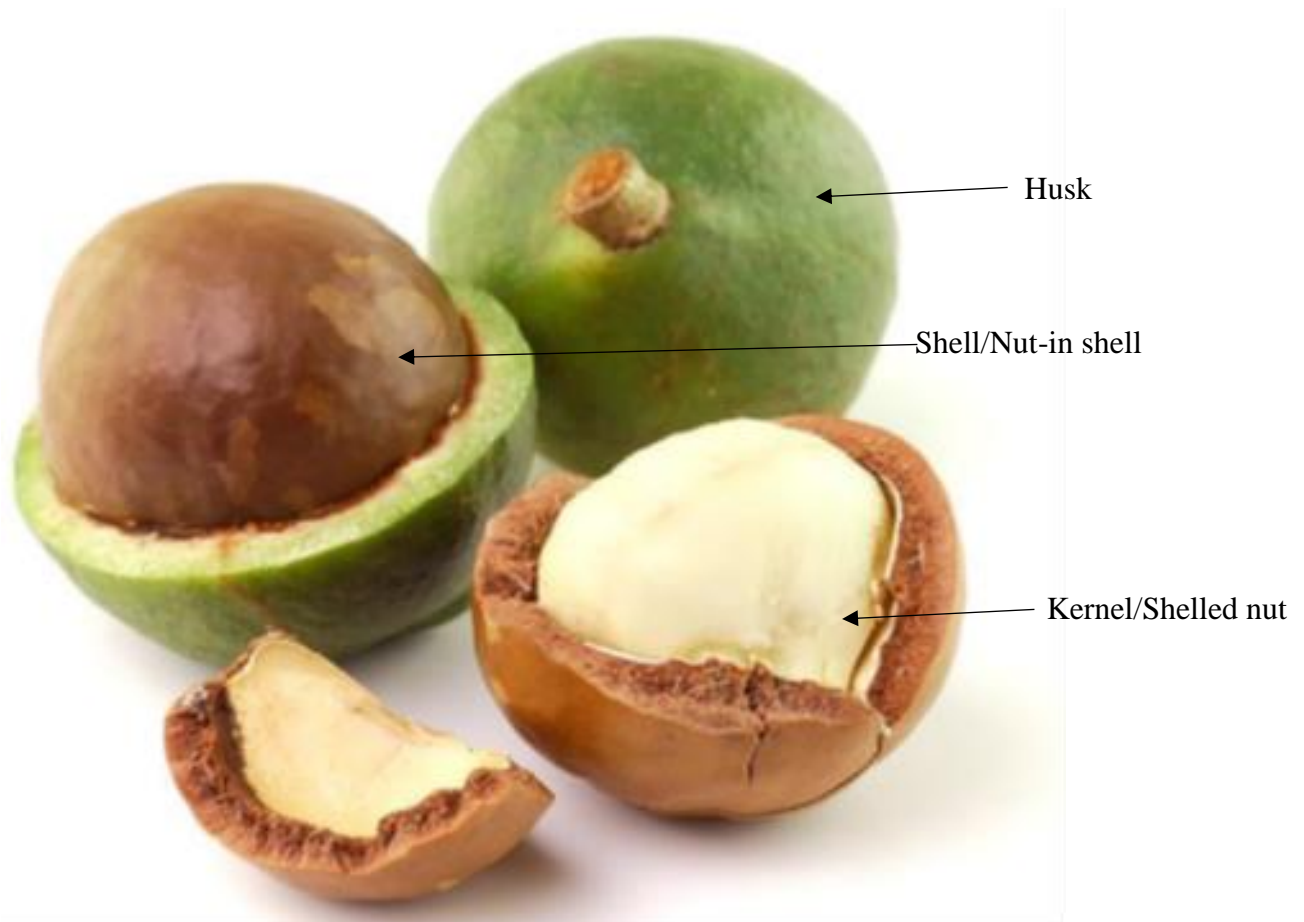
Fig. 1: Macadamia nut (DAFF, 2016).

3. Nut quality parameters

Nuts are rich in nutrients and are well known for their fat content, ranging from 44 to 76 % and energy, ranging from 20 to 30 kJ/g (Table 1). Nuts contain the highest percentage of mono-unsaturated fatty acids (MUFA) and polyunsaturated fatty acids (PUFA) (Ros, 2010; Shakerardekani et al., 2013). Monounsaturated fatty acids available in nuts includes oleic, palmitoleic and gadoleic acids and polyunsaturated fatty acids include linoleic acid and α-linolenic acid (Ros, 2010; Rengel et al., 2015). Nuts are also rich in other phytochemicals such as protein, dietary fiber, essential minerals, vitamin E, and plant sterols (Ros, 2010; Ros et al., 2010), which are linked with elevated health benefits including prevention of cardiovascular diseases, diabetes and cholesterol (Navarro and Rodrigues, 2016).

Table 1: Nutrient composition of nuts per 100 g

Nuts	Energy (kJ)	Fat (g)	SFA (g)	MUFA (g)	PUFA (g)	LA (g)	ALA (g)	Protein (g)	Fiber (g)	Folate (μg)	PS (mg)
Almonds	2418	50.6	3.9	32.2	12.2	12.2	0.00	21.3	8.8	29	120
Brazil nuts	2743	66.4	15.1	24.5	20.6	20.5	0.05	14.3	8.5	22	NR
Cashews	2314	46.4	9.2	27.3	7.8	7.7	0.15	18.2	5.9	25	158
Hazelnuts	2629	60.8	4.5	45.7	7.9	7.8	0.09	15.0	10.4	113	96
Macadamia nuts	3004	75.8	12.1	58.9	1.5	1.3	0.21	7.9	6.0	11	116
Peanuts	2220	49.2	6.8	24.4	15.6	15.6	0.00	25.8	8.5	145	220
Pecans	2889	72.0	6.2	40.8	21.6	20.6	1.00	9.2	8.4	22	102
Pine nuts	2816	68.4	4.9	18.8	34.1	33.2	0.16	13.7	3.7	34	141
Pistachios	2332	44.4	5.4	23.3	13.5	13.2	0.25	20.6	9.0	51	214
Walnuts	2738	65.2	6.1	8.9	47.2	38.1	9.08	15.2	6.4	98	72

Saturated fatty acids (SFA), monounsaturated fatty acids (MUFA), polyunsaturated fatty acids (PUFA), linoleic acid (LA), α-linolenic acid (ALA), plant sterols (PS), not reported (NR)

Source: United States Department of Agriculture Nutrient Data Base (https://www.nal.usda.gov/fnic, Accessed: 21/11/2018).

Nuts are sold as both in-shell and shelled nuts. In-shell nuts are mainly intended for fresh consumption while shelled ones are consumed either as raw, roasted whole nuts or as ingredients in various processed food. Shelled nuts are commonly used for making spreads, in bakery and in confectionary products (Moscetti et al., 2013; Pannico, 2014). Size, shape, shell, kernel defect, fatty acids, peroxide value and protein contents are among the main characteristics considered in the evaluation of nut quality (Pannico, 2014; Moscetti et al., 2014; Canneddu et al., 2016). Rancidity, internal browning, moldy and shriveled kernels are the main nut defects decreasing yield, kernel percentage and market value (Moscetti et al., 2014; Pannico, 2014). These nut defects are mainly influenced by kernel chemical composition (Özdemir et al., 2001; Pannico, 2014).

However, there is currently no adequate information in the literature about factors that determine kernel biochemical composition in hazelnuts and the techniques that can improve it, apart from the known facts that ecological conditions, cultivar, location, technical practices, and cultural practices can affect quality traits and biochemical composition in many nut species (Pannico, 2014). Wall and Gentry (2007) reported that the quality of processed macadamia nut depends on the initial quality of nuts at harvest, and the methods of processing (drying or roasting), packaging and storage conditions.

Harvest practices may lead to a vast variability in quality parameters such as maturity level, moisture content, disease and insect damage for wet-in-shell nuts delivered to the processor. However, oil content remains the most significant quality indicator of kernels (Walton and Wallace, 2012). Ebrahem (1992) reported that the flavour of pecan kernel is related to the oil content, volatile constituents, and possibly to the carbohydrates, especially sugars. The author further stated that the higher the oil content (which may vary from 50-75 %), the higher the flavour ratings. Because of high fat content in nuts, that is high in unsaturated fatty acids as indicated in Table 1, the development of lipid oxidation is the most significant quality parameter in unshelled nuts (Jensen et al., 2001; Pannico, 2014; Canneddu et al., 2016). High levels of lipid oxidation lead to disagreeable rancid taste due to the formation of oxidation products (Jensen et al 2001; Baker, 2002). High moisture content in nuts at harvest, during processing or in postharvest storage leads

to an increased microbial invasion as well as lipid oxidation which results in rancidity (Baker, 2002; Nahm, 2011; Canneddu et al 2016).

3.1. Moisture content

Freshly harvested macadamia nut has a moisture content of about 81.8 % in husk and 33.3 % in nut-in-shell (NIS) and are prone to deterioration (Borompichaichartkul et al., 2009). Such high moisture content quickens the growth of micro-fungi, that produce specific enzymes that break down carbohydrates into their monomers and hydrolyze fats to free fatty acids, forming rancidity (Borompichaichartkul et al., 2009; Moscetti et al., 2013; Pannico, 2014; Wang et al., 2014). Free fatty acids (FFA's) are the main catalyst of rancidity, resulting in a progressive increase of food acidity therefore, causing much stronger off-flavours (Saponaro et al., 2015; Walton et al., 2017). Also, kernels with high moisture brown more quickly during roasting due to soft texture (Phatanayindee et al., 2012). Therefore, drying is a most crucial step during the processing of nuts for maximizing kernel quality and storage (Borompichaichartkul et al., 2009). Moisture content essential for microbial development, enzyme activity, and chemical reactions is reduced in dried nuts (Wall and Gentry, 2007; Wang et al., 2014).

Previous studies recommend that moisture in raw kernels be minimized to about 1.5 % for macadamia nuts, 8 % for walnuts and cashew and 6-10 % for peanuts (Baker, 2002; Mursalim and Dewi, 2002; Phatanayindee et al., 2012). Nuts within this commercial range of moisture content have an increased kernel recovery during cracking and higher stability against oxidation during storage (Walton, 2005). Various drying techniques such as sun-drying, in-bin drying, hot air drying, heat pump drying, di-electric drying using microwave or radio frequency, vacuum drying, and freeze-drying have been studied and employed by the nut industry to improve kernel quality before storage (Mursalim and Dewi, 2002; Zhang et al., 2006; Nahm, 2011).

3.2. Oil content

Tree nuts have higher oil contents (± 60 %) than peanuts (± 40 %) (Pannico, 2014; Rengel et al., 2015; Navarro and Rodrigues, 2016). Nuts are rich in unsaturated fatty acids (Table 1), therefore, undergo hydrolytic and oxidative deterioration during postharvest processing and storage, leading to degraded sensory and chemical kernel quality and reduced shelf life (Nahm, 2011; Rengel et al., 2015; Srichamnong and Srzednicki, 2015). Oxidative rancidity occurs when unsaturated oil reacts with low molecular weight oxygenated constituents such as alcohols, ultimately resulting in the development of off-flavours, while in hydrolytic rancidity the hydrolysis of the triglycerides produces glycerol and free fatty acids which can also produce a disagreeable flavor (Borompichaichartkul et al., 2009; Rengel et al., 2015; Walton et al., 2017).

3.3. Lipid oxidation

Lipid oxidation is a vital deteriorative reaction associated with unsaturated fatty acids causing off-flavours that develop as a consequence of autoxidation which is a self-sustaining free radical mechanism that yield hydroperoxides (main products) (Phatanayindee et al., 2012). Autoxidation is usually autocatalytic, with oxidation products accelerating the reaction so that the rate accumulates over time (Kashani et al., 2003; Nahm, 2011; Walton et al., 2017). The hydrolysis of lipids is known to result in a continuous increase of food acidity due to the formation of fatty acids (Moscetti et al., 2013). Therefore, lipid hydrolysis accelerates lipid oxidation due to the formation of fatty acids that can be substrates of oxidation reaction (Saponaro et al., 2015).

Hydroperoxides, are the main products of lipid oxidation and can ultimately break down in a sequence of composite reactions, to generate secondary products such as alcohols and carbonyl compounds (aldehydes and ketones). These secondary products can then be oxidized to carboxylic acids (Moigradean et al., 2012). The secondary metabolites are usually volatile substances and can result in the formation of rancidity in nuts (Jensen et al., 2001; Pannico, 2014). Lipid oxidation products (secondary metabolites, peroxides and lipid-free radicals) can also lead to several deteriorative reactions in proteins, amino acids and vitamins, causing severe loss of nutrients and

functionality properties of kernel constituents (Bail et al., 2009; Pannico, 2014). Moscetti et al. (2013) reported that free fatty acids concentration exceeding 1 % decreases the shelf life of hazelnuts. Therefore, lipid oxidation is of great importance in nut storage and can be used to evaluate postharvest quality of nuts during processing and storage.

3.4. Peroxide value

Peroxide value is associated with the development of peroxides in unsaturated fat, initiated from the break of double bonds, which produces short chain volatile products responsible for the rancid odour (Canneddu et al., 2016). Peroxide value is the most common parameter often used for characterizing the quality of nuts (Moigradean et al., 2012; Borompichaichartkul et al., 2013). The number of peroxides available in edible oils indicates its oxidative level and therefore, its susceptibility to rancidity. Oils with high peroxide values (> 10 meq O_2/kg) are regarded unstable and easily become rancid while oils with relatively low peroxides values (< 10 meq O_2/kg) indicate that the products are stable against oxidation (Borompichaichartkul et al., 2013). Therefore, peroxide value is a major important quality parameter of nuts and can be used for classification of kernels. Nahm (2011) classified shea nut samples with the highest level of peroxides (> 15 mEq/kg), which was beyond an acceptable limit, to be within a 3rd grade.

4. Destructive Methods

4.1. Method for quantifying moisture content

Different drying methods used by researchers to determine moisture contents of macadamia, pistachios and walnuts are provided in Table 2.

Table 2: A summary of different drying methods used to determine moisture content as an important quality determinant of shelled nuts

Type of nuts	Drying method	Drying temperature (°C)	Drying time	Moisture content (%)	References
Macadamia	Hot air drying	40 – 60	6 days	1.5	Silva et al. (2006)
Macadamia	Fan-forced oven	38, 45, and 58	6 hours	1.5	Walton (2005)
Macadamia	Conventional oven	30 - 40	14 days	1.5	Wall and Gentry (2007)
Macadamia	Hot pump	40, 50 and 60	4.5 – 5.5 hours	1.5	Borompichaichartkul et al. (2013)
Pistachios	Sun-drying	26.5	2 days	< 4	Kashani et al. (2003)
Pistachios	Bin drying	65	8 days	< 4	Kashani et al. (2003)
Pistachios	Vertical continuous	40 - 45	10 hours	< 4	Kashani et al. (2003)
Pistachios	Vertical cylindrical	55	8 hours	< 4	Kashani et al. (2003)
Pistachios	Funnel cylindrical	80	5.5 hours	< 4	Kashani et al. (2003)
Walnut	Air oven	100	24 hours	5.73 - 6.95	Khir et al. (2013)

Other industrial effective drying methods for quantifying moisture content includes microwave or radio frequency in fruits and vegetables (Zhang et al., 2006), vacuum drying in grapes (Clary et al., 2005) and freeze-drying in skim milk (Wang et al., 2005), among others.

To accelerate the drying process, joint hot air and microwave method is used for drying fresh macadamia nuts to a low moisture content of 11.1 % on dry basis (d.b.); microwave device is further used to dry nuts to a lower moisture content of 1.5 % (d.b.) (Silva et al., 2006). Even though the joint method is quicker and requires only 4.5 to 5.5 hours to dry macadamia, it is expensive and requires high investment and operating cost (Borompichaichartkul et al., 2013). Another alternative for accelerating the drying process and enhancing the quality of numerous produce including nuts, such as hazelnut (Ceylan and Aktaş, 2008), macadamia nut (Kowitz, 2004) and stone fruit (Sunthonvit, 2005), is the use of advanced combination of superheated steam and heat pump drying method (Namsanguan et al., 2004).

Borompichaichartkul et al. (2009) used the combined technique to speed up drying process of macadamia nuts with the first-stage heat pump drying conducted at 40 °C and relative humidity of 20 % to reduce the nut-in-shell moisture content from the initial value of 20 to 22 % (d.b.) to the intermediate moisture content of 8.7 to 11.1 % (d.b.). Immediately after the first drying stage, hot air drying at 50, 60 and 70 °C was used to decrease moisture content to 1.5 % at the same relative humidity. Wall and Gentry (2007) reported that increase in drying temperature can encourage hydrolysis of sucrose to glucose and fructose in the kernel, leading to intensive kernel browning. Also, a study conducted by Borompichaichartkul et al. (2009) revealed that temperature above 60 °C promoted browning and resulted in high peroxide value as an indication of the onset of rancidity. Therefore, it is endorsed that the drying temperature for combined techniques in the second stage be kept at temperatures below 60 °C to avoid internal browning.

Khir et al. (2001) used oven drying on walnuts and observed a strong relationship between the moisture content of shells ($R^2 = 0.97$) and kernels ($R^2 = 0.96$). Mason et al. (1998) determined that the moisture content of macadamia nut-in-shell (shells) (3.5 %) correspond to the kernel moisture content of 1.5 %. Therefore, kernel moisture content can be predicted as a dependent factor of shell moisture content. The moisture content of tree nuts is commonly measured after dehusking or dehulling nuts using mechanical dehuskers (Walton and Wallace, 2015). A typical moisture content measurement procedure can be based on a method according to Khir et al. (2011) and Wang et al. (2014), shells and kernels were discretely placed in a pre-weighing aluminium dishes

and weighed on an electronic scale with a precision of 0.01 g. The samples were afterwards placed in an oven dryer and dried at desired temperature and time to reach the stable dry weight and then removed from the oven dryer and cooled in a desiccator and then weighed again. The moisture content of in-shell and shelled nuts was based on initial and final (dry) weight. Mass changes in nuts were used to calculate moisture content on a dry basis. According to Khir et al. (2011), moisture content was measured for husks, shells, and kernels based on the initial and final sample weight using the following equation:

$$MC_{wb}(\%) = \frac{W_i - W_d}{W_i} \times 100 \tag{1}$$

where MC_{wb} is the moisture content on a wet mass basis, W_i and W_d are the initial and the dry sample weights, respectively. The MC of nuts-in-shell was measured as follows:

$$MC_{wb} = \frac{(W_{si} - W_{sd}) + (W_{ki} - W_{kd})}{(W_{si} + W_{ki})} \times 100 \tag{2}$$

where W_{si} and W_{ki} are initial weights of shells and kernels and W_{sd} and W_{kd} are the final weights of shells and kernels, respectively. The moisture contents of samples were calculated on wet weight basis.

4.2. Method for quantifying oil content

Several methods are used for oil extraction from seed kernels of diverse origins. Common extractions comprise solvent extraction (Abdulkarim et al., 2005; Miraliakbari and Shahidi, 2008), cold-pressing (Prescha et al., 2014; Rabrenović et al., 2014), supercritical fluid extraction (Silva et al., 2008), and aqueous enzymatic extraction (AEE) methods (Yusoff et al., 2016). The most prevalent and precise method used for oil evaluation in chemical or food industries is the solvent extraction used to determine the oil content (Carvalho et al., 2014; Danlami et al., 2015). The nut industry, especially macadamia and hazelnut, use solvent extraction method, where the oil is

extracted from the known mass of the dry kernel sample using petroleum ether or hexane as a solvent (Miraliakbari and Shahidi, 2008; Santos et al., 2012). After which, the free oil yield (%) and oil recovery (%) can be calculated according to Yusoff et al. (2016) who used Eq. 3 and Eq. 4 for aqueous enzymatic extraction method where the difference between the initial and final mass of the crucible used was quantified as the oil yield from the tissue by normalizing this against the kernel mass initially taken.

$$\text{Free oil yield (\%)} = \frac{\text{Mass crucible containing the oil (g)} - \text{Mass of crucible (g)}}{\text{Mass of kernels initially taken (g)}} \times 100 \quad (3)$$

$$\text{Oil recovery (\%)} = \frac{\text{Mass of oil extracted from a given mass of kernel (g)}}{\text{Mass of oil contained in the kernels initially taken (g)}} \times 100 \quad (4)$$

Navarro and Rodrigues (2016) reported that, the wanted characteristics of a solvent such as the non-toxicity, low flammability and simplicity of recovery from the defatted sample, should be taken into consideration when selecting a solvent type. Hexane is frequently used as a solvent because of high stability, less evaporation loss, less corrosiveness, lower greasing residue, and better smell and flavour of the extracted sample (Magwaza and Tesfay, 2015). However, even though n-hexane is the most dominant solvent used in the food industry and can achieve crude oil yield of above 96 % (Liu et al., 2016), it is extremely flammable, explosive and severe inhalation of humans results in the nervous system effects, such as dizziness and headache making it a hazardous solvent for humans and plants (Liu et al., 2016).

Another oil extraction method in the macadamia industry is the subcritical fluid extraction, where ground macadamia are subjected to several subcritical extractions with different solvents such as *n*-butane (98 %), propane (94 %), dimethyl ether (95 %) and tetrafluoroethane (96 %) (Navarro and Rodrigues, 2016). Liu et al. (2014) suggested that *n*-butane should be a commonly used solvent in subcritical extraction because of its supreme ability to dissolve lipophilic compounds. In addition, it is colourless and can be regarded as a clean solvent by not leaving residual solvent in

the produce. However, Navarro and Rodrigues (2016) reported that the use of this solvent has the disadvantage of high flammability. Also, Zhu (2013) evaluated five techniques of macadamia oil extraction and obtained the following yields: extraction solvent (petroleum ether) 50.4 %, ultrasound-assisted extraction (petroleum ether), 57.2 %, Soxhlet (petroleum ether), 74.6 %, extraction by supercritical fluid (CO_2), 68.5 % and subcritical extraction (butane), 71.6 %. Although Soxhlet extraction method is accurate and showed higher oil content, this technique is slow and requires operation at high temperatures. Moreover, it is time-consuming to be effective to the nut industry (Özkal et al., 2005; Meyer and Terry, 2008; Carvalho et al., 2014). However, although solvent extractions are useful, they have several disadvantages, such as expensive equipment, operational expenditure and concerns for environmental pollution (Magwaza and Tesfay, 2015).

The nut industry still employs mechanical oil expression, where mechanical oil expression from kernels is a solid-liquid phase separation process. This process includes the use of pressure by hydraulic press with or without heat (Ogunsina et al., 2014). Navarro and Rodrigues (2016) reported that macadamia oil extraction is traditionally accomplished by cold pressing, an operation that comprises the use of pressure to the kernels while maintaining the temperature below 30 °C to avoid flavour deterioration. Although this method is useful and has benefits of extensive choice of application and cheap equipment, the oil and protein content is relatively low due to deterioration during mechanical processing (Ogunsina et al., 2014; Prescha et al., 2014). Rodríguez-Millán et al. (2011) reported that the yield of extraction using cold pressing was determined to be less than Soxhlet extraction (35 to 40 % and 40 to 60 %, respectively), indicating that the solid sample tissue remaining after the cold pressing operation still comprises considerable quantity of the oil. Sarkis et al. (2014) determined a residual oil content in a partly defatted sample tissue of about 52 %. Altogether, the partly defatted sample tissue is an exceptional raw material to be subjected to a second oil extraction process. Restrictions and the destructive nature of the solvent and mechanical oil extraction methods validate the necessity for the development of an alternative accurate and non-invasive method for determining oil quantity and quality in nuts. Furthermore, the knowledge and research gap on the application of non-destructive methods

especially in the nut industry also demonstrate a need for further research on the feasibility of non-destructive techniques to predict kernel quality.

4.3. *Method for quantifying peroxide value*

Peroxide value is the most effectively used parameter to quantify the onset and the degree of oxidation in oils as it is a measure of hydroperoxides formed in the primary stages of oxidation (Borompichaichartkul et al., 2013). The deterioration of nut quality during processing and storage can be quickly identified by variations in peroxide value (Baker, 2002; Borompichaichartkul et al., 2013). High quality nuts are characterized by peroxide value below 10 meq O_2/kg (Borompichaichartkul et al., 2013). Peroxide values can be determined according to Walton et al. (2017) who dissolved 1 g of sample oil in 0.01N $Na_2S_2O_3$ and titrated using 100 µL HPLC syringe, peroxide value of samples were expressed as milliequivalents per kilogram and calculated as follows:

$$PV \text{ (meq per kg)} = \frac{(S - B) \times N \times 1000}{\text{sample wt (g)} \times 1000} \tag{5}$$

where S = sample titration (µL); B = Blank titration; and N = normality of $Na_2S_2O_3$.

5. Non-destructive Methods

The strict and increasing requirements for quality assurance particularly in the fresh produce industry has urged the development of a broad variety of advanced accurate, fast, real-time, effective and non-destructive techniques for quality evaluation (Magwaza and Opara, 2015). Traditional analytical methods are invasive, slow, require the use of dangerous chemicals and are labor intensive, and some are only possible in laboratories due to the required specific instruments for quality analysis (Magwaza and Tesfay, 2015).

In recent years, non-invasive techniques for quality evaluation of various dry fruit, including hazelnut, peanut, walnut, macadamia, shea nut and chestnut have become popular and a significant attempt have been made to develop them (Jensen et al., 2001; Pannico et al., 2015). Non-invasive techniques predict produce quality parameters via differences in optical characteristics, sound, and density (Magwaza and Tesfay, 2015). The online non-invasive grading and sorting lines have been used for the evaluation of internal quality atributes including those based on electrical properties such as visible to near infrared (Vis/NIR) spectroscopy in walnuts and mango (Jensen et al., 2001; Saranwong et al., 2011), vibration energy in avocado (Magwaza and Tesfay, 2015), ultrasound, nuclear magnetic resonance (NMR) in pomegranate (Zhang and McCarthy, 2013), X-ray in chestnuts (Donis-González et al., 2012), volatile emission and others in fresh fruits and vegetables (Butz et al., 2005). Even though various non-destructive techniques have been developed and verified, near infrared (NIR) spectroscopy (NIRS) is currently the most often used method for prediction of internal disorders, moisture content, lipid oxidation and fatty acid profile in nuts (Jensen et al., 2001; Guthrie et al., 2004; Moscetti et al., 2014; Pannico et al., 2015). X-ray and NMR spectroscopy are scarcely used in the nut industry and there is currently very limited research reported on these techniques.

5.1. Vis/NIRS

Visible and near infrared spectroscopy (Vis/NIRS), with adequate chemometric analysis, has been implemented and proven to be an accurate, fast, and non-invasive alternative to invasive techniques for giving non-visible information regarding relative proportions of C–H, O–H, and N–H bonds (Magwaza and Tesfay, 2015). Nuts quality attributes such as moisture content, oil content, lipid oxidation, fatty acid composition and internal disorders are mainly based on organic molecules that include C–H, O–H, C–O, and C–C bonds. Thus, it is possible to use NIRS techniques to measure these quality attributes (Guthrie et al., 2004; Pannico et al., 2015). Moscetti et al. (2014) used a portable Luminar 5030 Acousto-Optic Tunable Filter-Near Infrared (AOTF-NIR) miniature analyzer to detect internal mold damaged chestnuts using ranges from 1100 to 1400 nm and 1650 to 1720 nm. This NIR region corresponds to combination and overtone vibrations of functional groups such as hydrogen (C–H, N–H and O–H), enabling the analysis of

kernel internal quality parameters such as moisture, protein, starch content and tissue damage. Canneddu et al. (2016) used Fourier Transformed Near Infrared (FT-NIR) spectroscopy to predict moisture content in macadamia nuts using ranges from 1300 to 1500 nm and 2300 to 2350 nm. For oil quality in hazelnuts, a robust electromagnetic absorption is reported around 2200 to 2400 nm (CH_2 stretch bend and combination) and around 1750, 1200 and 900 nm (first, second and third overtone of CH_2 stretching) (Pannico et al., 2015). In a study by Pannico et al. (2015), NIRS was used to predict lipid oxidation in hazelnuts, satisfactory PLS model ($R^2 = 0.85$ and RMSEP = 0.33 %) was created in the ranges from 2100 to 2200 nm. The authors argued that this spectral range had peaks corresponding to the C (C=C) double bond. Several researchers have also used spectral ranges including the 2100 to 2200 nm and different ranges for calibrating models to predict nut quality parameters (Guthrie et al., 2004; Moscetti et al., 2014; Pannico, 2014; Canneddu et al., 2016). From the statistical data, higher coefficient of determination (R^2) and lower root mean square error of cross validation (RMSECV) as indicated in Table 3, it can be concluded that Vis/NIRS is an adequate non-invasive technique for predicting nut quality.

Accurate predictive findings by Guthrie et al. (2004) showed that root mean square error of prediction (RMSEP) for macadamia kernels using Foss NIRS 6500 (Silicon-Lead Sulfide detector), Zeiss MMSI-NIR Enhanced (Silicon detector) and Zeiss MMS-NIR (Indium Gallium Arsenide detector) were 5.3 %, 2.4 % and 1.7 % for oil content and 0.11 %, 0.16 % and 0.29 % for moisture content, respectively (Table 3). A good performance of the indium gallium arsenide unit, comparative to the silicon unit for the evaluation of oil content, was credited to the detection of wavelengths pertinent to lower order overtones of the oil CH_2 bond. This advantage probably exceed the drawback of the more restricted penetration of wavelengths higher than 1000 nm and may suggest that macadamia kernel is comparatively homogeneous regarding oil content (Guthrie et al., 2004). Osborne et al. (1993) reported strong electromagnetic absorption for oil content prediction around 2200 to 2400 nm (CH_2 stretch bend and combination) and around 1750, 1200 and 900 nm (first, second and third overtones of CH_2 stretching). Kawano et al. (1993) further reported that shorter wavelengths enable improved penetration of produce and that these wavelengths are useful in the evaluation of macadamia kernels.

Jensen et al. (2001) reported prediction results of walnut quality parameters where the best description of nutty taste (R^2 = 0.77, RMSECV = 11.7), sweet taste (R^2 = 0.76, RMSECV = 7.8) and rancid taste (R^2 = 0.86, RMSECV = 13.4) were accurately attained using the second derivatives of 400 to 2498 nm (Table 3), while bitter taste (R^2 = 0.82, RMSECV = 7.7) and peroxide value (R^2 = 0.68, RMSECV = 1.5) were excellently described with the second derivatives of 650 to 750 nm spectral range. Pannico et al. (2015) reported that when the entire NIR wavelength range of 1100 to 2400 nm was used with six partial least square (PLS) factors, the calculated model permitted a precise prediction of hazelnuts kernel defect as indicated by high R^2 (0.89) and low RMSECV (0.88) (Table 3). These authors further reported the highest residual predictive deviation (RPD) of 2.18 and 2.58 for nut-in-shell and kernels, respectively and the lowest RMSEV values of 0.38 and 0.33 for nut-in-shell and kernels, respectively, which were obtained for the model predicting the K_{232} extinction coefficient. K_{232} is regarded as the most important variable for lipid oxidation and values above 2 are attributed to taste defect while values above 2.5 are considered rancid on hazelnuts (Lopez et al., 1997).

Although it is arguable, most Vis/NIRS researchers report that RPD values above 2 indicates the possibility of quantitative predictions, whereas values above 3 are considered to correspond to the best accurate prediction (Nicolai et al., 2007). This indicates that the prediction model for K_{232} was accurate and sufficient for both nut-in-shell and kernels. Furthermore, the finding that lipid oxidation (based on K_{232}) can be precisely predicted for both in-shell and shelled hazelnut is beneficial in commercial scales because it shows that lipid oxidation can as well be determined without shelling nuts. Canneddu et al. (2016) assessed the possibility of Fourier Transformed Near Infrared (FT-NIR) spectroscopy to non-invasively predict PV and AI in in-shell macadamia nuts and reported that the prediction of PV using the Kennard–Stone algorithm resulted in a square error of prediction (SEP) of 3.45 meq/kg, and a prediction coefficient determination value (R^2_p) of 0.72. The best AI values prediction result in comparison to PV values was precisely obtained with FT-NIR spectra without any pretreatment (SEP = 0.14 %, R^2_p = 0.80) (Table 3). Another study conducted by Hirano et al. (1998) assessed the use of NIRS and PLS regression chemometric techniques to predict mold and the degree of hydrolysis in peanuts. The authors found results that

indicated that there was a good correlation between the transmittance ratio and the level of the hydrolysis of triglycerides (R2 = 0.84) (Table 3).

Table 3: An overview of applications of visible to near infrared spectroscopy (Vis/NIRS) to measure quality parameters of nuts

Nut	Measure parameter	Spectrophotometer	Wavelength range (nm)	Accuracy	RMSEP (%)	Reference
Hazelnut (NIS and SN)	Kernel defect K$_{232}$	Perkin-Elmer Spectrum One NTS spectrophotometer (Perkin-Elmer, Beaconfield Bucks, UK)	700 – 2500	$R^2 = 0.89$ $R^2 = 0.79$ $R^2 = 0.85$	0.88 0.38 0.33	Pannico et al. (2015)
Macadamia (NIS)	PV (meq/kg SEP)	Fourier transformed near infrared (FT-NIR) spectroscopy (PerkinElmer, Shelton, Conn., U.S.A.)	1000 – 2500	$R^2_p = 0.72$	3.45	Canneddu et al. (2016)
	AI			$R^2_p = 0.80$	0.14	

Macadamia (kernel)	OC (%)	Foss NIRS 6500 (Silver Spring, USA)	400 – 2500	$R^2_c = 0.94$	5.3	Guthrie et al. (2004)
		Zeiss MMSI-NIR Enhanced (Germany)	300 – 1100	$R^2_c = 0.98$	2.4	
		Zeiss MMS-NIR (Germany)	800 – 1700	$R^2_c = 0.99$	1.7	
	MC (%)	Foss NIRS 6500 (Silver Spring, USA)	400 – 2500	$R^2_c = 0.89$	0.11	
		Zeiss MMSI-NIR Enhanced (Germany)	300 – 1100	$R^2_c = 0.78$	0.16	
		Zeiss MMS-NIR (Germany)	800 – 1700	$R^2_c = 0.37$	0.29	
Peanuts	Mold (hydrolysis)	Transmittance NIR, Spectrophotometer U-4000 (Hitachi Co.)	500 - 1500	$R^2 = 0.84$	NS	Hirano et al. (1998)
Walnut (kernel)	Nutty taste	Visible/near-infrared (Vis/NIR) spectroscopy (model 6500, NIRS ystems Inc., Silver Spring, MD)	400 - 2498	$R^2 = 0.77$	11.7	Jensen et al. (2001)
	Sweet taste			$R^2 = 0.76$	7.8	
	Bitter taste			$R^2 = 0.75$	8.8	
	Rancid taste			$R^2 = 0.86$	13.4	
	PV			$R^2 = 0.55$	1.9	
	Hexanal content			$R^2 = 0.72$	26.2	

Coefficient of determination of cross-calibration (R^2), root mean square error of prediction (RMSEP), peroxide value (PV), acidity index (AI), nut-in-shell (NIS), shelled nuts (SN), moisture content (MC), oil content (OC), not specified (NS)

In conclusion, NIRS can be successfully used to evaluate quality parameters such as lipid oxidation, PV, AI, oil and moisture content of in-shell and shelled nuts. This method can be precisely used as a valid non-invasive technique for monitoring internal quality of in-shell and shelled nuts, however there is limited research on the use of NIRS to determine quality parameters such as lipid oxidation, peroxide value and oil content (Guthrie et al., 2004; Pannico, 2014; Canneddu et al., 2016). Although there is limited published research regarding the use of NIRS to determine the quality of in-shell and shelled nuts, the few published studies show that non-destructive methods are beneficial to the nut industry as quality evaluation tool of certain quality parameters. Further research should consider the optical configuration for improving nut sampling (Guthrie et al., 2004). Further research experiments are needed to include more data variability (growing location districts, cultivars and times) to improve robustness and demonstrate the classification accuracy of Vis/NIRS (Canneddu et al., 2016).

5.2. X-ray and nuclear magnetic resonance (NMR) imaging

X-ray techniques such as radiography and computed tomography (CT) are influential tools for non-invasive internal quality assessment (Hirano et al., 1998; Kotwaliwale et al., 2014; Schoeman et al., 2016). After being successfully used in medical diagnostics and other industrial implementations, researchers are recently using these techniques for internal quality assessment of numerous agricultural products such as pistachio nuts, wheat kernels, pineapples, olives and tomatoes (Haff and Toyofuku, 2008). X-rays have low wavelength range of 0.01 to 10 nm and high energy electromagnetic radiation of 120 eV to 120 keV and are able to penetrate through numerous materials and are often called soft X-rays (Kotwaliwale et al., 2014). Neethirajan et al. (2007) stated that the soft X-ray technique was quick, taking only less than 5 seconds to produce an X-ray image. These authors further reported that due to the low power to penetrate and capability to show the internal density changes, soft X-rays are more adequate to be implemented on wheat kernels.

Nuclear magnetic resonance (NMR) technique includes resonant magnetic energy absorption by nuclei positioned in an alternating magnetic field. The quantity of energy absorbed by the nuclei

is directly proportional to the number of a particular nucleus in the produce such as the protons in water or oil (Jha and Matsuoka, 2000). NMR is considered as an excellent alternative to traditional analytical techniques because it is fast, simple and have the potential for online measurements (Santos et al., 2014). In agriculture, NMR may be used for the evaluation of several quality attributes such as moisture content, oil content and fatty acids (Jha and Matsuoka, 2000; Vigli et al., 2003). Since these quality parameters have not yet been evaluated in nuts, there is a need for further experiments on the ability of X-ray and NMR to predict internal quality of nuts.

Hirano et al. (1998) examined the potential of X-ray-Computed Tomography (X-ray-CT) and ^{1}H-NMR- Computed Tomography (^{1}H-NMR-CT) imaging techniques to effectively predict the internal mold defect in peanuts. Hirano et al. (1998) further reported that NMR scans were able to excellently predict internal mold in peanuts ($R^2 = 0.84$). However, the loss of signal to noise ratio in the images as the speed of the system increases is the limiting factor for the majority of desired detection abilities (Haff and Toyofuku, 2008). Although NMR has proven to be able to predict mold in peanuts, higher installation and running costs and challenges for in-line use limits it commercial application (Hirano et al., 1998; Pasikatan and Dowell, 2001). With improvements in instrumentation and in hardware and software, these techniques are expected to become more field-worthy in the future.

6. Future prospects

The quality of nuts is assessed by size, colour, visible defect, oil content, oxidation, peroxide value or acidity index and internal mold defect (Moscettie et al., 2014; Pannico, 2014; Canneddu et al., 2016). Previous research of non-invasive techniques for evaluating nuts quality have been focusing on inspecting specific quality parameters such as rancidity which is related to flavour (Jesnsen et al., 2001; Canneddu et al., 2016) and do not combine quantitative evaluation of both external and internal quality parameters in one system. Therefore, future studies should involve the development of non-invasive techniques for integrated non-invasive prediction of external and internal quality parameters (Magwaza and Tesfay, 2015). Even though Vis/NIRS have been successfully used to predict rancidity (lipid oxidation, and peroxide value) in nuts (Pannico et al.,

2014; Canneddu et al., 2016), there is a need for further research due to the lack of considering each parameter during tests. Magwaza and Tesfay (2015) reported that even though researchers have used various Vis/NIRS frameworks and chemometrics to improve prediction, the selection of these parameters might influence accuracy and robustness, therefore, future studies should attentively focus on this. A study by Pannico et al. (2015) revealed that NIR diffuse reflectance spectroscopy was a sufficient, fast and precise method for predicting kernel defect and lipid oxidation in hazelnuts. Their study revealed the possibility of developing a two-step NIR procedure that uses a first PLS model to predict and distinguish unsound kernels, and the second PLS model to classify sound kernels by lipid oxidation levels.

6.1. Calibration models

Calibration models to be implemented should be based on enormous datasets, involving various orchards, climate conditions, seasons and operational conditions, such as temperature, and optimized towards robustness by including suitable preprocessing techniques (Herrera et al., 2003; Nicolai et al., 2007). Nicolai et al. (2007) further stated that more research is needed regarding calibration methods which depend on the actual physics of NIR radiation penetration in produce tissue rather than on a purely statistical analysis, such as PLS on empirically preprocessed spectra. Light transport simulations based on the diffusion estimation, the adding-doubling technique may provide effective guidance to these research attempts, making it possible to distinguish the information associated with the physical (scattering) and chemical (absorption) properties of the biological sample. A study by Pannico (2014) showed that PLS models for parameters linked to lipid oxidation (K_{270}, ΔK and free acidity) for hazelnuts were not adequate for detecting lipid oxidation because the standard error of the laboratory method (SEL) was lower than the standard error of cross validation (SECV) for K_{232}. However, the toughness of shells in nuts such as hazelnuts, macadamia, cashew nuts etc. may cause wavelength scatter and specular reflection before penetration which can reduce precision. Therefore, studies investigating an increased light intensity for application on nuts are necessary for improved calibration techniques in future models.

The future of NMR and X-ray CT techniques applied to food inspection particularly for the assessment of quality attributes such as maturity, moisture content, oil content and fatty acids, as well as the quality of food after processing is promising as both the industry and consumers are increasingly becoming more knowledgeable about the necessity of ensuring food quality and safety. Mature tree nuts usually abscise when the husk is still green. The husk dries and splits along the suture to release nut-in-shell. This technology is an essential tool for the automatic evaluation and monitoring of these attributes (Hirano et al., 1998; Yee et al., 2005). It can locate quality defects such as mold in a kernel, thus measuring entire samples, rapidly and accurately (Williams and Kucheryavskiy, 2016). Although these techniques give a precise image and quantification of parameters, they are not suitable for small-scale businesses. Their high cost limits implementation only to highly successful entrepreneurs and developed countries (Jha and Matsuoka, 2000). A challenge with NMR and X-ray-CT techniques is that the obtained results depend on laboratory conditions such as lighting and calibration or on the statistical methods implemented and are not really related with internal compounds or physical-chemical properties that might support these results from the commodity point of view (Lorente et al. (2012), while NIR techniques are effectively used to evaluate the nutritional quality of produce (Jha and Matsuoka, 2000). However, it is not yet possible to produce an image of the internal physical quality of produce. Nuclear magnetic resonance and X-ray-CT methods are expensive, and their operation requires scientific knowledge (Jha and Matsuoka, 2000). There is currently limited published research regarding the use of NMR and X-ray-CT techniques to estimate external or internal quality parameters of nuts, demonstrating a need for further research. Future research must also focus on making the use of NMR and X-ray-CT techniques easier and cost effective to make it accessible to the research of small businesses or growers without huge capitals.

7. Conclusion

This literature review revealed that the non-destructive technology is an interesting alternative to destructive method which can be expensive, slow and time-consuming and has limitations as some of the equipment can only be operated in the laboratory. NIRS is an effective technique for thoroughly screening of nuts for their chemical quality such as lipid oxidation (peroxide value and

acidity index) and oil content. X-ray-CT and ^{1}H-NMR-CT techniques can be used as a tool for studying the incidence of pathogens such as mold in nuts. Literature found in this review evidently indicated that Vis/NIRS is the most promising and advanced technology for future application because of simplicity in instrumentation, application, accessories and chemometric software packages. Vis/NIRS can estimate chemical or nutritional properties of nuts, which is its advantage compared to X-ray-CT and ^{1}H-NMR-CT techniques which are currently well established to only detect the mold defect in nuts. Moreover, X-ray-CT and ^{1}H-NMR-CT are expensive and time-consuming, which limits extensive application in an industry that requires real-time evaluation, whereas Vis/NIRS is rapid and of lesser cost, therefore, a commercially possible alternative for nut quality evaluation. However, Vis/NIRS is not yet as advanced with nuts as it is with fruits such as apples and mango where spectrophotometers have been used in the pack house. Therefore, more research is necessary for the nut industry regarding the use of X-ray-CT, ^{1}H-NMR-CT and Vis/NIRS non-destructive techniques, including ultrasonic system, ultrasound imaging, hyperspectral imaging, and fluorescence imaging which have not yet been used to estimate the quality of nuts.

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CHAPTER 3: EFFECT OF POSTHARVEST PRE-STORAGE PROCESSING IN MACADAMIA (*MACADAMIA INTEGRIFOLIA*) NUTS' ANTIOXIDANTS AND QUALITY

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Abstract

Macadamia nut is rich in monounsaturated fatty acids which are known to reduce the risk of cardiovascular diseases. On the negative side, high concentrations of unsaturated fatty acids lead to oxidative reactions, which result in rancidity thus decreases the quality of the nut. Drying and roasting are used to reduce moisture content and alleviate the above-mentioned problems. This research was conducted to evaluate and compare quality parameters of raw and roasted macadamia nuts during the accelerated storage of 70 d. Two commercially important macadamia cultivars, namely, 'A4' and 'Beaumont' were used as model cultivars. Nuts were dried for three consecutive days, starting with 35 °C on the first day, 38 °C for the second day and 50 °C for the third day to attain a target 1.5 % of nut moisture, after which, nuts were roasted at 125 °C for 15 min using hot air oven dryer. Raw kernels of 'A4' and 'Beaumont' cultivars had significantly higher concentration of polyphenol oxidase activity, peroxide value, low concentration of flavonoids, phenols and antioxidant activity compared to roasted kernels which had significantly lower concentration of peroxide value, high concentration of flavonoids, phenols and antioxidants activity. Also, according to the sensory panelists, raw kernels of 'A4' and 'Beaumont' had poor texture, aroma, rancid taste, appearance and marketability during the storage period of 70 d. In contrast, roasting significantly improved kernel quality and shelf life of both cultivars with kernel texture rated as crispy, rancidity as none and aroma, appearance and marketability as good during the storage. Overall, roasting significantly improved kernel quality and shelf life of 'A4' and

'Beaumont', as indicated by low peroxide value and high phytochemical quality and sensory quality as roasted kernels were marketable throughout the storage duration.

Keywords: Roasted kernels; Raw kernels; Polyphenol oxidase; Peroxide value; Antioxidant activity; Sensory evaluation

1. Introduction

Macadamia (*Macadamia tetraphylla*) is one of the utmost valuable nuts in the world with the highest content of monounsaturated fatty acid, mainly oleic (60 %) and palmitoleic (20 %) acids that may possibly reduce cholesterol and triglyceride levels, hence minimizing the risk of heart diseases (Sinanoglou et al., 2014; Wang et al., 2013). Macadamia is also rich in bioactive macronutrients such as protein, dietary fiber, essential minerals, vitamin E, and plant sterols (Ros, 2010) and contain significant amount of antioxidants (Rengel et al., 2015). The global production of *Macadamia* sp. is approximately 44 000 metric tons (kernel), 86 % of which comes from five top producing countries which include Australia (32 %), South Africa (30 %), Kenya (12 %), the United States (8 %), and Malawi (4 %) (Jaskiewicz, 2015; Navarro and Rodrigues, 2016). The kernel is either consumed raw, roasted or as constituents in various processed food particularly confectionery products (Borompichaichartkul et al., 2009). In addition, macadamia is the richest oil-yielding nut with about 75 % oil content that is mainly consumed by the food, pharmaceutical and cosmetic industry (Mbora et al., 2008; Navarro and Rodrigues, 2016). The macadamia industry uses oil content as a major indicator of kernel quality since it is rich in unsaturated fatty acids (> 80 %) (Gitonga et al., 2009; Rengel et al., 2015).

Ebrahem (1992) indicated that the flavour of nut kernel is related to the oil content, volatile constituents and possibly to carbohydrates, especially sugars and further stated that the greater the oil content, the greater the flavour ratings. However, the economic profit of macadamia nuts depends on yield, kernel recovery (percentage of whole kernel after cracking nuts), nut style of distribution such as whole kernel, halves and pieces (du Preez, 2015). Also, kernel quality is primarily indicated by appearance including size, shape, colour, texture, freedom from defects and shelf life or storability (Pannico, 2014).

Macadamia nuts can be stored for about 3 months at room temperature and 12 months at 2 °C, quality loss is one of the major challenges facing the macadamia industry (Kaijser et al., 2000; Wall and Gentry, 2007). One of the economically important quality loss in macadamia nuts is mainly caused by mold and its germination during storage as a consequence of high initial moisture

content (> 30 %) after harvest (Borompichaichartkul et al., 2009; Wang et al., 2014). Such high moisture content promotes the growth of microbes such as fungi, which produce specific enzymes that break down carbohydrates and accelerate the hydrolysis of lipids into free fatty acids, leading to the development of rancidity (Pannico et al., 2015). Since macadamia nuts contain high amount of unsaturated fatty acids they are prone to hydrolytic and oxidative rancidity when they contain high levels of free moisture (Borompichaichartkul et al., 2009).

Lipid oxidation termed oxidative rancidity is a major deteriorative reaction affecting the quality of macadamia nuts by causing off-flavours that develop as a consequence of autooxidation (Nahm, 2011; Walton et al., 2017). Autooxidation is a self-sustaining free radical mechanism that produces primary products such as hydroperoxides (Márquez-Ruiz et al., 2007; Phatanayindee et al., 2012). Hydroperoxides primarily accumulates as main oxidation product, subsequently breaking down to form low molecular weight oxygenated constituents such as alcohols, aldehydes, ketones and free fatty acids, eventually resulting in the development of rancidity (Kanner, 2007; Moigradean et al., 2012; Pannico, 2014). Furthermore, hydroperoxides can react with amino acids residues in the Maillard reaction, causing excessive browning (Walton, 2005). Therefore, it is essential to reduce high moisture content to a level at which lipid oxidation and mold development are prevented (Walton, 2005).

Drying is the primary preservation technique of macadamia nuts (Borompichaichartkul et al., 2009). The drying technique removes the available water to reduce microbial development, enzyme activity and chemical reactions thereby extending the shelf life of nuts (Wall and Gentry, 2007). The current practice by the macadamia industry is that nut-in-shell should be dried to approximately 3.5 % moisture content before shelling, which corresponds to a kernel moisture content of about 1.5 %. This is done to increase the kernel recovery during shelling and to prevent flavour degradation during storage (Wall and Gentry, 2007; Wang et al., 2014). Several drying techniques such as in-bin drying, hot air drying, fan-forced oven drying, microwave or radio frequency drying, vacuum drying, and freeze-drying have been implemented by the macadamia industry (Borompichaichartkul et al., 2009; Wang et al., 2014). Walton (2005) and Borompichaichartkul et al. (2013) reported that low initial drying temperature of less than 40 °C

is essential to prevent kernel internal browning due to reactions between proteins and reducing sugars enhanced by enzymatic activity at high moisture content and temperature. Furthermore, this will prevent excessive browning during roasting (Borjian Borojeni et al., 2016).

Roasting is the most frequent form of processing macadamia nuts in order to maximize overall palatability and storability of nuts (Nikzadeh and Sedaghat, 2008). It improves flavour, aroma, colour, texture and appearance of the nuts through non-enzymatic (Maillard browning) reactions, resulting from the reaction between sugars and amino acids (McDaniel et al., 2012; Schlörmann et al., 2015; Taş and Gökmen, 2017). Roasted kernels are more delicate, uniquely nutty and extensively consumed compared to raw kernels (Özdemir and Devres, 1999). Roasting also inactivates enzymes that accelerates nutrient deterioration, removes microorganisms and food contaminations and reduces degradative reactions such as lipid oxidation and rancidity which are the major limiting factors for the shelf-life (Birch et al., 2010; Marzocchi et al., 2017).

Industrial roasting is conducted at temperatures ranging from 100 to 180 °C for 5 to 60 minutes (Belviso et al., 2017; Taş and Gökmen, 2017). Furthermore, roasting can be accomplished by using different methods, such as commercial electrical ovens, hot air dryers or even by exploiting other techniques, such as infrared heating and the dielectric processes of radiofrequency and microwave (Belviso et al., 2017). Although roasting is a commercial standard in the macadamia industry, little is known about the effect of roasting on kernel nutritional quality and shelf life. Also, there is limited information on postharvest quality and storability of dried kernels compared to roasted ones. Therefore, the objective of the study was to evaluate and compare quality parameters of raw and roasted macadamia kernels during the accelerated postharvest storage of 70 days.

2. Materials and methods

2.1. Macadamia samples

Two hybrids of Australian-bred cultivars of *Macadamia integrifolia* namely, 'Beaumont' and 'A4' were harvested from the commercial orchards of Elliot Farm in Port Shepstone, South Coast of

KwaZulu-Natal, South Africa (latitude: 30°44′28″ S, longitude: 30°27′17″ E and altitude: 36 m). Harvesting of nuts was conducted at two different times, early season (May 2017) and late season (June 2017) based on industry practice. About 50 kg of nuts per cultivar were harvested per sampling date. At each date, nuts were dehusked within 24 h after harvest using a dehusker (01-one-lane, WMC sheet metal works, Tzaneen, South Africa), getting nut-in-shell (NIS) at the dehusking facility at Ukulinga Research Farm of the University of KwaZulu-Natal (UKZN).

2.2. Drying and cracking process

Drying temperatures were selected according to the nut industry practice to avoid quality deterioration (Belviso et al., 2017; Taş and Gökmen, 2017; Walton et al., 2017). Following a method described by Walton et al. (2013) with slight modifications, NIS were separately placed in a mechanical convection oven (RY-EB-550, Rongyao factory, Mainland, China) at Postharvest Research Laboratory of UKZN. Dehusking and drying was started on the same day of harvesting. After dehusking, nuts were weighed and dried for three consecutive days, starting with 35 °C on the first day, 38 °C on the second day and 50 °C on the third day. Dried nuts were checked for moisture content and were only removed from the oven when moisture content has reached 1.5 %. The moisture content of nuts was measured based on initial and final (dry) weight. Mass changes in nuts were used to calculate moisture content on a dry basis (d.b.) (Wang et al., 2014). Moisture content was determined according to Khir et al. (2011) as follows:

$$MC_{db} = \frac{W_i \text{-} W_d}{W_d} \times 100 \qquad (1)$$

where MC_{db} is moisture content on a dry mass basis, W_i and W_d are the initial and the dry sample weights, respectively. Furthermore, macadamia nuts were mechanically cracked into wholes, halves and pieces using a commercial mechanical macadamia nutcracker (TZ-150 macadamia nut cracker, Alibaba Group Houlding (PTY) LTD , Hangzhou, China). The shell and kernel were separated manually or by hand and the percentage of kernel recovery was calculated and expressed as a percentage weight of the nut that is kernel at 1.5 % moisture content, the rest being shell (Eq.

79

2). Only full kernels were used for the experiment. Nuts that are dried to 1.5 % kernel moisture content for the purpose of dehusking and cracking are referred to as raw kernels (du Preez, 2015).

$$KR = \frac{NIS - Shell}{NIS} \times 100$$

2

where KR is kernel recovery and NIS is nut-in-shell.

2.3. Roasting process

Dried kernels were roasted using a method described by Nikzadeh and Sedaghat (2008) and Birch et al. (2010), with slight modifications. Kernels were roasted at 125 °C for 15 min using a convection oven (RY-EB-550, Rongyao factory, Mainland, China). This roasting temperature was selected based on the nut industry practice to avoid quality deterioration (Belviso et al., 2017; Taş and Gökmen, 2017; Tonfack Djikeng et al., 2018).

2.4. Storage conditions

Raw and roasted kernels of 'A4' and 'Beaumont' cultivars were stored in a labcon growth chamber (Labotec, Model FSIM16, Labotec (PTY) LTD, Durban, South Africa) at 20 °C and 60 % RH for 70 d for the evaluation of sensory and chemical changes during the accelerated storage.

2.5. Experimental treatments

Raw and roasted kernels of 'A4' and 'Beaumont' cultivars were used as two distinct treatments. Only full kernels with no visible defects were used for sampling. A randomly sampled set of 15 replicates per treatment per cultivar, each weighing 2 kg were packed in commercial brown paper bags for postharvest storage trials. Kernels were stored for the total of 70 d and were sampled before storage and at 10 d interval until the end of storage. Kernels were evaluated for sensory quality: texture, aroma, rancid taste (bitterness), appearance and marketability, according to a

visual standard scale or hedonic scale and chemical quality: polyphenol oxidase, peroxide value, flavonoids, phenols and antioxidants activity (DPPH and ABTS).

2.6. Quantification of polyphenol oxidase activity

The enzymatic activity of polyphenol oxidase (PPO; EC 1.14.18.1) activity was determined according to Tesfay and Magwaza (2017) using an assay formerly described by Van Lelyveld et al. (1984). A sample of 100 mL of extracted protein was added to a mixture of 1.45 mL of 20 mM 4-methyl-catechol and 1.45 mL of 10 mM (pH 5.0) acetate buffer. Total activity of PPO was read in a spectrophotometer at 420 nm and expressed as U kg^{-1} DW.

2.7. Quantification of peroxide value

Kernels were ground into fine powder using pestle and mortar. Kernel oil content was measured from ground sample material and quantified using a method described by Meyer and Terry (2008), with slight modifications. Hexane (9.0 mL) was added into a test tube containing 3 g of ground kernel sample and the test tube was placed into an ultrasonic bath (Labotec, Model No. 132, Labotec (PTY) LTD, Johannesburg, South Africa) for 10 min. The supernatant was filtered under vacuum and another 6 mL hexane was added to the residue in the test tube. This was left for 5 min before the test tube was emptied into the Buchner funnel. After filtration, 15 mL hexane was dried off the supernatant using a GenVac® concentrator (SPScientific, Genevac LTD., Suffolk, UK) under vacuum leaving the oil content of the sample. The residual oil was weighed and presented on dry weight basis.

Peroxide value (PV) was determined according to Walton et al. (2017), with minor modifications. A 1 g of oil sample was dissolved in 20 mL of acetic acid/chloroform (3:2 v/v) followed by adding 1 mL of saturated potassium iodide solution by an additional burette. The reaction took place and iodine was formed. A 50 mL of deionized water was added. Iodine was titrated with $Na_2S_2O_3$ using a burette. Peroxide value (expressed as milliequivalents of peroxide per kilogram of sample) was calculated according to the following formula:

$$PV \text{ (meq per kg)} = \frac{(S\text{-}B) \times N \times 1000}{\text{Sample wt (g)} \times 1000} \qquad 3$$

where S = sample titration (µL); B = Blank titration; and N = normality of $Na_2S_2O_3$.

2.8. Quantification of free and membrane bound phenols

Phenols were determined based on Hertog et al. (1992), with slight alterations. Freeze dried kernel sample (1 g each) was mixed with 10 mL 99.8 % (v/v) methanol and vortexed for 30 s. Thereafter, the mixture was shaken overnight at room temperature to extract the free phenols. Afterward, the mixture was centrifuged, and supernatant was filtered through Whatman® no. 1 filter paper and the sample was again rinsed with 10 mL of solvent until colour was no longer released. Then, the acid hydrolysis was also used for the remaining kernel residue to efficiently release cell wall-bound phenols. Briefly, a 10 mL portion of acidified (2 M hydrochloric acid) 60 % aqueous methanol was added to each sample and placed in a hot water bath at 90 °C for 90 min. Glass tubes were allowed to cool, and supernatants were filtered through a 0.45 µm filter. The total phenolic content was determined spectrophotometrically using Folin-Ciocalteu reagent (5 mL of distilled water + 1 mL of extract + 1 mL Folin-Ciocalteu reagent + 10 mL of 7 % Na_2CO_3 + 8 mL of distilled water and left at room temperature for overnight) at 750 nm using gallic acid monohydrate as a standard and the total phenolic content was expressed as mg Gallic Acid Equivalents (GAE) kg^{-1} DW.

2.9. Quantification of total flavonoids concentration

The total flavonoids concentration was determined using aluminium chloride ($AlCl_3$) (kernel extract prepared for phenolic concentration determination) following a method described by Eghdami and Sadeghi (2010), with slight modifications, using quercetin as a standard. The kernel extract (0.10 mL) was added into a glass tube, followed by adding 5 % $NaNO_2$ (0.03 mL) and the reaction mixture was allowed to stand at room temperature for 5 min. A 0.03 mL of 10 % $AlCl_3$ was added and incubated for 6 min, after that 0.2 mL of 1 mM NaOH was added to the solution and the reaction mixture was diluted to 1 mL with distilled water. The absorbance of the reaction

mixture was read at 510 nm, against methanol used as blank. The results were expressed as mg quercetin kg^{-1} DW.

2.10. Quantification of total antioxidants activity

2.10.1. 2,2'-diphenyl-1-picrylhydrazyl (DPPH) assay

The 2,2'-diphenyl-1-picrylhydrazyl (DPPH) free radical scavenging activity was determined according to Ahmed et al. (2015), with slight modifications. The stock solution of the radical was prepared by dissolving 1.94 mg DPPH in 50 mL of methanol and was kept in a refrigerator at -20 °C until further use. The working solution of the radical was prepared by diluting the DPPH stock solution with methanol to obtain an absorbance of about 0.98 (±0.02) at 517 nm. A 20 µL of garlic acid or sample extract were measured into polystyrene 4.5 mL cuvette. A 800 µL of absolute methanol was added, followed by 1 mL of 0.1 mM DPPH solution which was added in the dark and covered with aluminium foil and was allowed to stand at room temperature for 60 min. The absorbance was measured at 517 nm against blank (absolute methanol) under dim light and the results were expressed as mg DPPH GAE kg^{-1} DW.

2.10.2. 2,2'-azinobis-3-ethylbenzothiazoline-6-sulfonic acid (ABTS) assay

The 2,2'-azinobis-3-ethylbenzothiazoline-6-sulfonic acid (ABTS) was determined based on Tesfay et al. (2011), with slight alterations. 2,2'-azinobis-3-ethylbenzothiazoline-6-sulfonic acid was prepared as a 7 mM solution in water or ethanol, for measuring hydrophilic and lipophilic antioxidant fractions, respectively. The ABTS radical cation (ABTS$^{·+}$) was produced by reacting the 7 mM ABTS solution with 2.45 mM ammonium persulfate and allowing the mixture to stand in the dark at room temperature for 3 to 6 h. Thereafter, 1.0 mL activated ABTS solution (A$_{734}$ nm $= 0.700 \pm 0.5$) was added to 10 µL sample solution from extracts of freeze-dried material in acetate buffer (pH 4.0). The decrease in absorbance at 734 nm was recorded after 6 min and the results were expressed as mg ABTS GAE kg^{-1} DW.

2.11. Sensory evaluation

A randomized set of macadamia kernels were examined immediately after drying and roasting and during the accelerated storage of 70 d at 10 d intervals at University of KwaZulu-Natal, Department of Horticulture laboratory. The panelists (5 males and 5 females) ranging from the age of 21 to 46 were requested to assess the quality of 'A4' and 'Beaumont' kernels in terms of texture, aroma, rancid taste (bitterness), overall appearance and marketability. The quality of kernels was rated using the hedonic scale (Sanful, 2009; Wang, 2015). The texture of kernels was assessed on a 1 to 5 scale where 1: very smooth, 2: smooth, 3: neutral, 4: crispy and 5: very crispy. Rancid taste was also evaluated on a scale of 1 to 5 where 1: none, 2: slight, 3: moderate, 4: moderately severe and 5 severe. Aroma, overall appearance and marketability were also assessed on a 1 to 5 scale where 1: poor, 2: fair, 3: good, 4: very good and 5: excellent. The average of these indices was used as an estimation of kernel storability and marketability (Agüero et al., 2011).

2.12. Statistical analysis

The collected data was subjected to the analysis of variance (ANOVA) using GenStat statistical software (GenStat®, 18.1 edition, VSN International, UK) 18.1. Least significant difference values (LSD; $p < 0.001$) were calculated for mean separation. In order to gain a better insight of how measured phytochemical and sensory properties correlate with each other and how these properties change during roasting and storage, data was subjected to principal component of analysis (PCA). PCA was performed with Unscrambler 10.3 software (CAMO Software, Oslo, Norway).

3. Results and discussion

3.1. Polyphenol oxidase

Roasting results to inactivation of microorganisms and denaturation of several enzymes such as peroxidase and polyphenol oxidase (PPO), which are responsible for the development of off-flavours and darkening reactions through the development of browning pigments (Borjian

Borojeni et al., 2016; Rabelo et al., 2016). Therefore, PPO activity is inactivated during roasting (Walton et al., 2013) hence Figure 1 shows the PPO activity of raw kernels. Polyphenol oxidase activity for both 'A4' and 'Beaumont' kernels significantly increased ($p < 0.001$) throughout the storage period (Fig. 1). At day 60 and 70 of accelerated storage, kernels of 'A4' and 'Beaumont' had significantly ($p < 0.001$) higher PPO activity which could be attributed to the oxidation of several phenols such as procynidins and monomeric catachins to o-quinones which can undergo non-enzymatic secondary reactions to form dark brown secondary products such as polymers (Taranto et al., 2017). The increase of PPO activity in raw kernels could also be attributed to the reaction between proteins and reducing sugars enhanced by enzymatic and non-enzymatic reactions forming brown pigment as their end product (Bittner, 2006; Srichamnong and Srzednicki, 2015). Furthermore, browning of kernels may be evident as surface discolouration, or hidden internally as 'concealed damage' of nuts (Wakeling et al., 2003). Browning may cause the formation of off-odours and off-flavours (Le Lagadec, 2009), thereby affecting the nutritional properties and storability of nuts (Camargo et al., 2016).

Furthermore, the PPO activity of 'A4' was two-fold higher than that of 'Beaumont', ranging from 0.105-5.003 U kg^{-1} during storage. These findings suggest that 'A4' is more sensitive to internal browning and the development of off-odours and off-flavours which could result to limited shelf-life of kernels (Camargo et al., 2016; Taranto et al., 2017).
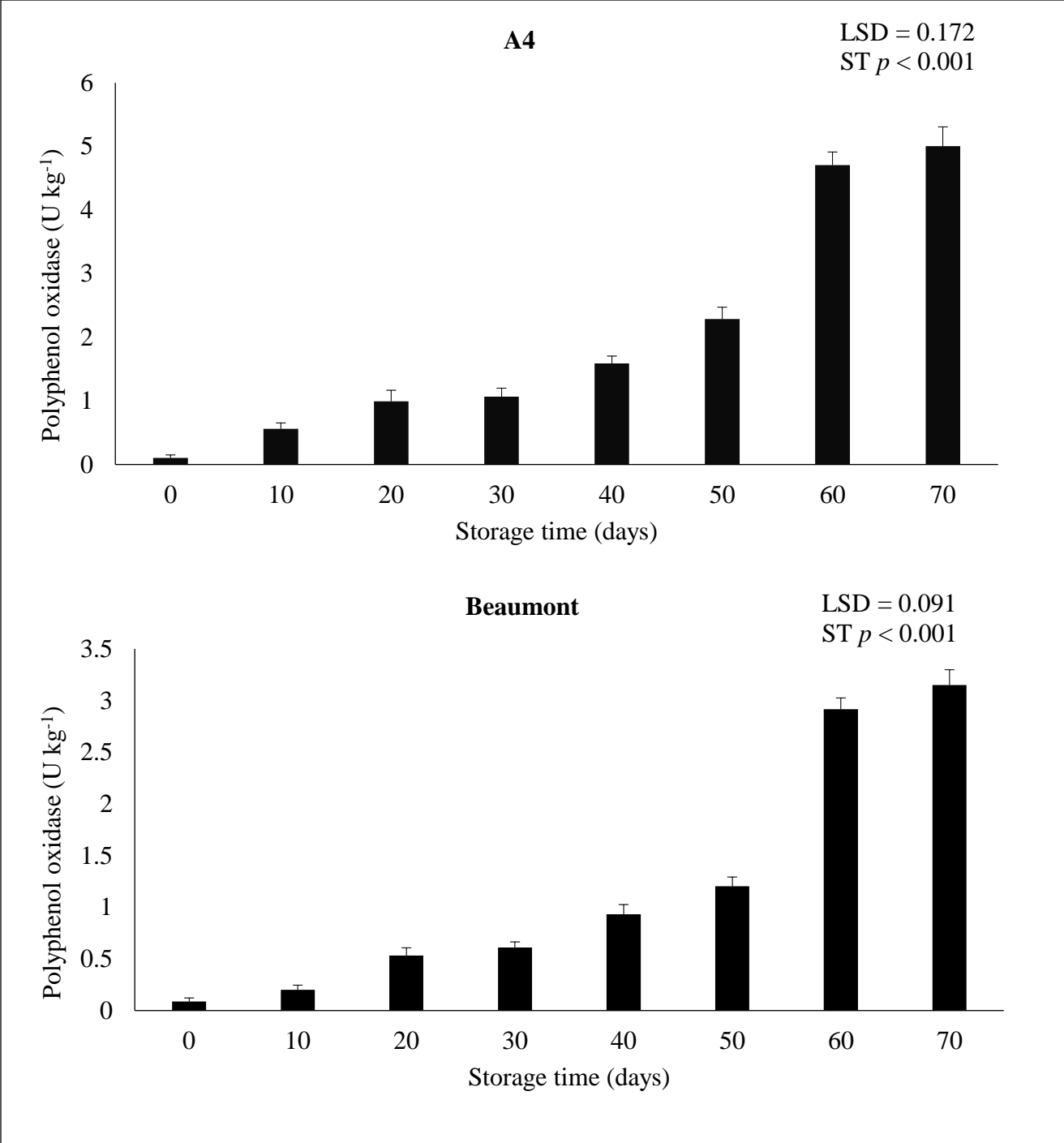
Fig. 1: Polyphenol oxidase (PPO) activity of raw kernels of 'A4' and 'Beaumont' during accelerated postharvest storage. Vertical bars represent standard errors of differences of means. LSD, least significant difference; ST, storage time.

3.2. Peroxide value

Peroxide value (PV) is the most commonly used parameter and a good technique for determining the onset of oxidation as it is a measure of the hydroperoxides formed in the initial stages of oxidation (Borompichaichartkul et al., 2013). The deterioration of macadamia nuts during processing and storage can be rapidly characterized by the changes in PV (Gölge and Ova, 2008). A high-quality macadamia product is characterized by low PV of less than 1 meq O_2 kg^{-1} which is considered acceptable for freshly refined fat and is classified at low oxidation state; that between 5 and 10 meq O_2 kg^{-1} at moderate oxidation and above 10 meq O_2 kg^{-1} is classified at high oxidation state (Walton, 2005; Borompichaichartkul et al., 2013). Kaijser et al. (2000) and Domı et al. (2007) reported that the development of an inacceptable rancid taste is also a feature of nuts that have been stored for too long. The significant increase of PV during storage of macadamia nuts was also observed in the current study. The PV of raw and roasted kernels of 'A4' and 'Beaumont' cultivars significantly ($p < 0.001$) increased during the accelerated storage of 70 d (Fig. 2). These results are in agreement with those previously reported by Baker (2002), Gölge and Ova (2008) and Belviso et al. (2017), confirming that peroxide value tend to increase with increasing storage as an indication of quality deterioration.

In Fig. 2, it can be observed that processing significantly ($p < 0.001$) affected PV of kernels during the storage. Raw kernels of 'A4' and 'Beaumont' cultivars had the highest amount of PV (19.417 meq O_2 kg^{-1} and 8.199 meq O_2 kg^{-1}), respectively at the end of the storage period. The increase of PV during the storage period could be due to the high PPO activity (Fig. 1) observed in these cultivars which might have promoted the formation of rancidity. Polyphenol oxidase is hydroxylated to o-diphenols and o-quinones. The quinones condense and react nonenzymatically to accelerate reaction of proteins with reducing sugars to produce dark brown, black or red pigments as their end product which are associated with off-flavours (Bittner, 2006; Srichamnong and Srzednicki, 2015). Furthermore, kernels with PV above 10 meq O_2 kg^{-1} are not acceptable to the macadamia industry (Borompichaichartkul et al., 2013). Therefore, our findings demonstrated that raw kernels are more susceptible to the development of off-flavours during storage.

Furthermore, Fig. 2 shows that roasting significantly ($p < 0.001$) preserved the quality of kernels throughout the storage period as indicated by PV lower than 10 meq O_2 kg^{-1} for both cultivars. 'Beaumont' had the PV of 5.139 meq O_2 kg^{-1} on day 70, indicating that kernels were fresh throughout the storage period (Moigradean et al., 2012). This could be attributed to the fact that roasting further reduces moisture content needed for microbial growth, enzyme activity and chemical reactions such as hydrolysis of lipids into free fatty acids, often leading to the development of rancidity therefore, extending the storability of kernels (Borompichaichartkul et al., 2013; Das et al., 2014; Pannico et al., 2015).
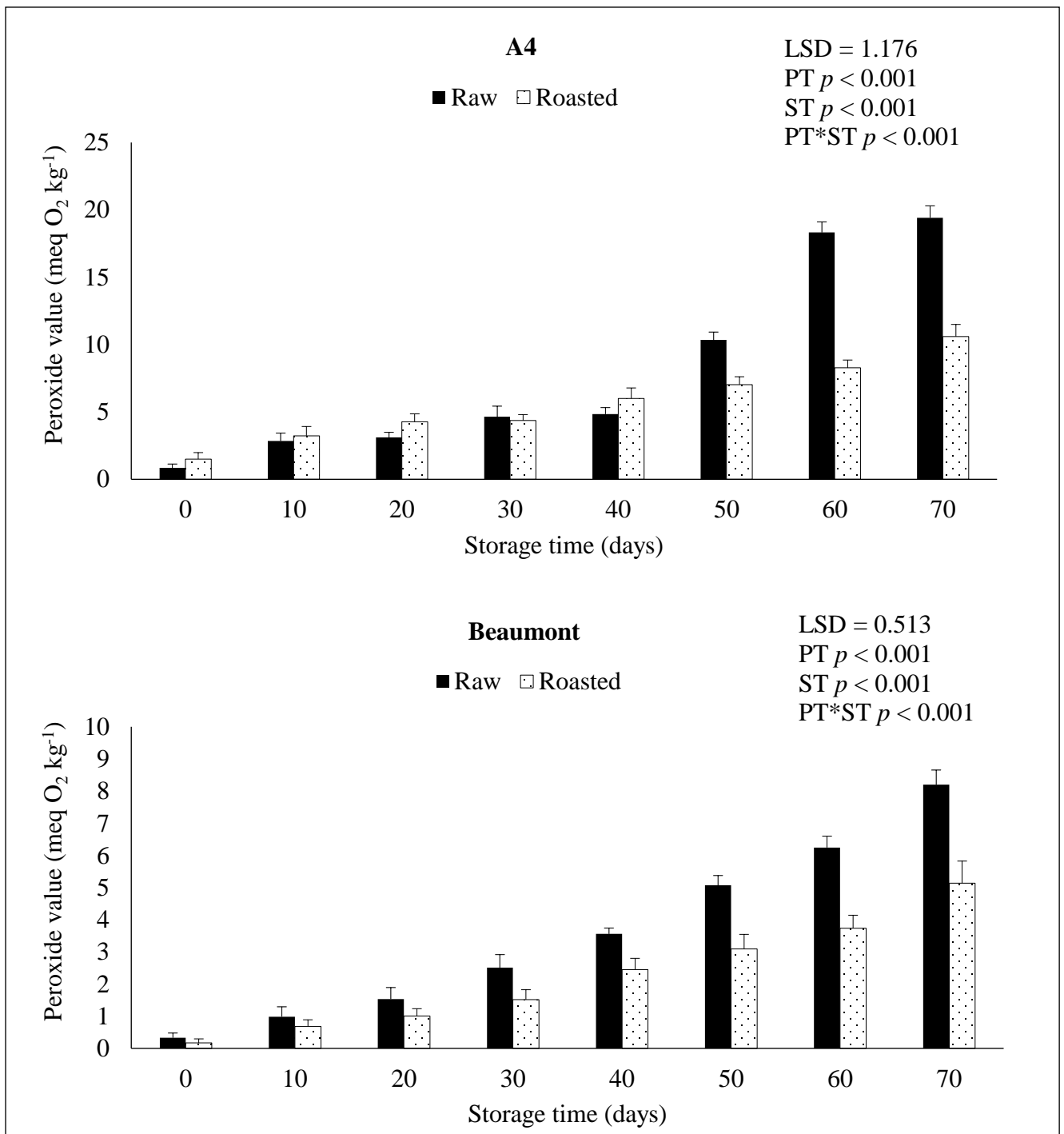
Fig. 2: Peroxide value of raw and roasted kernels of 'A4' and 'Beaumont' during the accelerated postharvest storage. Vertical bars represent standard errors of differences of means. LSD, least significant difference; PT, processing treatments; ST, storage time; PT*ST, processing treatments and storage time.

3.3. Flavonoids

Both raw and roasted kernels showed a significant ($p < 0.001$) depletion of flavonoids during the accelerated storage period (Fig. 3). Raw kernels of 'A4' and 'Beaumont' had significant ($p < 0.001$) lower concentration of flavonoids (0.158 to 0.036 mg quercetin kg^{-1} and 0.182 to 0.039 mg quercetin kg^{-1}, respectively) during the storage. This could be due to high levels of enzymatic browning (PPO) and rancidity (PV) observed in raw kernels (Fig. 1 and 2), which could promote the progressive loss of quality (Chutichudet and Chutichudet, 2011; Pannico, 2014). Pannico et al. (2015) reported that during storage, nuts can be exposed to microbial contamination and undergo changes in their chemical composition as a consequence of rancidity. Also, a significant fluctuation of flavonoids was observed in Fig. 3 where raw kernels of 'A4' cultivar showed a significant increase of flavonoids on day 40 and 50 and a gradual decrease on day 60 and 70. Our findings are similar to Šamec and Piljac-Žegarac (2015) who reported similar trend of fluctuating flavonoids in several crops and further stated that the decrease in flavonoids could be due to oxidation, hydrolysis or isomerization of polyphenolic compounds that takes place during long-term storage. Bakowska-Barczak and Kolodziejczyk (2008) reported that the storability of flavonoids greatly depends on cultivar which could be the reason for the significant ($p < 0.001$) fluctuation of flavonoids observed in raw kernels of only 'A4' cultivar during storage. Bakowska-Barczak and Kolodziejczyk (2011) reported that quercetin pentosides are the most storage-sensitive and unstable flavonoids which could be the cause of fluctuation of quercetin flavonoids during prolonged storage as a consequence of quality deterioration such as the increase of polyphenol oxidase enzyme during storage (Šamec and Piljac-Žegarac, 2011). The flavonoids concentration of roasted kernels of 'A4' (0.161 to 0.030 mg quercetin kg^{-1}) and 'Beaumont' (0.330 to 0.063 mg quercetin kg^{-1}) was slightly higher than that of raw kernels during the storage period of 70 days. These findings are in agreement with McDaniel et al. (2012) who reported that during roasting some antioxidants are formed through chemical reactions such as Maillard browning. Also, roasting inactivates degradative reactions such as lipid oxidation or rancidity which are responsible for quality loss during storage (Marzocchi et al., 2017).
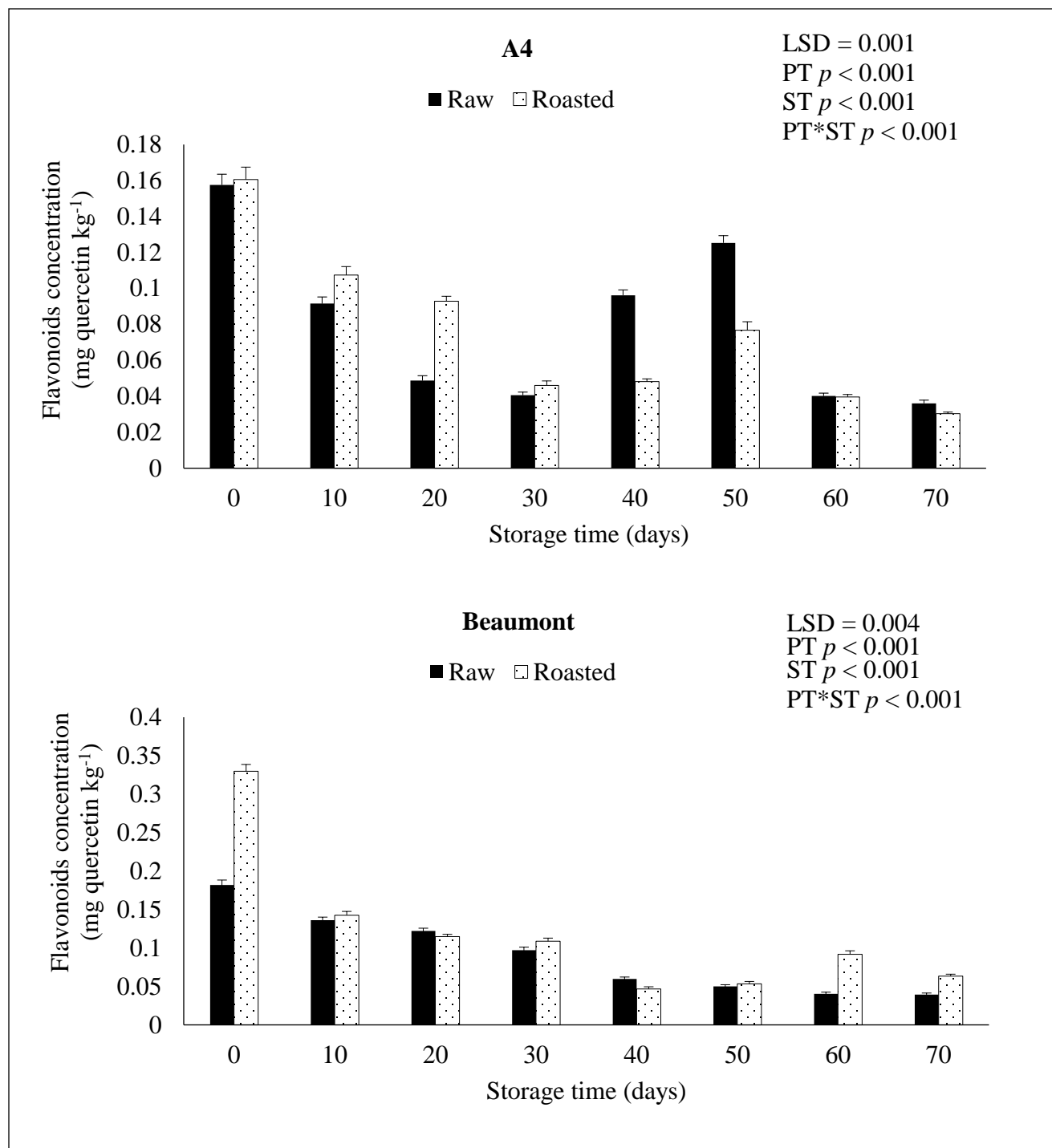
Fig. 3: Flavonoids content of raw and roasted kernels of 'A4' and 'Beaumont' during accelerated postharvest storage. Vertical bars represent standard errors of differences of means. LSD, least significant difference; PT, processing treatments; ST, storage time; PT*ST, processing treatments and storage time.

3.4. Phenols

The changes of phenolic concentration of raw and roasted kernels of 'A4' and 'Beaumont' cultivars during the accelerated storage are shown in Fig. 4. Phenolic concentration of both raw and roasted kernels significantly increased ($p < 0.001$) with increasing storage. Shiri et al. (2011) reported that the phenolic compounds are generally synthesized by the shikimate pathway in which phenylalanine ammonialyase (PAL) is the key enzyme. The physical damage of kernels during drying and roasting may increase PAL activity, which leads to an increase in phenolic compounds during processing and storage (Fan, 2005). Roasting significantly ($p < 0.001$) increased phenolic concentration of 'A4' (0.098 to 0.508 mg GAE kg^{-1}) and 'Beaumont' (0.132 to 0.521 mg GAE kg^{-1}) throughout the storage period in comparison to raw kernels (0.088 to 0.479 mg GAE kg^{-1} and 0.096 to 0.310 mg GAE kg^{-1}, respectively). Other authors have observed the similar behavior in other nuts and have linked the increase in extractable phenolic compounds after roasting with the formation of Maillard products (McDaniel et al., 2012; Srichamnong and Srzednicki, 2015). Also, roasting may cause complex physical and chemical reactions on phenolics, including leaching of water soluble phenolics, freeing phenolics from bond forms, degradation of polyphenols, breakdown and the transformation of phenolics, such as the formation of complex products from phenolics and proteins, and the formation of Maillard reaction products having antioxidative activity (Belviso et al., 2017).
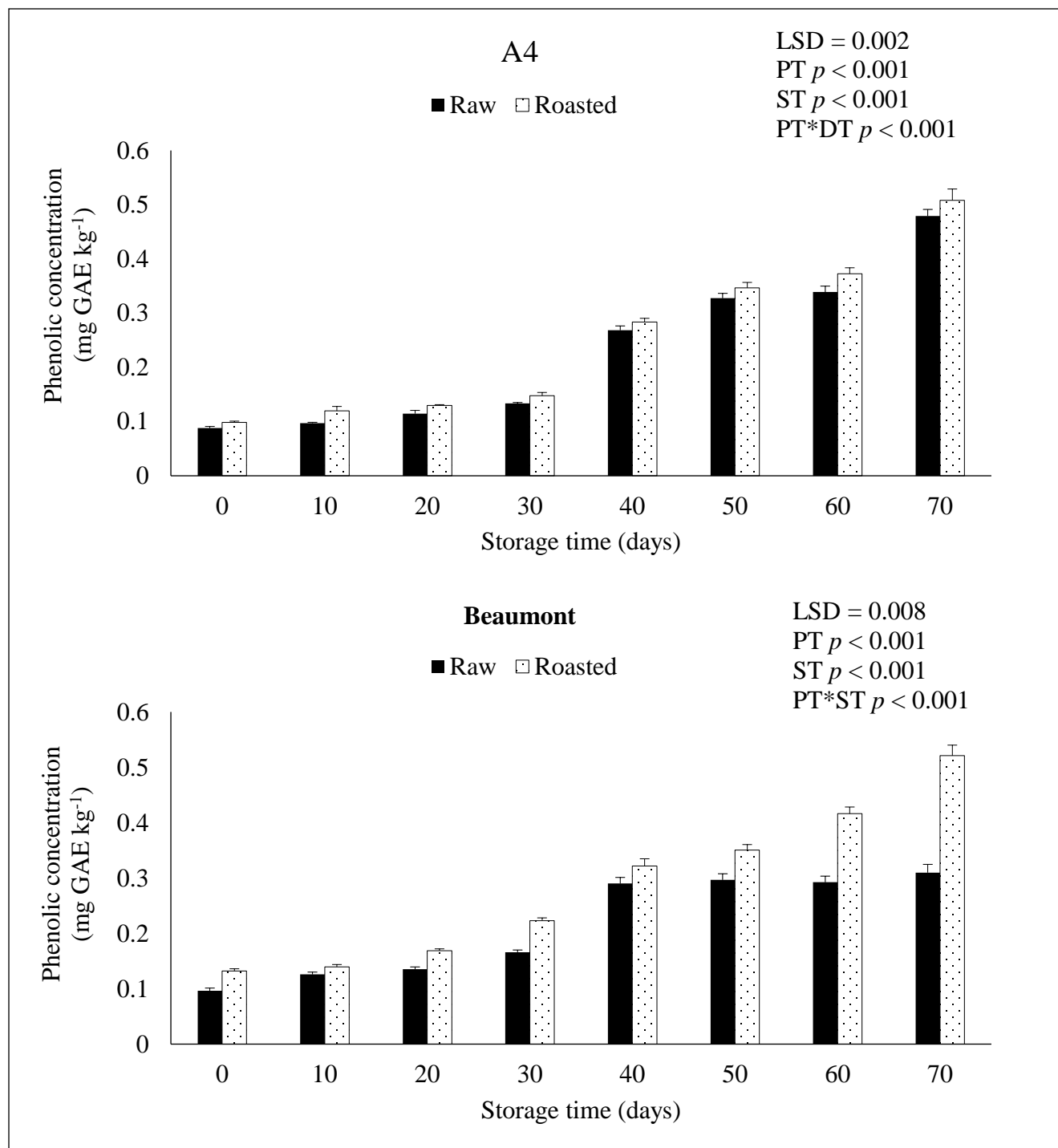
Fig. 4**:** Phenolic content of raw and roasted kernels during accelerated postharvest storage. Vertical bars represent standard errors of differences of means. LSD, least significant difference; PT, processing treatments; ST, storage time; PT*ST, processing treatments and storage time.

3.5. Antioxidant activity [DPPH (2,2'-diphenyl-1-picrylhydrazyl) and ABTS (2,2'-azinobis-3-ethylbenzothiazoline-6-sulfonic acid) assay]

Antioxidant activity (DPPH and ABTS) of both raw and roasted kernels of 'A4' and 'Beaumont' significantly increased ($p < 0.001$) throughout the storage period which is similar to the results observed for phenols (Fig. 4). These results are in agreement with Taş and Gökmen (2015) who reported similar trend of accumulation of antioxidant activity in hazelnuts. Roasting significantly ($p < 0.001$) enhanced antioxidant activity during storage compared to raw kernels which had low concentration of antioxidants (Fig. 5 and 6). The enhancement of antioxidant activities could be attributed to release some bound antioxidant phenolic compounds acting as free radical scavengers from the cell matrix and increase phenolic extractability upon roasting (Kumar and Pandey, 2013). Our results are also in agreement with Lin et al. (2016) who suggested that antioxidant activity of almond kernels increased upon roasting due to Maillard reaction products, resulting from the reaction between sugars and amino acids (McDaniel et al., 2012; Schlörmann et al., 2015; Taş and Gökmen, 2017).

Fig. 5: Antioxidant activity (DPPH) of raw and roasted kernels of 'A4' and 'Beaumont' during accelerated the postharvest storage. Vertical bars represent standard errors of differences of means. LSD, least significant difference; PT, processing treatments; ST, storage time; PT*ST, processing treatments and storage time.
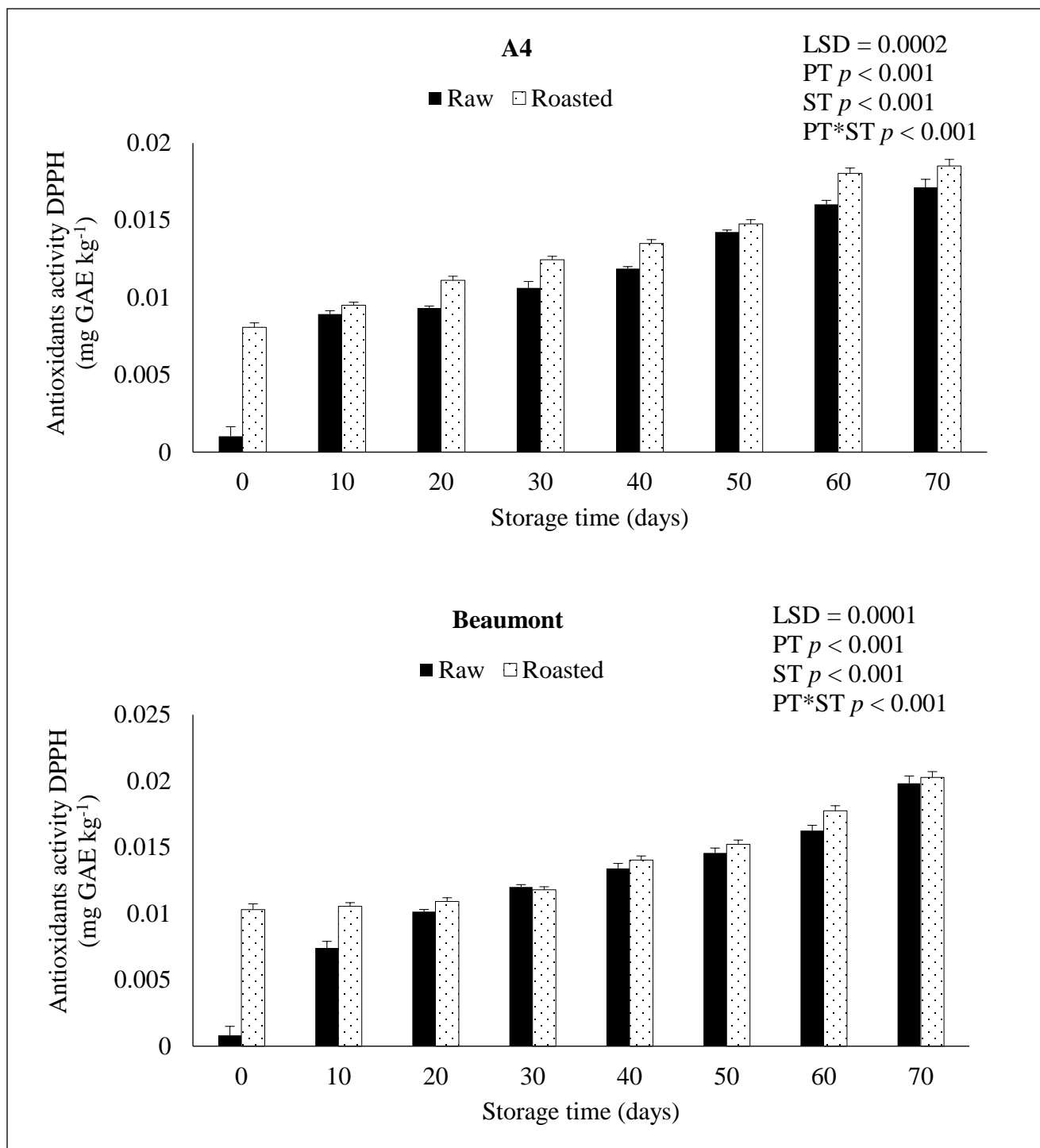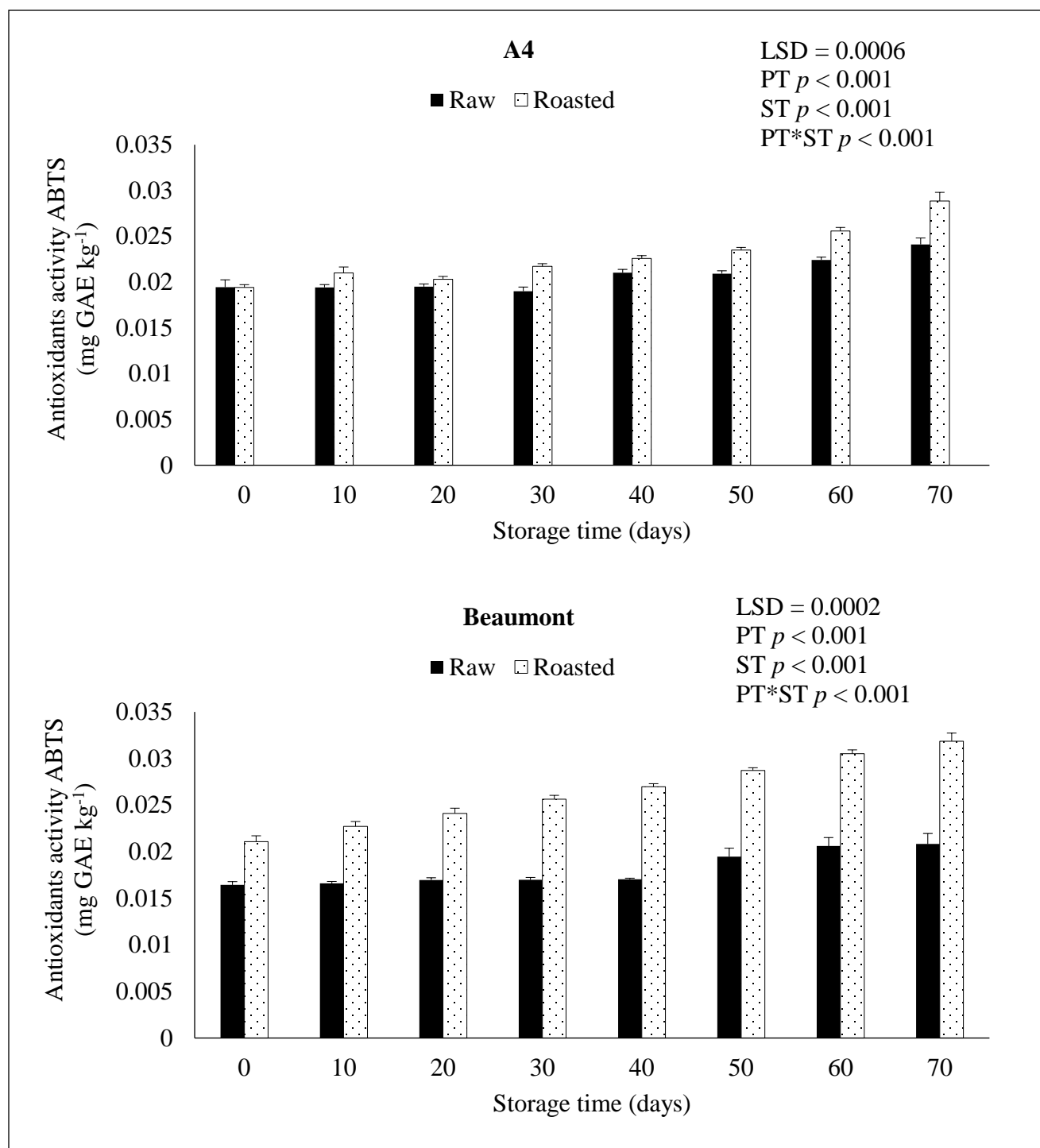
Fig. 6: Antioxidant activity (ABTS) of raw and roasted kernels of 'A4' and 'Beaumont' during the accelerated postharvest storage. Vertical bars represent standard errors of differences of means. LSD, least significant difference; PT, processing treatments; ST, storage time; PT*ST, processing treatments and storage time.

3.6. Sensory evaluation

Sensory evaluation is very important in the food industry, providing insight to the food development and market strategy (Wang, 2015). It helps producers understand the consumers' attitude and preference towards their products (Lawless and Heymann, 2010). The following figures demonstrate the average scores on comparative sensory evaluation of raw and roasted kernels of macadamia.

3.6.1. Kernel texture

According to the panelists, raw kernels of 'A4' and 'Beaumont' had a smooth texture throughout the accelerated storage (du Preez, 2015; Navarro and Rodrigues, 2016). Roasted kernels had a crispy texture throughout the storage period (Fig. 7). The moisture loss and changes in protein content are considered as the main factors in texture development of roasted kernels, leading to increased crispiness (Shi, 2015). Varela et al. (2008) and Soleimanieh et al. (2015) reported that the crisp texture of roasted kernels makes them more delicious hence more preferred by consumers.

Fig. 7: Texture of raw and roasted kernels of 'A4' and 'Beaumont' during the accelerated postharvest storage. Vertical bars represent standard errors of differences of means. LSD, least significant difference; PT, processing treatments; ST, storage time; PT*ST, processing treatments and storage time.

3.6.2. Aroma

In Fig. 8, it can be observed that aroma was significantly ($p < 0.001$) lost with increasing storage time. Raw kernels of 'A4' and 'Beaumont' showed poor and fair aroma, respectively, at the end of storage. This could be attributed to lipid oxidation products such as aldehydes which are responsible for the loss of aroma and development of off-odours and off-flavours (Shi, 2015; Wang, 2015). Also, raw kernels had high levels of PV (Fig. 2) which might have contributed to the loss of aroma (Walton et al., 2017). However, it can be observed from Fig. 8 that roasting significantly ($p < 0.001$) improved the aroma of kernels. Panelists rated the aroma of roasted kernels of 'A4' and 'Beaumont' as good and very good, respectively, at the end of storage. This could be attributed to the aromatic compounds such as benzaldehyde, methylphenol, alcohol and alkylbenzenes generated during roasting (Xiao et al., 2014). Also, Purlis (2010) reported that aroma enhancement during roasting could be due to Maillard browning reaction and caramelization.
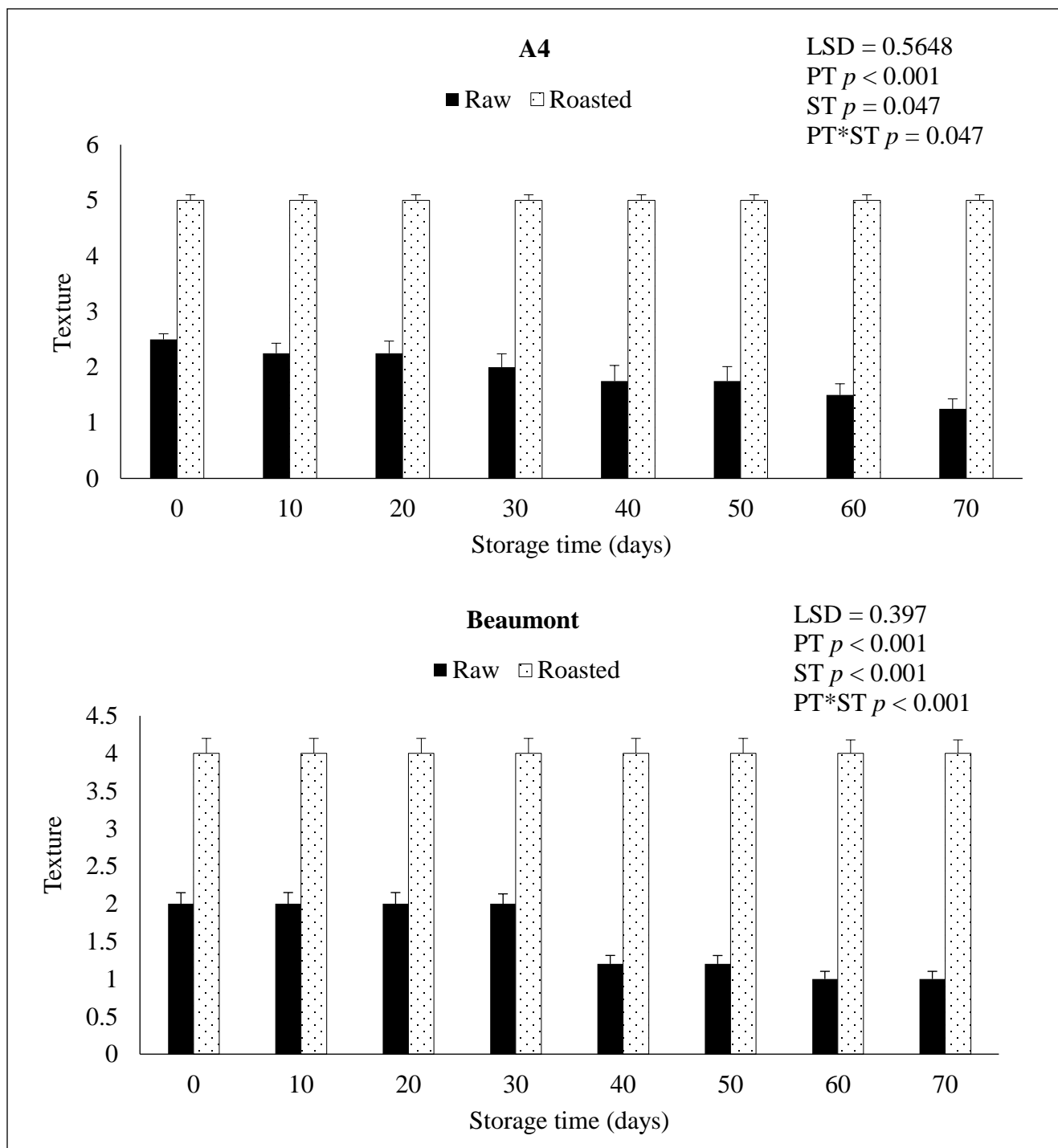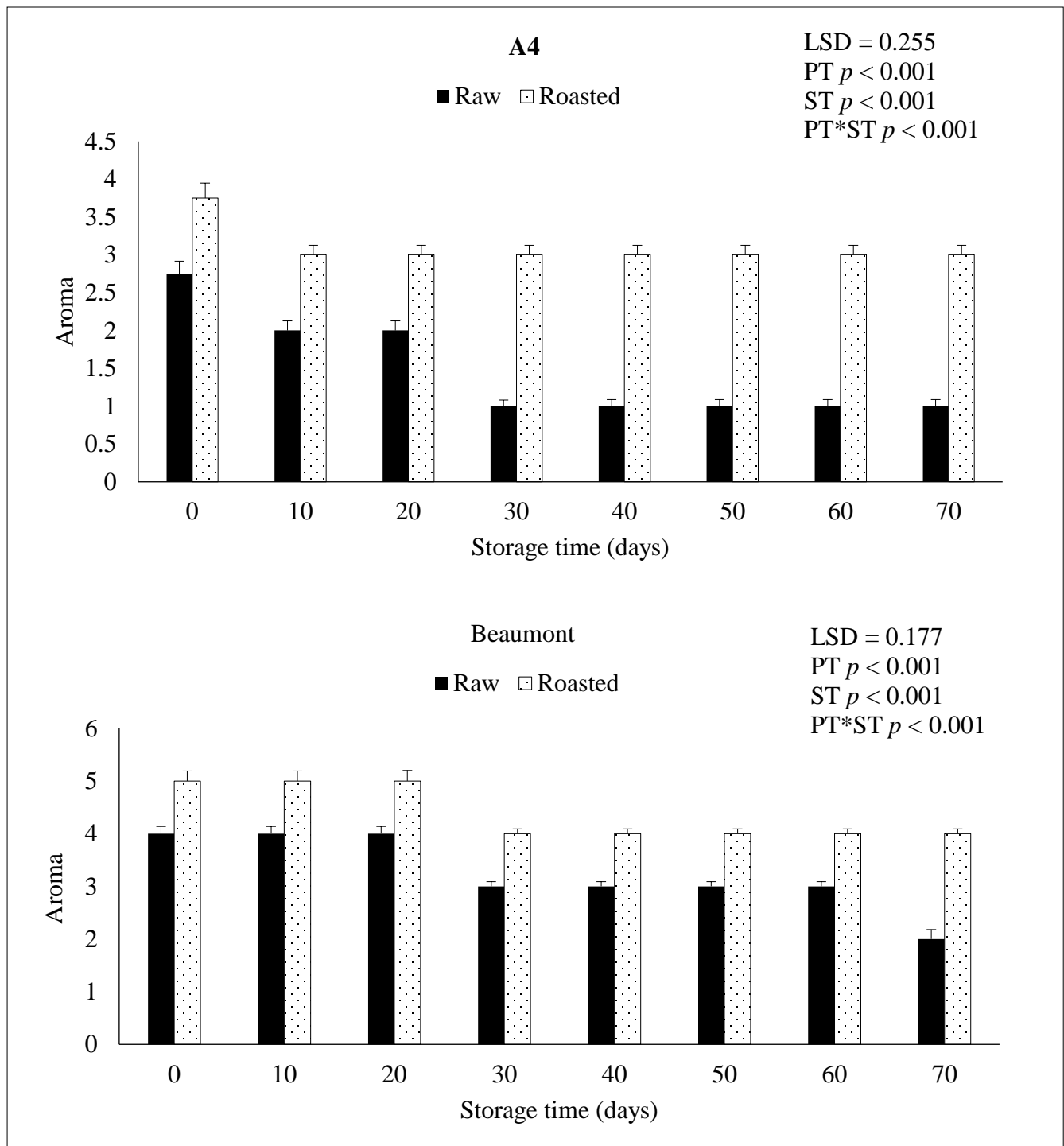
Fig. 8: Aroma of raw and roasted kernels of 'A4' and 'Beaumont' during the accelerated postharvest storage of. Vertical bars represent standard errors of differences of means. LSD, least significant difference; PT, processing treatments; ST, storage time; PT*ST, processing treatments and storage time.

3.6.3. Rancid taste (bitterness)

According to the panelists, rancidity significantly ($p < 0.001$) increased with storage time. Raw kernels of 'A4' and 'Beaumont' had a rancid taste towards the end of the storage period (Fig 9). This could be attributed to lipid oxidation which causes the reaction of fats and oils with molecular oxygen resulting in the development of off-flavours called rancidity (Márquez-Ruiz et al., 2007). Furthermore, during the oxidation process hydroperoxides which are primary non-volatile oxidation products decompose to various volatile aromatic secondary products such as alcohols, aldehydes and ketones which are responsible for off-flavours (Phatanayindee et al., 2012; Wang, 2015). However, roasting significantly ($p < 0.001$) improved flavour quality of kernels. The 'A4' cultivar showed slight rancid taste at the end of storage and the 'Beaumont' cultivar had no rancid taste throughout the storage period. This could be attributed to Maillard browning reaction resulting from the reaction between sugars and amino acids which enhances flavour of nuts (McDaniel et al., 2012; Schlörmann et al., 2015; Taş and Gökmen, 2017). Furthermore, Fig. 2 shows that roasted kernels had very low peroxide value which is a measure of hydroperoxides formed in the initial stages of oxidation (Borompichaichartkul et al., 2013; Das et al., 2014). These results indicate that roasted kernels did not develop unacceptable rancid taste during the storage period as suggested by low peroxide value which is similar to the observation of the panelists which is shown in Fig. 9.
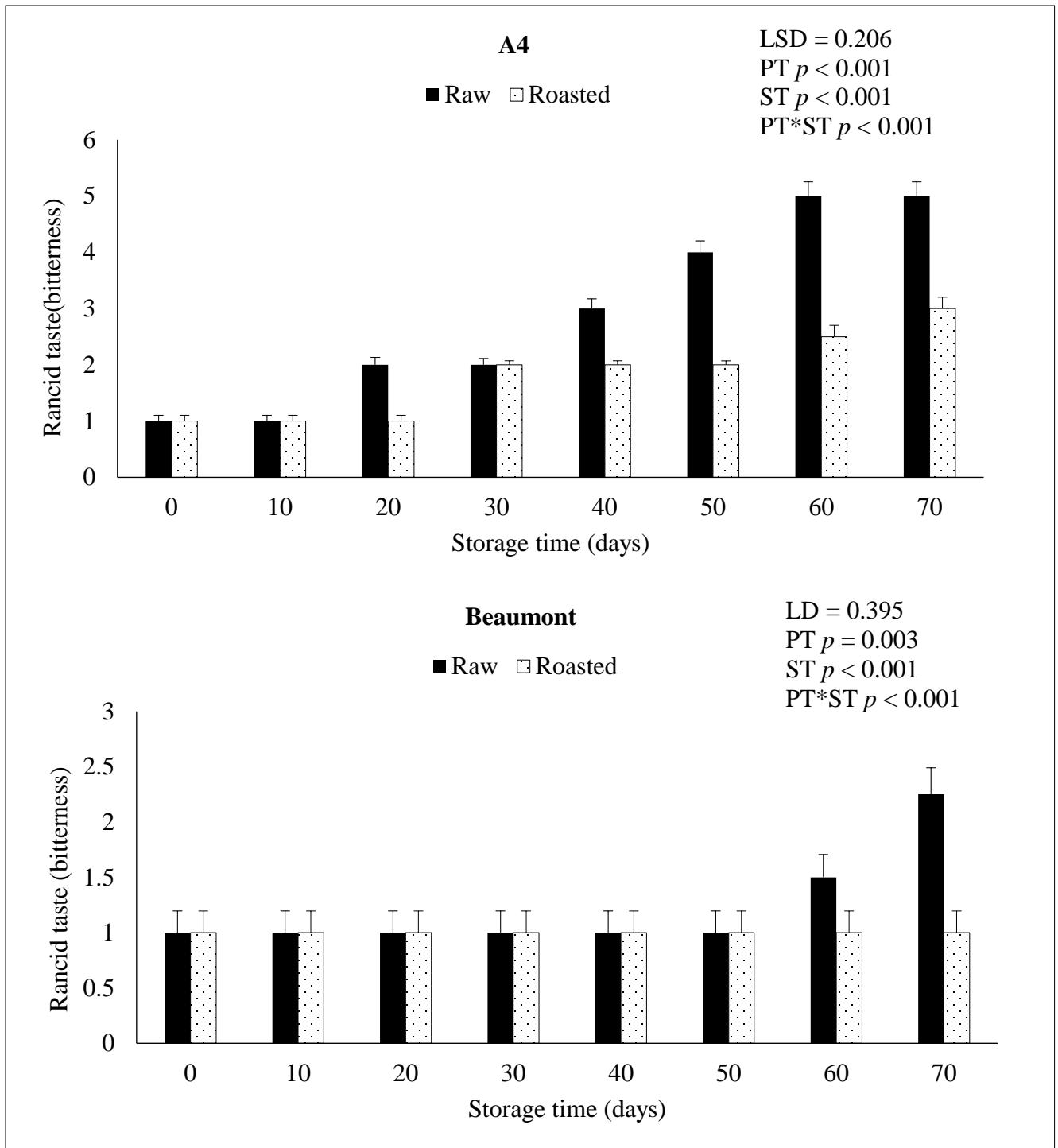
Fig. 9: Rancid taste (bitterness) of raw and roasted kernels of 'A4' and 'Beaumont' during the accelerated postharvest storage. Vertical bars represent standard errors of differences of means. LSD, least significant difference; PT, processing treatments; ST, storage time; PT*ST, processing treatments and storage time.

3.6.4. Overall appearance

Consumers consider good quality of macadamia kernels based on appearance (size, shape, colour, gloss, wholeness and freedom from defects) at the initial purchase (Walton and Wallace, 2009, 2011, 2015). From Fig. 10, it can be observed that raw kernels of 'A4' and 'Beaumont' cultivars had poor ($p < 0.001$) appearance with increasing storage. This could be due to high levels of PPO activity (Fig. 1) observed in raw kernels which is associated with excessive browning (Chutichudet and Chutichudet, 2011; Taranto et al., 2017). Roasting significantly ($p < 0.001$) enhanced the appearance of both 'A4' and 'Beaumont' kernels. The panelists rated the appearance of roasted kernels of 'A4' and 'Beaumont' as fair and good, respectively, at the end of the storage period which could be attributed to the brown colour of roasted kernels produced from non-enzymatic browning reactions such as Maillard browning and caramelization resulting from heat induced reactions among the amino groups of the amino acids present with the carbonyl groups of reducing sugars (Shi, 2015). Varela et al. (2008), Erten (2016) and Belviso et al. (2017) reported that roasting eliminates microorganisms and minimizes deteriorative reactions such as lipid oxidation, but improves sensory and nutritional quality of nuts (Nikzadeh and Sedaghat, 2008).

Fig. 10: Overall appearance of raw and roasted kernels of 'A4' and 'Beaumont' during the accelerated postharvest storage. Vertical bars represent standard errors of differences of means. LSD, least significant difference; PT, processing treatments; ST, storage time; PT*ST, processing treatments and storage time.

3.6.5. Kernel marketability

According to the panelists, roasted kernels of 'A4' and 'Beaumont' were marketable throughout the storage period while raw kernels were fairly or poorly marketable towards the end of storage (Fig. 11) which could be attributed to visible alteration such as kernel browning which is promoted by the PPO enzyme (Taranto et al., 2017). The marketability of roasted kernels could be due to enhanced crispy texture (Fig. 7) and appearance (Fig. 10) observed by panelists.
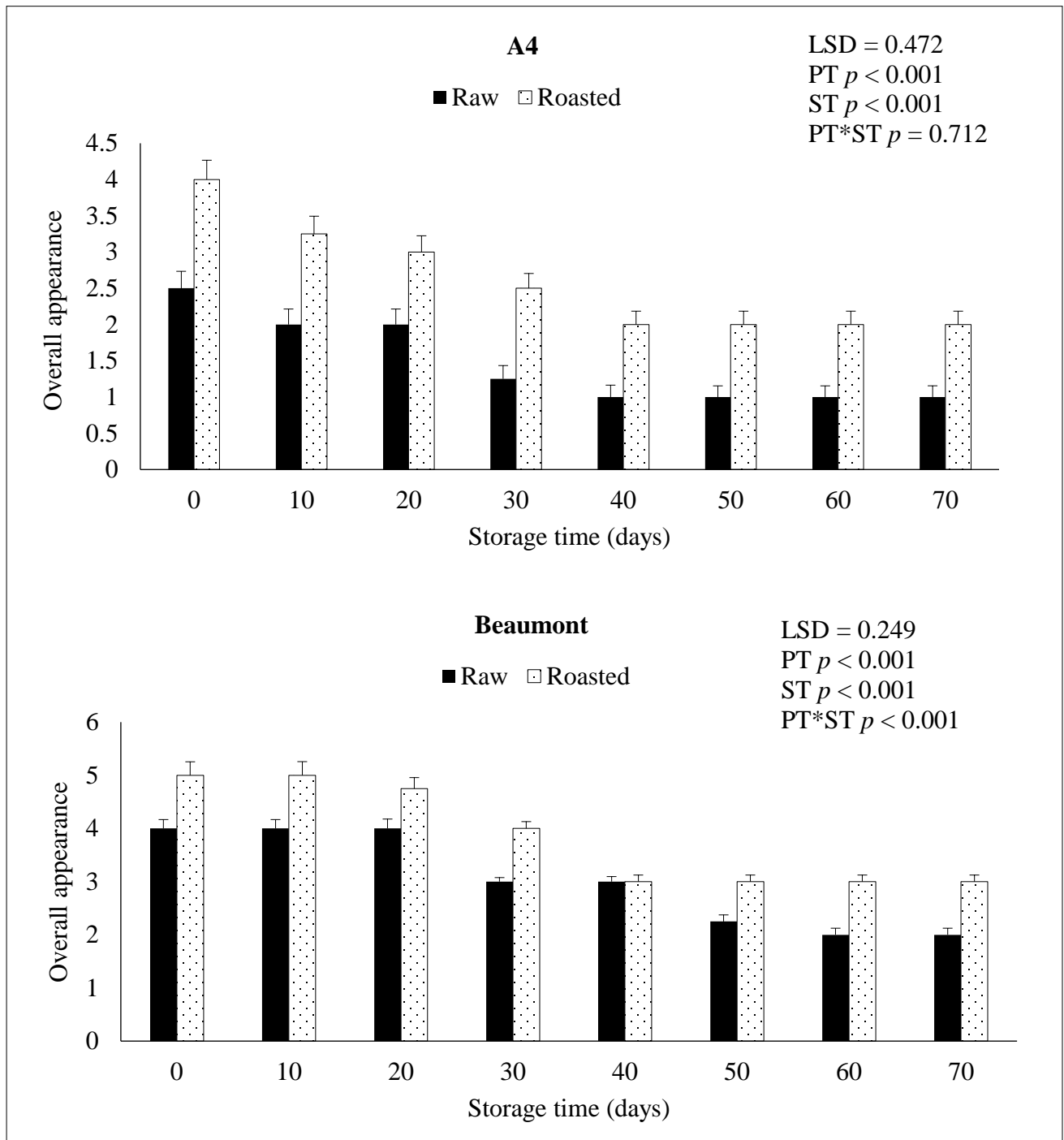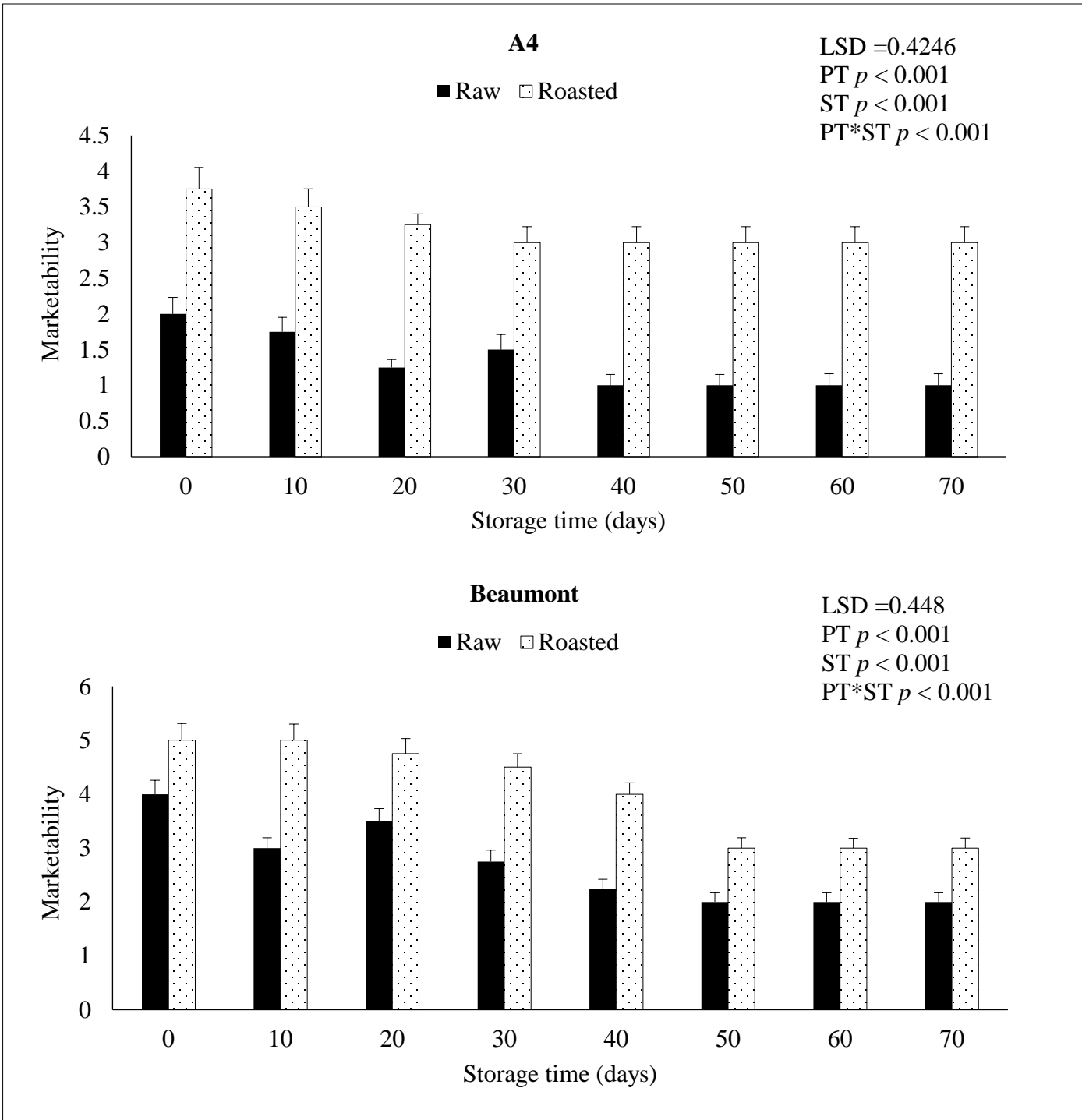
Fig. 11: Kernel marketability of raw and roasted kernels of 'A4' and 'Beaumont' during the accelerated postharvest storage. Vertical bars represent standard errors of differences of means. LSD, least significant difference; PT, processing treatments; ST, storage time; PT*ST, processing treatments and storage time.

3.7. PCA data analysis

3.7.1. 'A4' cultivar

In order to gain a better insight on how the quality parameters evaluated in this study correlate with each other and how they were influenced during the accelerated storage, data sets of raw and roasted kernels were subjected to PCA. The total variability was explained by the first two principal components (PCs) with PC1 and PC2 accounting for 68 % and 17 %, respectively (Fig. 12 a and b). Results of the PCA scores showed that quality parameters of raw kernels were positively affected by the storage whereas roasted kernels were only positively affected by storage from day 50 to 70, confirming that the quality of raw nuts deteriorate much quicker with prolonged storage whereas roasting nuts extends its shelf life (du Preez, 2015; Walton et al., 2017). Results of the PCA correlation loadings showed that the ratio of peroxide value, polyphenol oxidase, kernel appearance, bitterness, aroma and marketability were positively correlated with each other and with storage time. This confirms significant contribution of polyphenol oxidase and peroxide value to quality deterioration during prolonged storage. Supporting this, polyphenol oxidase (Fig. 1) and peroxide value (Fig. 2) of raw kernels significantly increased throughout the storage and significantly contributed to the loss of aroma (Fig. 8), development of rancid taste or bitterness (Fig. 9) therefore, leading to poor appearance (Fig. 10) and marketability (Fig. 11). Our results are similar to Le Lagadec (2009), Borompichaichartkul et al. (2013), du Preez (2015), Srichamnong and Srzednicki (2015) and Camargo et al. (2016) who reported similar trend of polyphenol oxidase and peroxide value in nuts and correlated with excessive visible kernel browning and the development of off-odours and off-flavours. Also, Fig. 12b showed that phenols and antioxidants (DPPH) clustered around storage time, indicating a strong correlation. Fig. 4 and 5 showed that phenols and antioxidant concentrations, respectively, significantly increased with increasing storage. Although ABTS was located in the same plane as DPPH, phenols and storage time, the correlation was not very strong. Flavonoids and kernel texture had no influence on other quality parameters as they were on the opposite quadrants of the plot. Kernel texture was negatively correlated with storage time. This further confirmed results presented in Fig. 7 that the texture of roasted kernels was not affected by storage time.

Fig. 12 a: 'A4' principal component analyses (PCA) scores plots of the first two principal components showing a correlation of measured quality parameters over the accelerated storage. RT = raw kernels; RD = roasted kernels.

Fig. 12 b: 'A4' principal component analyses (PCA) correlation loadings plots of the first two principal components showing a correlation between biochemical and sensory properties and storage time. T = storage time; PPO = polyphenol oxidase; PV = peroxide value; F = flavonoids; P = phenols; DPPH = 2,2'-diphenyl-1-picrylhydrazyl; ABTS = 2,2'-azinobis-3-ethylbenzothiazoline-6-sulfonic acid; T= texture; AR = aroma; B = bitterness; AP = appearance; M = marketability.

3.7.2. 'Beaumont' cultivar

The total variability was explained by the first two principal components (PCs) with PC1 and PC2 accounting for 53 % and 28 %, respectively (Fig. 13 a and b). Results of the PCA scores showed that quality parameters of raw kernels were positively affected by the storage whereas roasted kernels were only positively affected by storage from day 60 to 70, confirming that roasting does enhance quality and storability of nuts. Results of the PCA correlation loadings showed that the ratio of polyphenol oxidase, kernel appearance, bitterness, aroma and marketability were positively correlated with each other and with storage time. Peroxide value, phenols and DPPH were clustered around storage time, indicating a strong correlation. Although ABTS was located in the same plane as peroxide value, DPPH, phenols and storage time, the correlation was not very

strong. This confirmed result presented in Fig 1 and 2, the polyphenol oxidase and peroxide value of raw kernels significantly increased with increasing storage resulting to the loss of aroma (Fig. 8), bitterness (Fig. 9) poor appearance (Fig. 10) and marketability (Fig. 11). Our findings are similar to Siboza et al. (2014) who reported that polyphenol oxidase which is involved in tissue browning reduces the marketability of food. Walton (2005), Domı et al. (2007), Gölge and Ova (2008) and Borompichaichartkul et al. (2013) reported that high PV causes the loss of the above mentioned quality attributes through deteriorative reactions such as lipid oxidation. Fig. 4, 5 and 7 showed a significant increase of phenols, DPPH and ABTS, respectively, in roasted kernels throughout the storage period which could be due to increase in extractable phenolic compounds after roasting with the formation of Maillard products (McDaniel et al., 2012; Srichamnong and Srzednicki, 2015). Flavonoids and kernel texture were not correlated with other quality parameters as they were on the opposite quadrants of the plot. Kernel texture was negatively correlated with storage time as observed in Fig. 7 that the panelists rated the texture of roasted kernels as crispy throughout the storage period. The correlation of quality parameters with storage time suggest that polyphenol oxidase and peroxide value can be used as primary indicators of kernel quality during the storage of macadamia nuts.
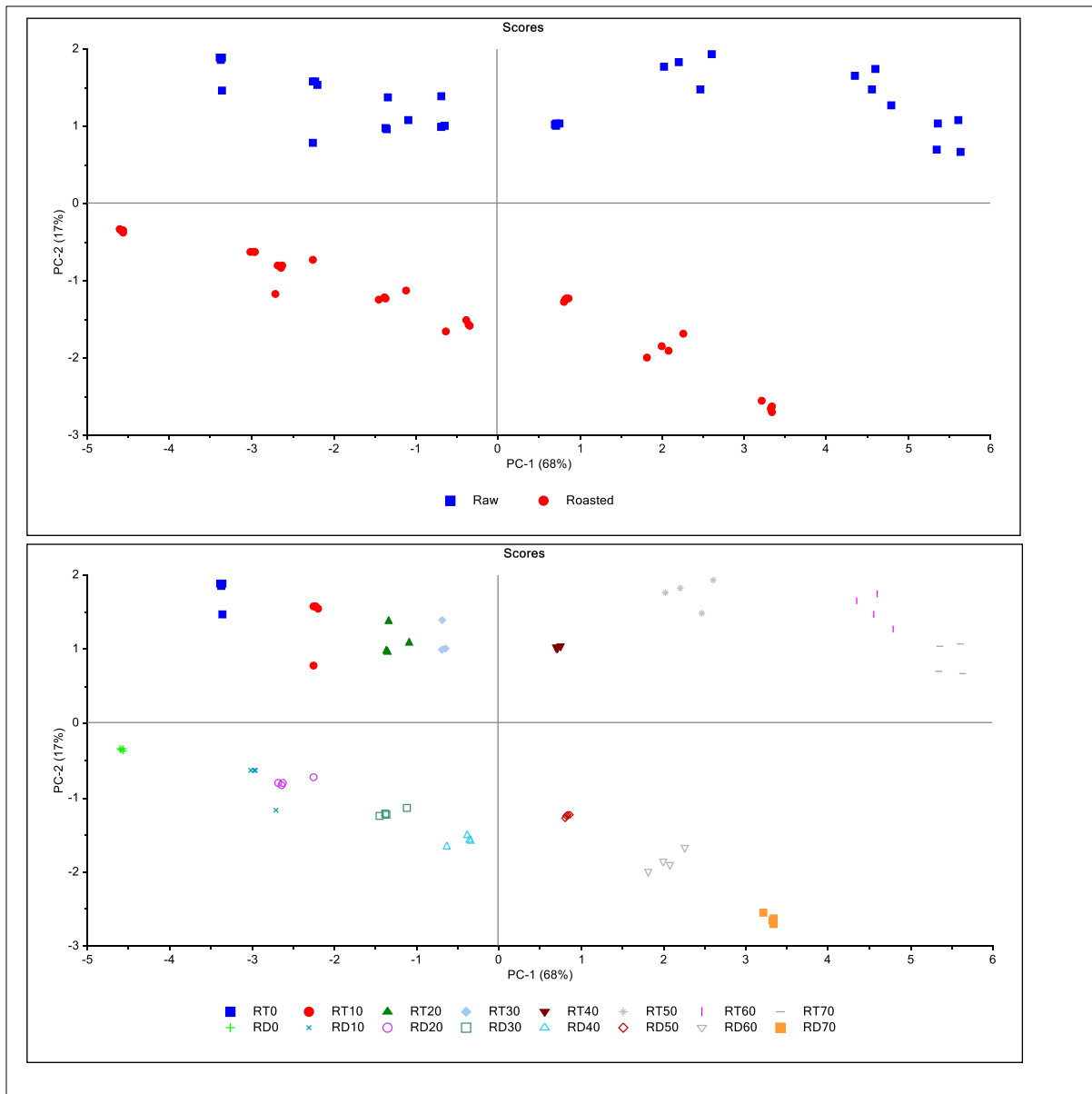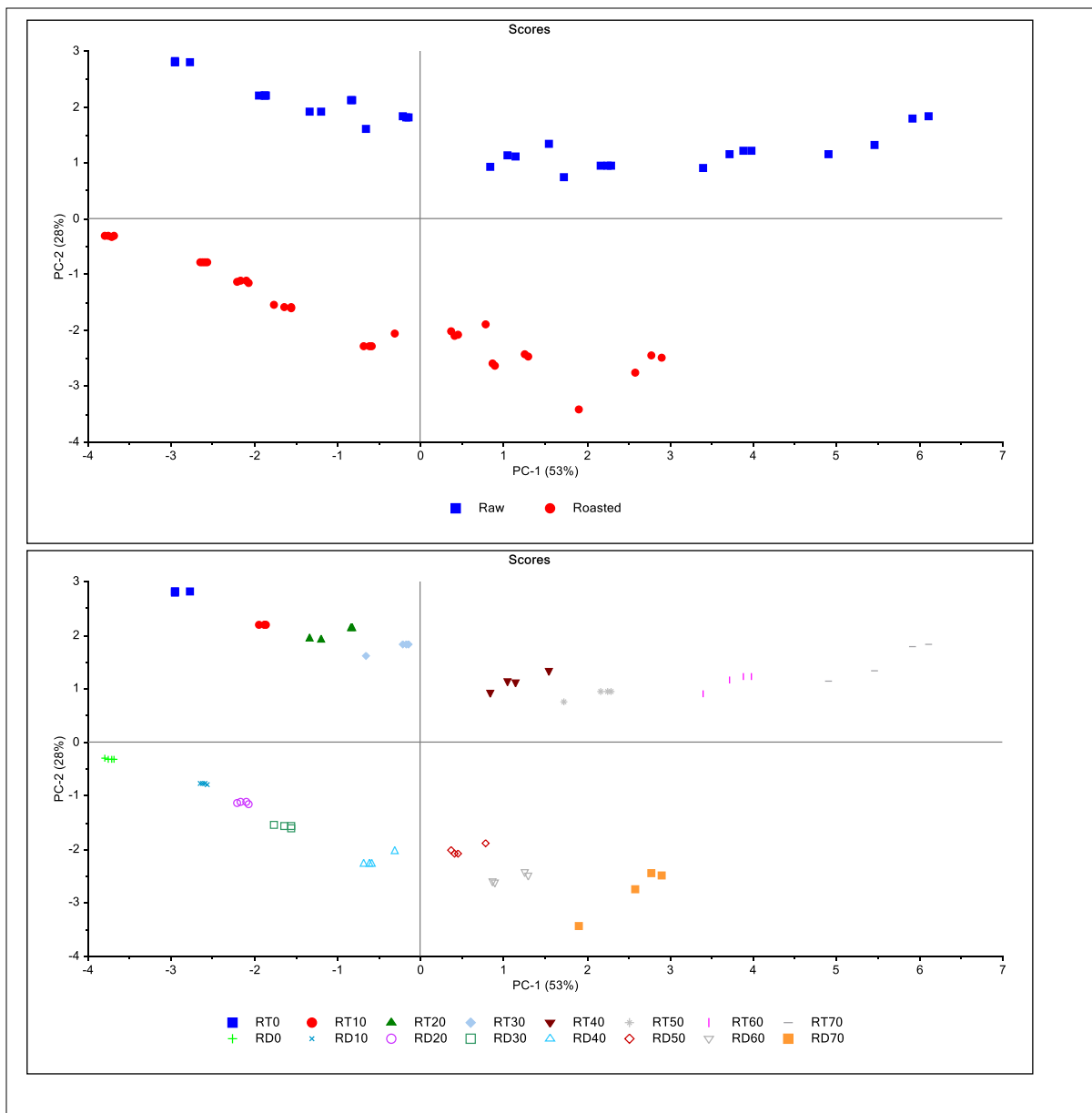
Fig. 13 a: 'Beaumont' principal component analyses (PCA) scores plots of the first two principal components showing a correlation of measured quality parameters over the accelerate storage. RT = raw kernels; RD = roasted kernels.
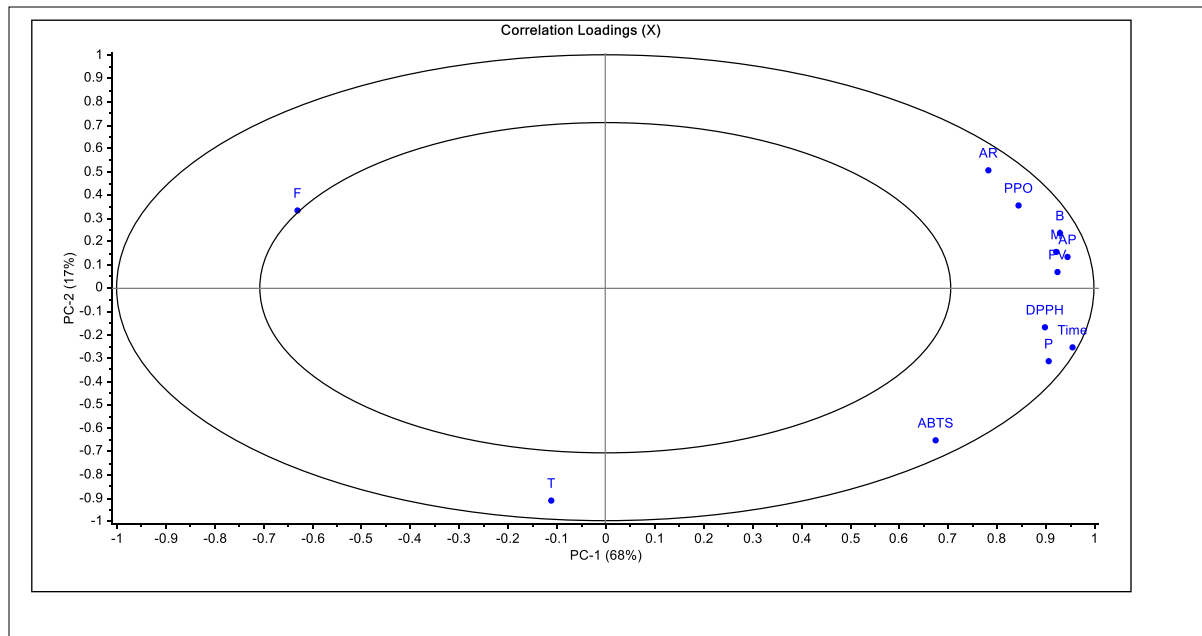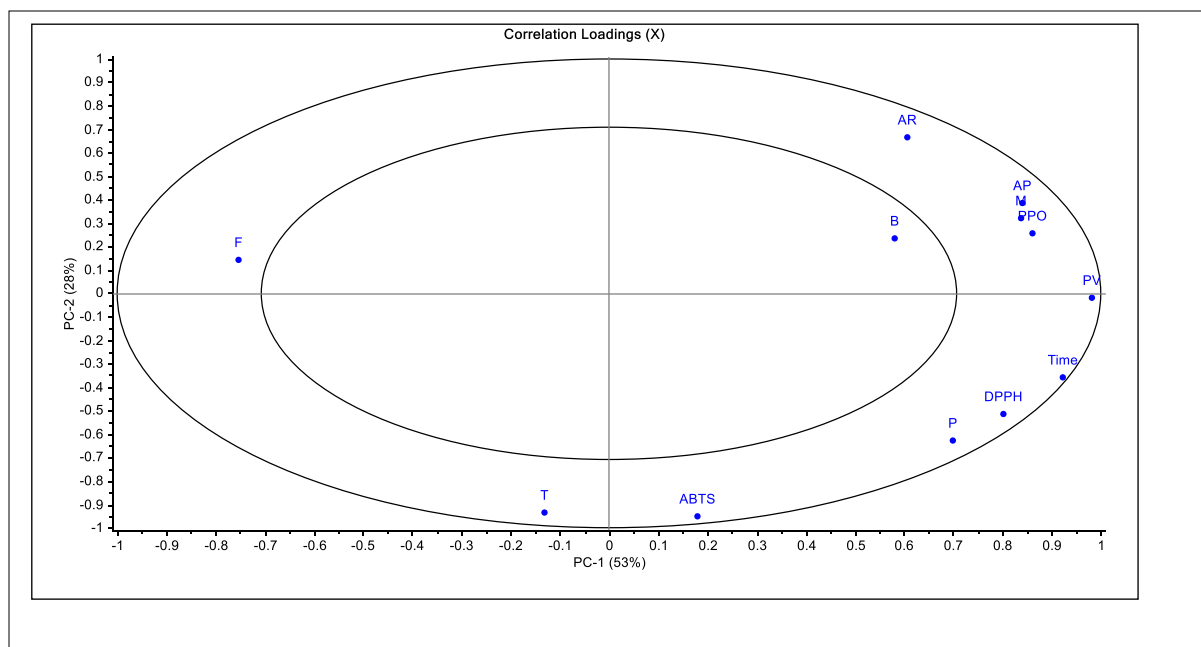
Fig. 13 b: 'Beaumont' principal component analyses (PCA) correlation loadings plot of the first two principal components showing a correlation between biochemical and sensory properties and storage time. T = storage time; PPO = polyphenol oxidase; PV = peroxide value; F = flavonoids; P = phenols; DPPH = 2,2'-diphenyl-1-picrylhydrazyl; ABTS = 2,2'-azinobis-3-ethylbenzothiazoline-6-sulfonic acid; T= texture; AR = aroma; B = bitterness; AP = appearance; M = marketability.

4. Conclusion

Overall, the study demonstrated that roasting enhanced and preserved the quality of kernels of both 'A4' and 'Beaumont' cultivars during the accelerated storage of 70 d. Roasted kernels had the lowest PV and the highest levels of phenolic and antioxidant concentration, confirming the vital role of antioxidant activity in delaying lipid oxidation or rancidity. Also, according to the panelists roasted kernels had enhanced texture, aroma, flavour, appearance and good marketability throughout the storage period. Therefore, it can be recommended that macadamia kernels be roasted for improved quality and longer storability or shelf life. Furthermore, it should be noted that although roasting may be favorable for many aspects, it could cause reactions leading to the loss of nutritional quality or development of disagreeable compounds such as 5-

hydroxymethylfurfural. Several physical and chemical changes such as microstructural and lipid modifications may enhance the susceptibility of roasted nuts to oxidation thus, reducing its shelf life. Heat treatment at high temperatures may result in the formation of some toxic compounds such as acrylamide, heterocyclic amines, polycyclic aromatic hydrocarbons and N-alkyl-N-nitrozamines which could decrease the nutrition value of nuts and put its safety in danger. Therefore, the consideration of mild roasting temperatures (30 to 180 °C) and minimal roasting time (15 to 60 min) depending on roasting temperature could be useful in reducing quality deterioration in nuts as a consequence of over-roasting.

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CHAPTER 4: THE EFFECT OF ROASTING TEMPERATURES ON ANTIOXIDANT, PHYTOCHEMICAL AND SENSORY ATTRIBUTES OF MACADAMIA NUTS (*MACADAMIA INTEGRIFOLIA*)

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Abstract

The effect of roasting temperatures on the sensory and biochemical quality of macadamia nuts was investigated using 'A4' and 'Beaumont' as model cultivars. Macadamia kernels were roasted at 50 °C, 75 °C, 100 °C, 125 °C and 150 °C for 15 min using the hot air oven dryer. After roasting, kernels were immediately evaluated for sensory quality and on the same day roasted kernels were ground into a fine powder using a blender and stored at – 20 °C for further analysis. Raw kernels were used as a control. Although 'A4' and 'Beaumont' kernels roasted at 50 °C, 75 °C and 100 °C had significant ($p < 0.001$) higher antioxidants, they were prone to deterioration, indicated by high levels of rancidity which might have been promoted by higher kernel moisture content and poor kernel texture, colour and taste observed by trained panelists. 'A4' and 'Beaumont' kernels roasted at a higher temperature (150 °C) had the lowest moisture content, flavonoids, phenols and antioxidants (DPPH and ABTS), higher levels of peroxide value and poor sensory quality; excessive browning, extremely crispy texture and bitter taste. 'A4' and 'Beaumont' kernels roasted at 125 °C had the lowest levels of peroxide value which is required by the macadamia industry for estimation of good quality and significant concentration of flavonoids, phenols and total antioxidants and had excellent sensory quality; ideal crispy texture, brown colour and very nutty taste. Therefore, roasting 'A4' and 'Beaumont' kernels at 125 °C could be recommended for enhancing kernel quality and palatability.

1. Introduction

Macadamia (*Macadamia integrifolia*) is regarded as the highest ranking nut globally and is widely consumed roasted or as an ingredient into various confectionary products (Eagappan and Sasikumar, 2014; Navarro and Rodrigues, 2016). The worldwide consumption of macadamia may be due to its high nutritional content and reported health benefits, including prevention of cardiovascular diseases and type 2 diabetes (Jiang et al., 2005; Lovejoy, 2005; Rengel et al., 2015). These health benefits are associated with low levels of cholesterol, high oil content (69 to 78 %) which is rich in monounsaturated fatty acid (80 %) mainly oleic (60 %) and palmitoleic (20 %) acids (Kaijser et al., 2000; Moreno-Pérez et al., 2011; Sinanoglou et al., 2014) and antioxidants due to several phytochemicals and polyphenols also present in kernels (Leja et al., 2001; Oboh, 2005; Rengel et al., 2015). Macadamia is also a rich source of bioactive macronutrients such as protein, fiber, minerals, vitamin E, and plant sterols (Ros, 2010). Since macadamia nuts contain a high content of monounsaturated fatty acids they are highly susceptible to hydrolytic and oxidative rancidity when it contains high levels of free moisture (Borompichaichartkul et al., 2009; Phatanayindee et al., 2012).

Roasting is one of the most effective processing methods for maximizing the overall palatability and preserving the quality of nuts (Nikzadeh and Sedaghat, 2008; Shakerardekani et al., 2011). This processing method leads to sensory and chemical changes in kernels (Saklar et al., 2001). It improves colour, flavour, aroma and texture of the nuts through non-enzymatic reactions such as Maillard browning (McDaniel et al., 2012; Schlörmann et al., 2015; Taş and Gökmen, 2017). The brown colour of roasted nuts is a result of pyrazines and pyridines compounds, which are characteristic products resulting from polymerization and Maillard reaction which needs reducing sugars for reaction with amino acids to form browning products (McDaniel et al., 2012; Phatanayindee et al., 2012; Srichamnong and Srzednicki, 2015).

Various volatile compounds responsible for kernel flavour and aroma are generated through the Maillard reaction during roasting (Saklar et al., 2001; Vázquez-Araújo et al., 2009). Pyrazines, furans and pyrroles are essential components of roasted kernel aroma (Vázquez-Araújo et al.,

2008). Pyrazines, which have nutty and roasted aromas, are formed during heating via Maillard sugar-amine reactions and Strecker degradation (Phatanayindee et al., 2012). Roasted kernels have a crispy texture, delicate, uniquely nutty taste and are widely consumed compared to raw kernels (Kita and Figiel, 2007; Nikzadeh and Sedaghat, 2008). Furthermore, roasting inactivates oxidative enzyme system (lipoxygenic enzymes), reduces moisture content therefore, eliminates microorganisms and minimizes deteriorative reactions such as lipid oxidation, which exhibit antioxidant activity (Belviso et al., 2017; Taş and Gökmen, 2017).

Although favourable for many aspects, roasting may lead to chemical changes that can affect nuts sensory attributes, nutritional value and the quality of its lipids (Tonfack Djikeng et al., 2018). Furthermore, high temperatures or over-roasting can promote lipid oxidation and non-enzymatic browning reactions, which can reduce the nutritional value of foods, causing the loss of essential fatty acids, essential amino acids and carbohydrates (Borompichaichartkul et al., 2013; Tonfack Djikeng et al., 2018) and further accelerates the development of lipid oxidation often referred to as oxidative rancidity related to the occurrence of disagreeable odours and flavours (Phatanayindee et al., 2012; Rengel et al., 2015). These chemical alteration reactions may generate toxic compounds in nuts which can be detrimental to consumers health (Garcıa-Pascual et al., 2003; Süvari et al., 2017b). Since macadamia nuts are rich in fats and prone to oxidation, they require mild roasting temperatures (Kita and Figiel, 2007; Rengel et al., 2015). The nut industry considers mild temperature to range from 30 to 180 °C in which roasting is carried out for 15 to 60 min using several methods such as commercial electrical ovens, infrared heating and dielectric processes of radiofrequency and microwave (Belviso et al., 2017; Marzocchi et al., 2017; Tonfack Djikeng et al., 2018). However, little is known about the effect of mild roasting temperatures on sensory and chemical quality of macadamia kernels. Therefore, the objective of this study was to evaluate the impact of different roasting temperatures on sensory and nutritional quality of macadamia.

2. Materials and methods

2.1. Macadamia samples

Two hybrids of Australian-bred cultivars of *Macadamia integrifolia* namely, 'Beaumont' and 'A4' were harvested from the commercial orchards of Elliot Farm in Port Shepstone, South Coast of KwaZulu-Natal, South Africa (latitude: 30°44′28″ S, longitude: 30°27′17″ E and altitude: 36 m). Harvesting of nuts was conducted at two different times, early season (May 2017) and late season (June 2017) based on industry practice. About 50 kg of nuts per cultivar were harvested per sampling date and transported to Ukulinga Research Farm of the University of KwaZulu-Natal (UKZN) for further processing.

2.2. Dehusking, drying and cracking process

Dehusking (01-one-lane dehusker, WMC sheet metal works, Tzaneen, South Africa) was done on the same day of harvesting at Ukulinga Research Farm of UKZN. Following a method described by Walton et al. (2013) with slight modifications, immediately after dehusking, NIS were weighed and dried using a mechanical convection oven (RY-EB-550, Rongyao factory, Mainland, China) at Postharvest Research Laboratory of UKZN for three consecutive days, starting with 35 °C on the first day, 38 °C for the second day and 50 °C for the third day. These drying temperatures were selected according to the nut industry practice to avoid quality deterioration (Belviso et al., 2017; Walton et al., 2017). Dried nuts were checked for moisture content and were only removed from the oven when moisture content had reached 1.5 %. The moisture content of nuts was based on initial and final (dry) weight. Mass changes in nuts were used to calculate moisture content on a dry basis (d.b.) (Wang et al., 2014). Moisture content was determined according to Khir et al. (2011) as follows:

$$MC_{db} = \frac{W_i\text{-}W_d}{W_d} \times 100 \tag{1}$$

Where MC_{db} is moisture content on a dry mass basis, W_i and W_d are the initial and the dry sample weights, respectively. Furthermore, macadamia nuts were mechanically cracked into wholes, halve and pieces using a commercial mechanical macadamia nutcracker (TZ-150 macadamia nut cracker, Alibaba Group Houlding (PTY) LTD , Hangzhou, China). The shell and kernel were separated manual or by hand and the percentage of kernel recovery was calculated and expressed as a percentage weight of the nut that is kernel at 1.5 % moisture content, the rest being a shell (Eq. 2) and only full kernels were used for the experiment. Nuts that are dried to 1.5 % kernel moisture content for the purpose of dehusking and cracking are referred to as raw kernels (du Preez, 2015).

$$KR = \frac{NIS\text{ -Shell}}{NIS} \times 100 \tag{2}$$

where KR is kernel recovery and NIS is nut-in-shell.

2.3. Roasting process

The roasting process was carried out according to Srichamnong and Srzednicki (2015), with slight modifications. The roasting temperatures were selected based on the nut industry practice to avoid quality deterioration (Belviso et al., 2017; Taş and Gökmen, 2017; Tonfack Djikeng et al., 2018). Only full kernels with no visible defects were used for sampling. The kernels were roasted using convection oven (RY-EB-550, Rongyao factory, Mainland, China) at 5 different temperatures, namely, 50 °C, 75 °C, 100 °C, 125 °C and 150 °C. Raw kernels were used as the control. A randomly sampled set of kernels of 15 replicates per treatment per cultivar per harvest season, each weighing 2 kg were packed in commercial brown paper bags for postharvest storage trials. After roasting, kernels were immediately evaluated for sensory quality and on the same day roasted kernels were ground into a fine powder using a blender (brabantia-table blender, BBEK1051, Massdiscounter (Pty) Limited, Johannesburg, South Africa) and stored at – 20 °C for further analysis.

2.4. Quantification of peroxide value

Oil content was quantified using a method described by Meyer and Terry (2008), with slight modifications. Hexane (9.0 mL) was added into a test tube containing 3 g of ground kernel sample and the test tube was placed into an ultrasonic bath (Labotec, Model No. 132, Labotec (PTY) LTD, Johannesburg, South Africa) for 10 min. The supernatant was filtered under vacuum and another 6 mL hexane was added to the residue in the test tube. This was left for 5 min before the test tube was emptied into the Buchner funnel. After filtration, 15 mL hexane was dried off the supernatant using a GenVac® concentrator (SPScientific, Genevac LTD., Suffolk, UK) under vacuum leaving the oil content of the sample. The residual oil was weighed and presented on dry weight basis.

Peroxide value (PV) was determined according to Walton et al. (2017), with minor modifications. A 1 mL of oil sample was dissolved in 20 mL of acetic acid/chloroform (3:2 v/v) followed by adding 1 mL of a saturated potassium iodide solution by an additional burette. The reaction took place and iodine was formed. A 50 mL of deionized water was added. Iodine was titrated with $Na_2S_2O_3$ using a burette. Peroxide value (expressed as milliequivalents of peroxide per kilogram of sample) was calculated according to the following formula:

$$PV \text{ (meq per kg)} = \frac{(S - B) \times N \times 1000}{\text{Sample wt (g)} \times 1000} \tag{3}$$

where S = sample titration (µL); B = Blank titration; and N = normality of $Na_2S_2O_3$.

2.5. Quantification of free and membrane bound phenols

Phenols were determined based on Hertog et al. (1992), with slight alterations. Roasted kernel sample (1 g each) was mixed with 10 mL 99.8 % (v/v) methanol and vortexed for 30 s. Thereafter, the mixture was shaken overnight at room temperature to extract the free phenols. Afterward, the mixture was centrifuged, and the supernatant was filtered through Whatman® no. 1 filter paper and the sample was again rinsed with 10 mL of solvent until rinsing solvent was clear. Then, the

acid hydrolysis was also used for the remaining kernel residue to efficiently release cell wall-bound phenols. Briefly, a 10 mL portion of acidified (2 M hydrochloric acid) 60 % aqueous methanol was added to each sample and placed in a hot water bath at 90 °C for 90 min. Glass tubes were allowed to cool, and supernatants were filtered through a 0.45 µm filter. The total phenolic concentration was determined spectrophotometrically using Folin-Ciocalteu reagent (5 mL of distilled water + 1 mL of extract + 1 mL Folin-Ciocalteu reagent + 10 mL of 7 % Na_2CO_3 + 8 mL of distilled water and left at room temperature for overnight) at 750 nm using gallic acid monohydrate as a standard and the total phenolic concentration was expressed as mg Gallic Acid Equivalents (GAE) kg^{-1} DW.

2.6. Quantification of total flavonoids concentration

The total flavonoids concentration was determined using aluminium chloride ($AlCl_3$) following a method described by Eghdami and Sadeghi (2010), with slight modifications, using quercetin as a standard. The kernel extract (0.10 mL) was added into a glass tube followed by adding 5 % $NaNO_2$ (0.03 mL) and the reaction mixture was allowed to stand at room temperature for 5 min. A 0.03 mL of 10 % $AlCl_3$ was added and incubated for 6 min, after that 0.2 mL of 1 mM NaOH was added to the solution and the reaction mixture was diluted to 1 mL with distilled water. The absorbance of the reaction mixture was read at 510 nm, against methanol used as blank. The results were expressed as mg quercetin kg^{-1} DW.

2.7. Quantification of total antioxidants activity

2.7.1. 2,2'-diphenyl-1-picrylhydrazyl (DPPH) assay

The 2,2'-diphenyl-1-picrylhydrazyl (DPPH) free radical scavenging activity was determined according to Ahmed et al. (2015), with slight modifications. The stock solution of the radical was prepared by dissolving 1.94 mg DPPH in 50 mL of methanol and was kept in a refrigerator at -20 °C until further use. The working solution of the radical was prepared by diluting the DPPH stock solution with methanol to obtain an absorbance of about 0.98 (±0.02) at 517 nm. A 20 µL of gallic

acid or sample extract were measured into polystyrene 4.5 mL cuvette. A 800 µL of absolute methanol was added, followed by 1 mL of 0.1 mM DPPH solution which was added in the dark and covered with aluminium foil and was allowed to stand at room temperature for 60 min. The absorbance was measured at 517 nm against a blank (absolute methanol) under dim light and the results were expressed as mg DPPH GAE kg^{-1} DW.

2.7.2. 2,2'-azinobis-3-ethylbenzothiazoline-6-sulfonic acid (ABTS) assay

The 2,2'-azinobis-3-ethylbenzothiazoline-6-sulfonic acid (ABTS) was determined based on Tesfay et al. (2011), with slight alterations. 2,2'-azinobis-3-ethylbenzothiazoline-6-sulfonic acid was prepared as a 7 mM solution in water or ethanol, for measuring hydrophilic and lipophilic antioxidant fractions, respectively. The ABTS radical cation (ABTS$^{.+}$) was produced by reacting the 7 mM ABTS solution with 2.45 mM ammonium persulfate and allowing the mixture to stand in the dark at room temperature for 3 to 6 h. Thereafter, 1.0 mL activated ABTS solution (A$_{734}$ nm = 0.700 ± 0.5) was added to 10 µL sample solution from extracts of roasted material in acetate buffer (pH 4.0). The decrease in absorbance at 734 nm was recorded after 6 min and the results were expressed as mg ABTS GAE kg^{-1} DW.

2.8. Sensory evaluation

A randomized set of macadamia kernels was examined raw and immediately after roasting (50 °C, 75 °C, 100 °C, 125 °C and 150 °C at the Department of Horticultural Science Postharvest Laboratory of UKZN. Samples were given to trained panelists (5 males and 5 females) ranging from the age of 25 to 44 to assess the quality of 'A4' and 'Beaumont' kernels in terms of their texture, colour and taste (Kita and Figiel, 2007; Nikzadeh and Sedaghat, 2008; Sanful, 2009). Sensory quality of kernels was assessed using hedonic scale. Hedonic scale represents one of the most important sensory methods in the food industry during product development and launching of new products in the market because it informs some measure of whether products are liked or not (Nicolas et al., 2010). This further assist both the marketing and Research and Development departments to develop better products that will satisfy and be accepted by consumers (Singh-

Ackbarali and Maharaj, 2014). Hedonic scale usually ranges from 1 to 9 which represent dislike to like. Recent modifications of the hedonic scale includes the range of 5 (like or excellent) to 1 (dislike or poor) (Mademgne and Dorys, 2016). In our study, the texture of kernels was assessed according to Nikzadeh and Sedaghat (2008) and Sanful (2009) with minor modifications using a five-grade hedonic scale where 1: very hard, 2: hard, 3: slightly crispy, 4: crispy and 5: very crispy; colour where 1: very light, 2: light, 3: slightly brown, 4: brown and 5: extremely brown and taste where 1: very nutty, 2: nutty, 3: slightly bitter, 4: bitter and 5: extremely bitter.

2.9. Statistical analysis

The collected data was subjected to the analysis of variance (ANOVA) using GenStat statistical software (GenStat®, 18.1 edition, VSN International, UK) 18.1. Least significant difference values (LSD; $p < 0.001$) were calculated for mean separation.

3. Results and discussion

3.1. Moisture content

The kernel moisture content of 'A4' and 'Beaumont' cultivars significantly ($p < 0.001$) decreased with increasing roasting temperature (Fig. 1). 'A4' and 'Beaumont' kernels roasted at 50 °C, 75 °C, 100 °C and 125 °C showed a significant decrease of moisture content of 1.474 and 1.432 %, 1.429 and 1.4 %, 1.393 and 1.318 % and 1.319 and 1.211 %, respectively, and kernels roasted at 150 °C had the lowest moisture content of 1.218 and 1.025 %, respectively. The significant decrease of kernel moisture content at 150 °C could be due to dehydration or loss of moisture or moisture evaporation and loss of volatile compounds such as reaction of free amino acids and short-chained peptides with free mono- and disaccharides during nonenzymatic browning and protein denaturation and degradation that might occur upon roasting nuts at higher temperatares above 130 °C (García-Alamilla et al., 2017; Marzocchi et al., 2017; Süvari et al., 2017b). These chemical changes might results in subsequent changes in kernel chemical and sensory quality (Belviso et al., 2017; Taş and Gökmen, 2017; Tenyang et al., 2017). A similar significant decrease

of moisture content from 2.4 to 1 % as influenced by applying higher temperatures (150 °C) during roasting has been previously reported by Kita and Figiel (2007), Nikzadeh and Sedaghat (2008) and Shakerardekani et al. (2011).
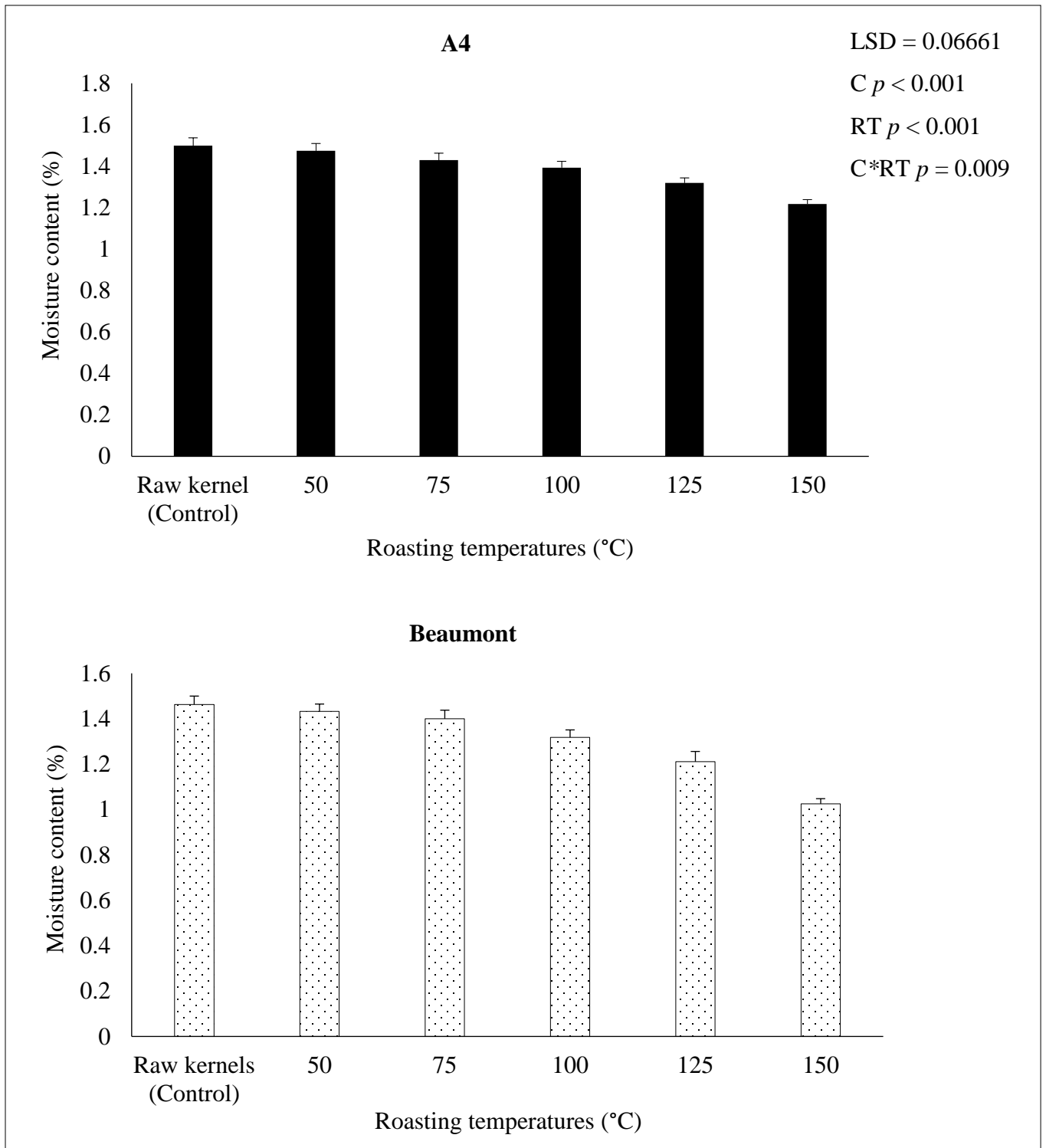
Fig. 1: Moisture content of 'A4' and 'Beaumont' after roasting for 15 min. Vertical bars represent standard errors of differences of means. LSD, least significant difference; C, cultivar; RT, roasting temperatures; C*RT, cultivar and roasting temperatures.

3.2. Peroxide value (PV)

Peroxide value is the most frequently used parameter to measure the extent of primary oxidation products, mainly hydroperoxides in edible oils (Phatanayindee et al., 2012; Tonfack Djikeng et al., 2018). Peroxide value is evidence of autoxidation (free radical reaction) which might be influenced by several factors including, roasting temperature, levels of unsaturated fatty acids, the presence of enzymes and levels of antioxidants (Garcıa-Pascual et al., 2003; Walton et al., 2017). Hydroperoxides produced from autoxidation react with other nut components such as amino acids and proteins leading to nut rancidity (Bai et al., 2017).

From Fig. 2, it can be observed that the PV of 'A4' and 'Beaumont' kernels roasted at 50 °C (2.203 and 1.303 meq O_2 kg^{-1}), 75 °C (1.72 and 1.232 meq O_2 kg^{-1}), 100 °C (1.569 and 1.011 meq O_2 kg^{-1}) and 125 °C (1.161 and 0.947 meq O_2 kg^{-1}) significantly ($p < 0.001$) declined with increasing roasting temperature. The lower PV observed in kernels roasted at 125 °C is regarded as an indication of high quality. Walton (2005) and Borompichaichartkul et al. (2013) reported that a high quality macadamia product is characterized by low PV of less than 1 meq O_2 kg^{-1} which is considered acceptable for a freshly refined fat and is classified at low oxidation state. Our results are consistent with Bai et al. (2017) who reported that PV of *Canarium indicum* L. (*Burseraceae*) kernels significantly decreased from 1.30 to 1 meq O_2 kg^{-1} with increasing roasting temperature (110 to 120 °C).

Roasting kernels at 150 °C lead to the increase of PV for both 'A4' (1.727 meq O_2 kg^{-1}) and 'Beaumont' (1.682 meq O_2 kg^{-1}) cultivars. This could be due to the fact that high roasting temperatures could cause the oil to undergo a series of chemical reactions such as oxidation, hydrolysis and polymerization (Makeri et al., 2011). During this process, many oxidative products such as hydroperoxide and aldehydes are produced, which can be absorbed into the roasted food (Alhibshi et al., 2016). Garcıa-Pascual et al. (2003) reported that the oxidation of edible oils and the rate of rancidity development are highly dependent on temperature; the higher the temperature the higher is the rate of rancidity. Our results are also in agreement with Tenyang et al. (2017) and Tonfack Djikeng et al. (2018) who reported that the increase of PV in sesame and walnuts,

respectively, due to thermal processing, could be attributed to the increase of hydroperoxides as a result of free radicals attacking the unsaturated fatty acids of the oil. Makeri et al. (2011) and Borompichaichartkul et al. (2013) reported that the increase of PV may result to the development of noticeable off-flavours, therefore, our findings suggest that roasting 'A4' and 'Beaumont' kernels at 150 °C should be avoided.

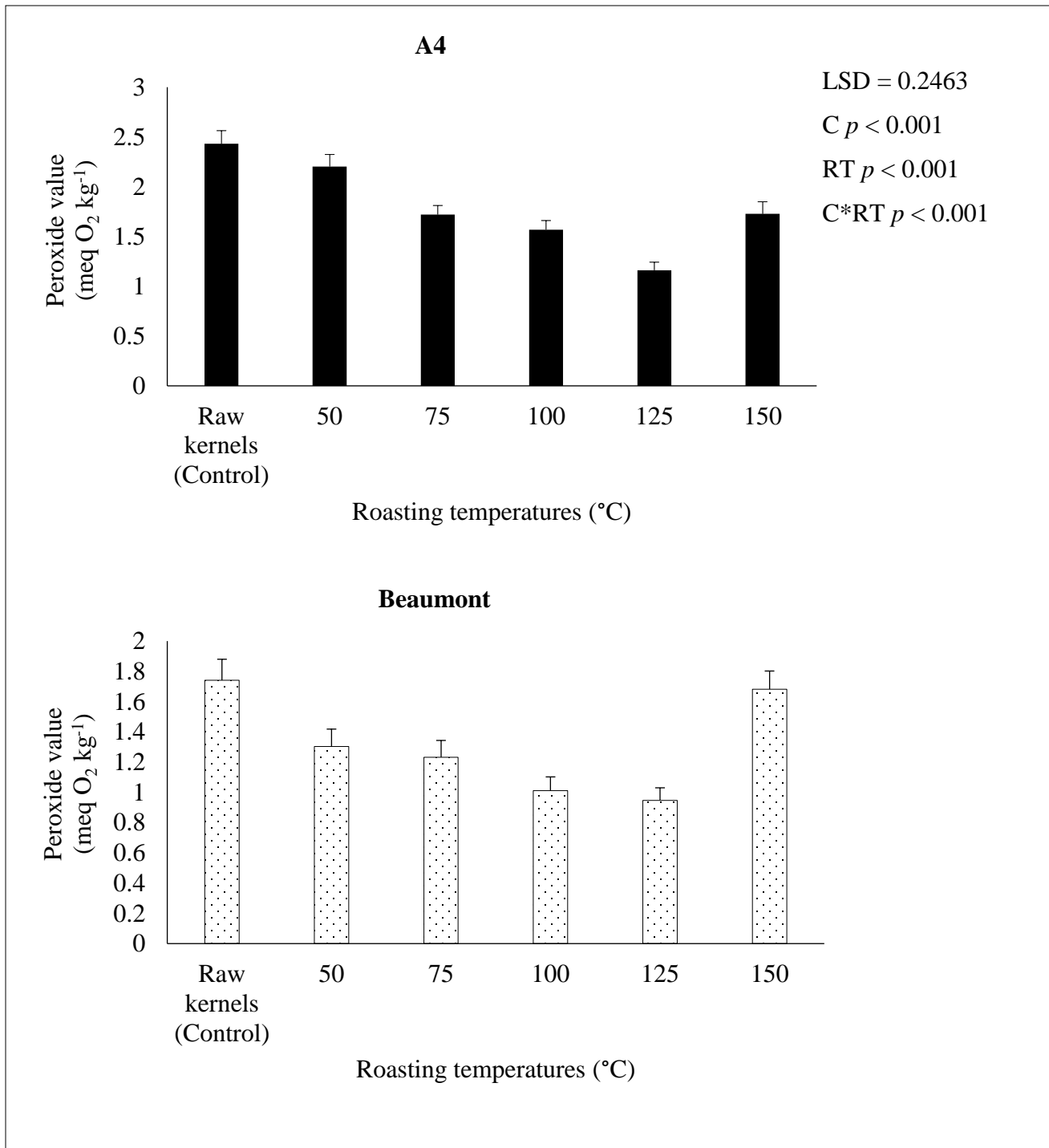Fig. 2: Peroxide value of 'A4' and 'Beaumont' after roasting for 15 min. Vertical bars represent standard errors of differences of means. LSD, least significant difference; C, cultivar; RT, roasting temperatures; C*RT, cultivar and roasting temperatures.

3.3. Flavonoids concentration

Flavonoids concentration of 'A4' and 'Beaumont' kernels roasted at 50 °C (0.071 and 0.097 mg quercetin kg^{-1}), 75 °C (0.071 and 0.089 mg quercetin kg^{-1}), 100 °C (0.067 and 0.075 mg quercetin kg^{-1}), 125 °C (0.066 and 0.071 mg quercetin kg^{-1}) and 150 °C (0.053 and 0.067 mg quercetin kg^{-1}) significantly ($p < 0.001$) decreased with increasing roasting temperature. Kunyanga et al. (2011) reported that flavonoids concentration of food and its functional properties could be altered during thermal processing, depending on temperatures used to roast products which could result to a decrease of flavonoids concentration (Randhir et al., 2008). McDaniel et al. (2012) reported that during roasting some antioxidants are lost due to chemical reactions such as Maillard browning reaction. In our study, roasting 'A4' and 'Beaumont' kernels at 150 °C further reduced the concentration of flavonoids (Fig. 3). This could be attributed to quality deterioration observed in kernels roasted at 150 °C such as high levels of PV (Fig. 2) which could potentially promote the development of off-flavours (Chutichudet and Chutichudet, 2011). The decrease of flavonoids concentration at 150 °C could further be attributed to polymerization reactions between 5-hydroxymethylfurfural (HMF) and flavonoids and the hydrolytic mechanisms since HMF formation and polymerization are enhanced at low moisture content. This supports our findings as Fig. 1 shows that kernels roasted at 150 °C had the lowest moisture content which could promote the loss of flavonoids. Duarte et al. (2005) reported that high roasting temperatures may cause evaporation of intracellular water, triggering profound changes in the chemical composition such as protein, amino acids, reducing sugars, sucrose, trigonelline, chlorogenic acid and melanoidins formation which is mainly due to Maillard reactions. These chemical reactions may potentially result to the loss of flavonoids. Although there is limited published studies reporting on the effect of processing on flavonoids concentration of macadamia nuts, our findings are similar to Yang (2009) who reported the similar range of flavonoids concentration (1.38 mg g^{-1}). This suggests the necessity of further research on effect of roasting temperatures on phytochemical quality such as flavonoids of macadamia nuts.
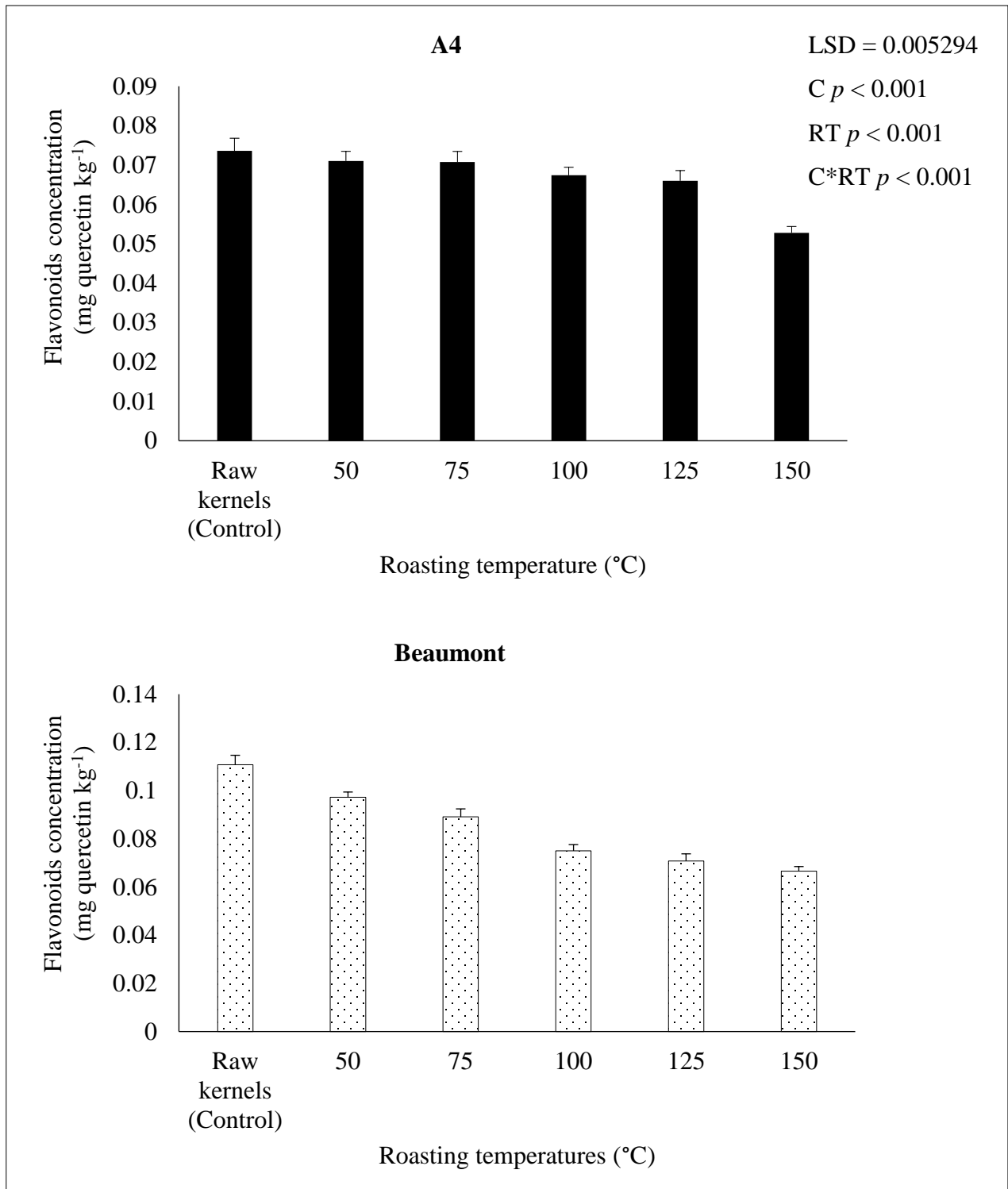
Fig. 3: Flavonoids concentration of 'A4' and 'Beaumont' after roasting for 15 min. Vertical bars represent standard errors of differences of means. LSD, least significant difference; C, cultivar; RT, roasting temperatures; C*RT, cultivar and roasting temperatures.

3.4. Phenolic concentration

Phenolic concentration was found to be in accordance with flavonoids concentration, where phenolic concentration of 'A4' and 'Beaumont' roasted at 50 °C (0.096 and 0.143 mg GAE kg^{-1}), 75 °C (0.095 and 0.137 mg GAE kg^{-1}), 100 °C (0.089 and 0.130 mg GAE kg^{-1}), 125 °C (0.082 and 0.127 mg GAE kg^{-1}) and 150 °C (0.038 and 0.087 mg GAE kg^{-1}) significantly ($p < 0.001$) decreased with increasing roasting temperature which could be attributed to the degradation of polymensed polyphenols, mainly hydrolysable tannins and the hydrolysis of other glycosylated flavonoids (Monagas et al., 2009). Jinap et al. (2004) reported that most phenolic compounds are highly unstable and might be lost during processing. In Fig. 4, it can be observed that roasting 'A4' and 'Beaumont' kernels at 150 °C further reduced phenolic concentration which is in agreement with García-Alamilla et al. (2017) who reported that roasting temperatures above 130 °C leads to a gradual decrease of total phenolic concentration as a consequence of thermal and oxidative degradation of polyphenols and intermediate products of brown reaction. Furthermore, Kotsiou and Tasioula-Margari (2016) reported that the degradation of phenols at high roasting temperatures could be due to oxidation and hydrolysis or rancidity. This further supports our findings as Fig. 2 shows that kernels roasted at 150 °C had high PV which is a measurement of oxidation or rancidity (Borompichaichartkul et al., 2013). Our findings are related to Munro (2008) who reported similar concentration of phenols (1.56 mg GAE g^{-1}) on roasted kernels of macadamia nuts.

Fig. 4: Phenolic concentration of 'A4' and 'Beaumont' after roasting for 15 min. Vertical bars represent standard errors of differences of means. LSD, least significant difference; C, cultivar; RT, roasting temperatures; C*RT, cultivar and roasting temperatures.

3.5. Antioxidant activity [DPPH (2,2'-diphenyl-1-picrylhydrazyl) and ABTS (2,2'-azinobis-3-ethylbenzothiazoline-6-sulfonic acid) assay]

Changes in antioxidants activity were consistent with the depletion of flavonoids (Fig. 3) and phenols (Fig. 4). The antioxidants activity (DPPH and ABTS) of 'A4' and 'Beaumont' cultivars significantly ($p < 0.001$) decreased with increasing roasting temperature. 'A4' and 'Beaumont' kernels roasted at 50 °C had high concentration of antioxidants (0.017 and 0.017 ABTS mg GAE kg^{-1} and 0.005 and 0.007 DPPH mg GAE kg^{-1}) compared to the kernels roasted at a higher temperature; 150 °C (0.003 and 0.005 ABTS mg GAE kg^{-1} and 0.001 and 0.006 DPPH mg GAE kg^{-1}), respectively. From Fig. 5 and 6, it can be observed that roasting 'A4' and 'Beaumont' kernels at 150 °C further reduced the antioxidants activity which is in agreement with Açar et al. (2009) who reported similar decrease of antioxidants in hazelnuts roasted at 180 °C, which could be due to the oxidation of phenols (Ali et al., 2018). Votavová et al. (2009) and Dybkowska et al. (2017) reported that higher roasting temperatures such as 160 °C promotes excessive browning in products often referred to as dark roast in beans and further decreases the total antioxidants activity due to oxidation, hydrolysis, decarboxylation and other degradative chemical reactions, leading to the deterioration of the products sensory and chemical quality. This further supports our findings as kernels roasted at 150 °C showed a significant increase of rancidity (Fig. 2).

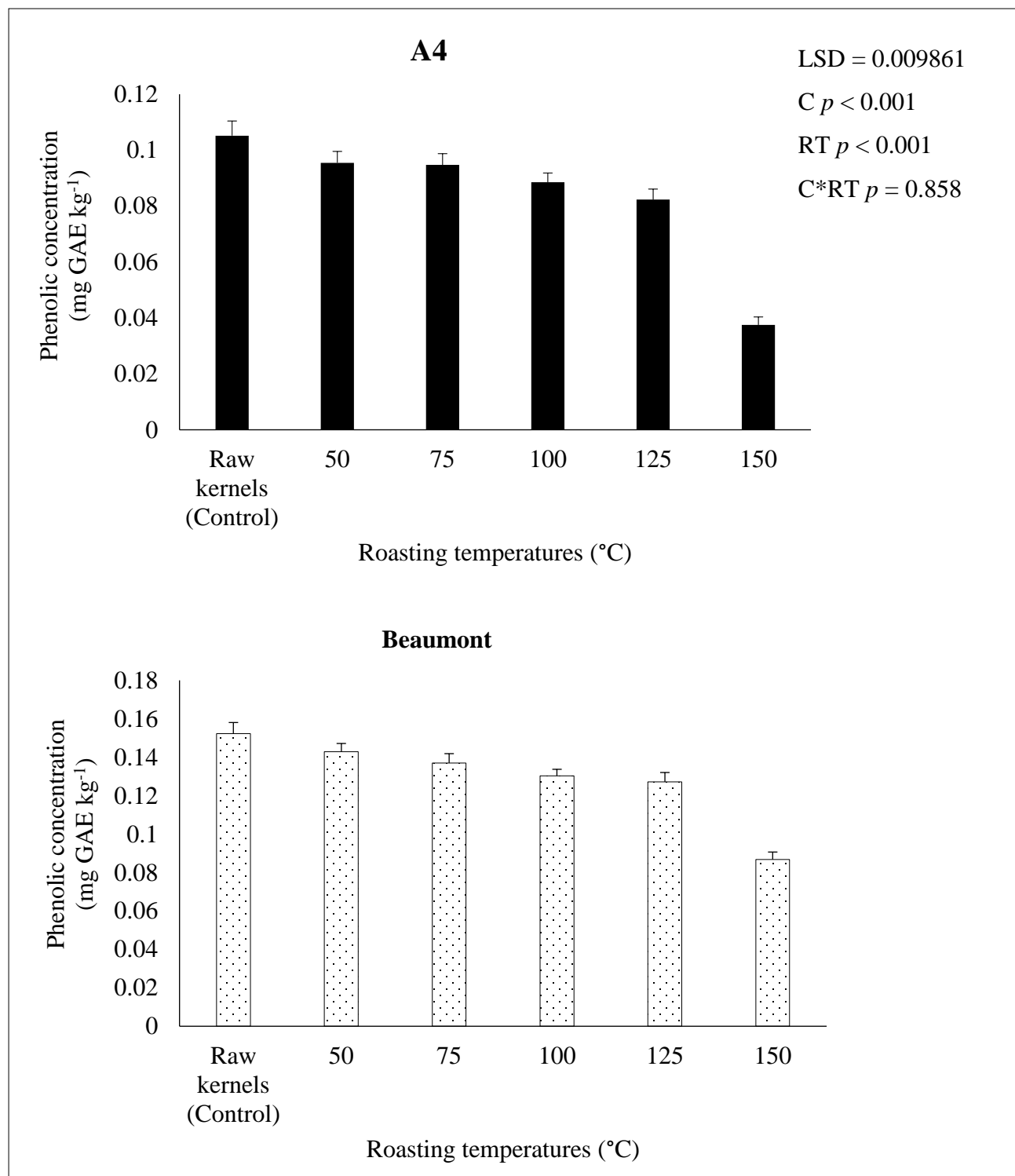Fig. 5: Antioxidants activity (DPPH) of 'A4' and 'Beaumont' after roasting for 15 min. Vertical bars represent standard errors of differences of means. LSD, least significant difference; C, cultivar; RT, roasting temperatures; C*RT, cultivar and roasting temperatures.
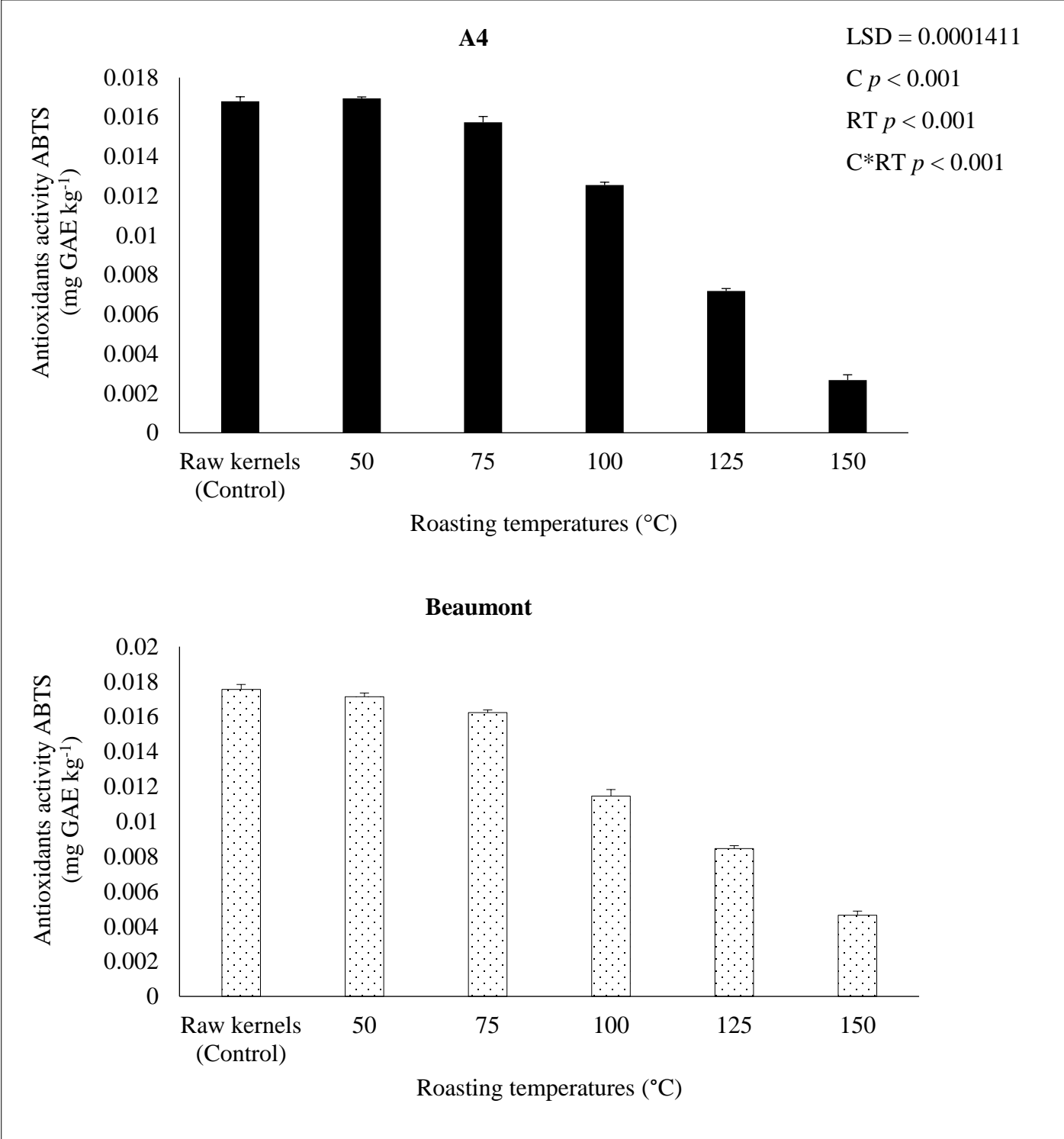
Fig. 6: Antioxidants activity (ABTS) of 'A4' and 'Beaumont' after roasting for 15 min. Vertical bars represent standard errors of differences of means. LSD, least significant difference; C, cultivar; RT, roasting temperatures; C*RT, cultivar and roasting temperatures

3.6. *Sensory evaluation*

3.6.1. *Kernel texture*

In Fig. 7, it can be observed that 'A4' and 'Beaumont' kernels became significantly ($p < 0.001$) crispy with increasing roasting temperature which is regarded as a basic characteristic of roasted kernels (Soleimanieh et al., 2015). This could be due to heat penetration into the kernels thus reducing the moisture content and making kernels crispy (Shi, 2015). Lee and Resurreccion (2006) and Boge et al. (2009) reported that the roasting process changes the internal microstructure of samples, resulting in a texture that is typically more brittle, crispy, and or crunchy. The panelists preferred kernels roasted at 125 °C due to the appealing crispy texture. Our findings are similar to Moghaddam et al. (2016) who reported that eight trained panelists preferred pistachio kernels roasted at 120 °C due to the appealing crispy texture of kernels. Fig. 7 also shows that kernels roasted at lower temperatures (50 °C, 75 °C and 100 °C) had a hard texture which is similar to Mridula et al. (2007), Jokanović et al. (2012) and Moghaddam et al. (2016) who reported that pistachio and soybeans kernels roasted at lower temperatures (< 100 °C) had a hard texture which is less crispy. 'A4' and 'Beaumont' kernels roasted at 150 °C had unappealing excessive crispiness due to heat stress (Nikzadeh and Sedaghat, 2008).
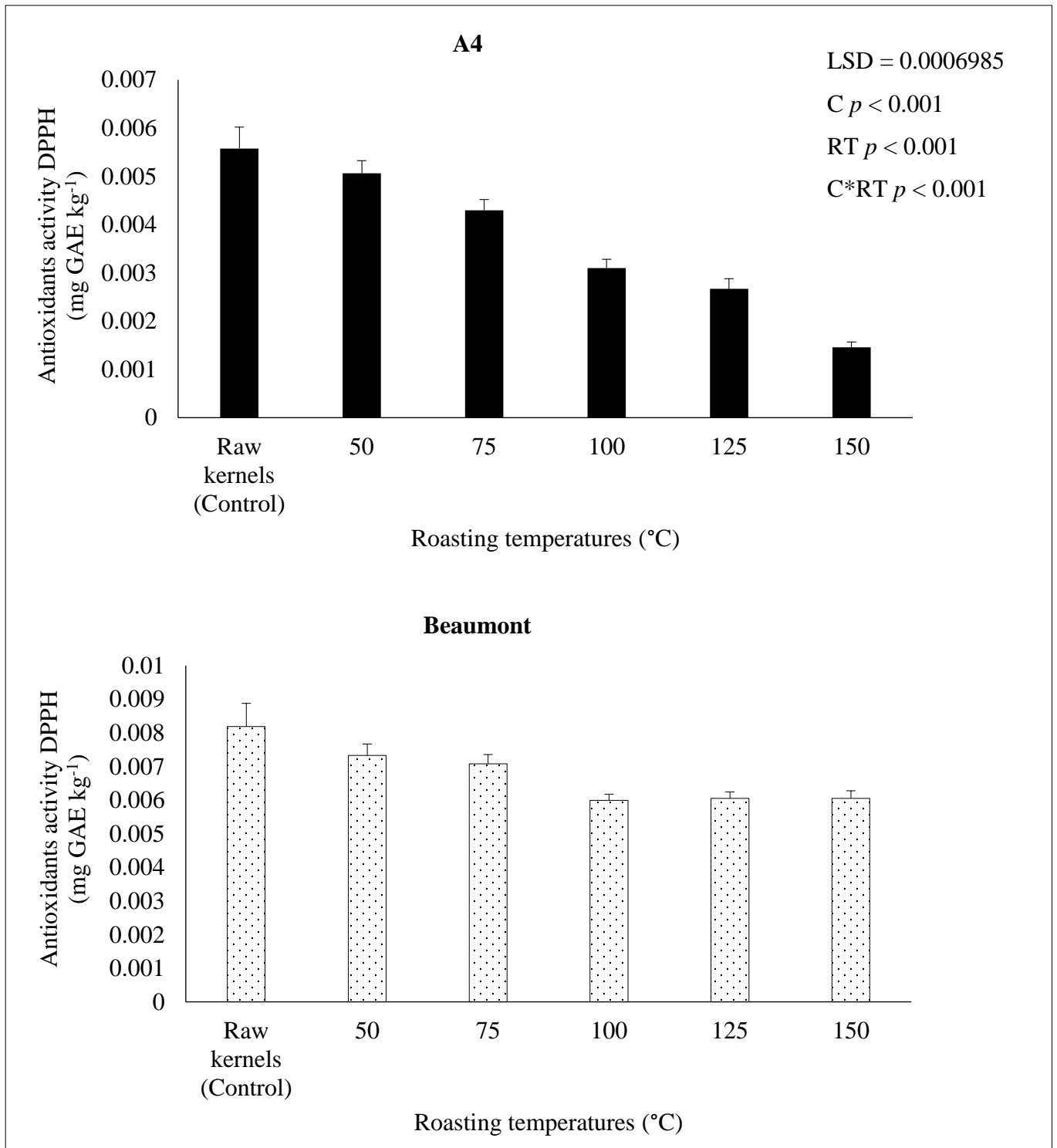
Fig. 7: Kernel texture of 'A4' and 'Beaumont' after roasting for 15 min. Vertical bars represent standard errors of differences of means. LSD, least significant difference; C, cultivar; RT, roasting temperatures; C*RT, cultivar and roasting temperatures.

3.6.2. Kernel colour

Colour is one of the parameters that are used for process control during roasting because the brown pigments increase as the browning and caramelization reactions progress (Moghaddam et al., 2016). It is also among the most important quality attributes of roasted nuts and as well as an indicator of kernel flavour (Shi, 2015; Soleimanieh et al., 2015; Wang, 2015). In our study, kernels roasted at lower temperatures (50 °C and 75 °C) had a light colour which was considered poor by the panelists whereas roasting temperatures above 75 °C significantly ($p < 0.001$) enhanced the colour of kernels (Fig. 8). 'A4' and 'Beaumont' kernels became more browner with increasing temperatures which could be attributed to the development of pyrazines and pyridines compounds, which are characteristic products resulting from non-enzymatic browning reactions such as Maillard browning and caramelization (Corzo-Martınez et al., 2012; Phatanayindee et al., 2012; Walton et al., 2013). Le Lagadec (2009) reported that during roasting enzymatic and non-enzymatic reactions occur, resulting in the conversion of sucrose into two reducing sugars: glucose and fructose. The reducing sugars, together with amino acids are key components of the Maillard reaction, which appears to cause the browning of the kernels (Srichamnong and Srzednicki, 2015). In our study, kernels roasted at 125 °C had the most desirable brown colour whereas those roasted at 150 °C were excessively brown which is considered as over roasting (Borjian Borojeni et al., 2016). Our findings are similar to Ng et al. (2014) who reported that roasting almond nuts at temperatures above 150 °C resulted in a darker colour of kernels which could be due to non-enzymatic reaction which occurs when a reducing sugar and protein are heated together (Kahyaoglu and Kaya, 2006).
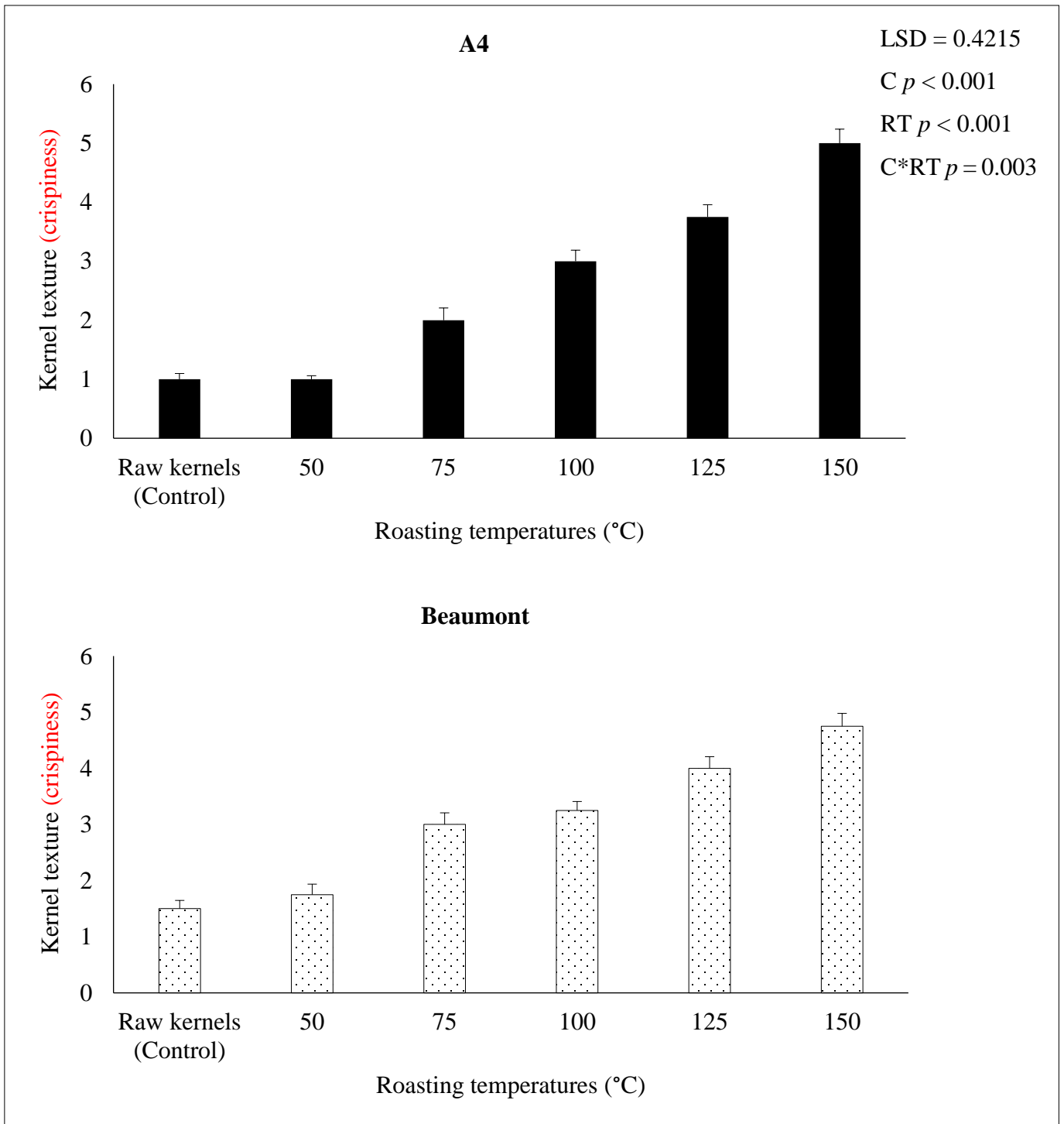
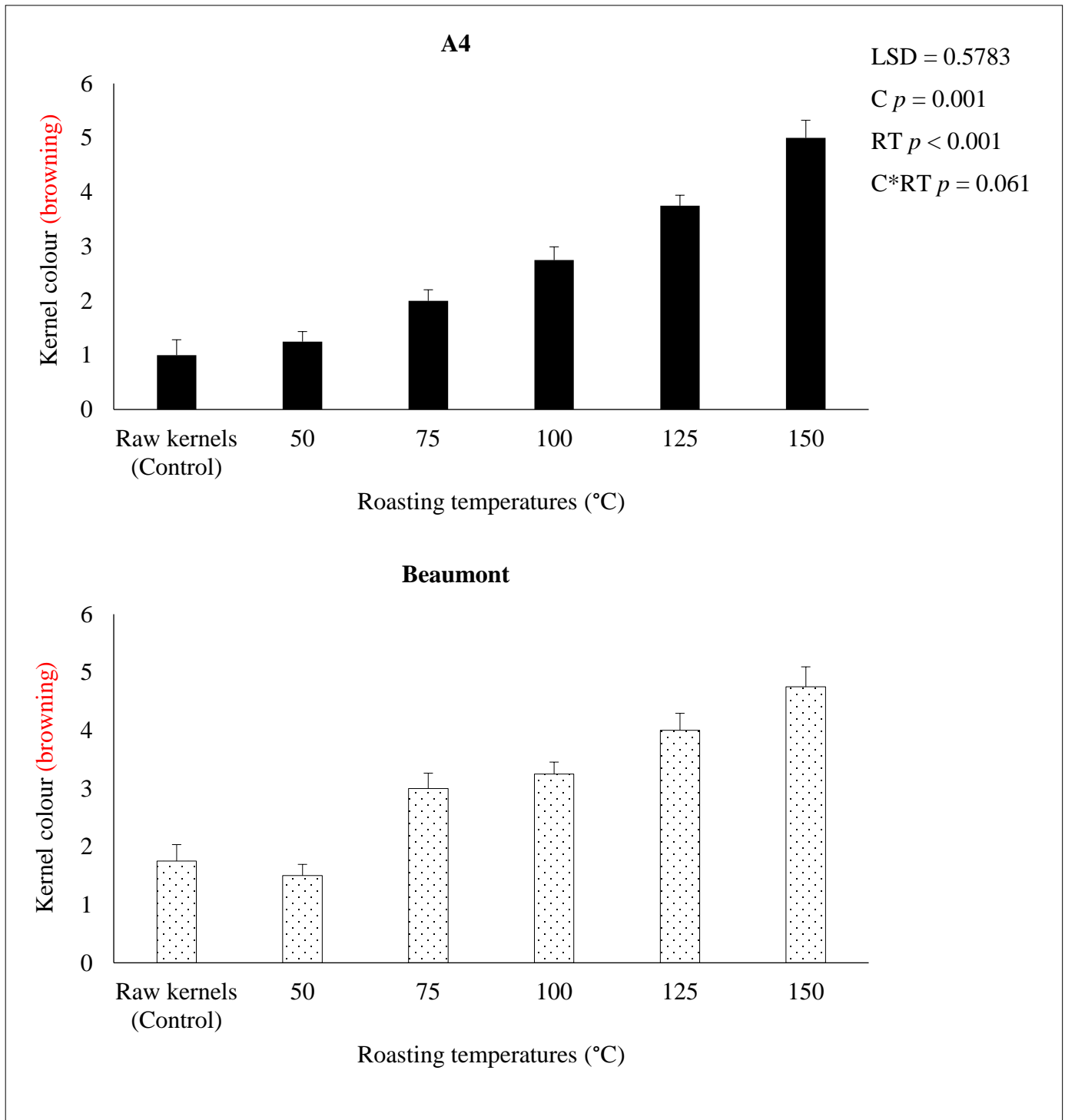Fig. 8: Kernel colour of 'A4' and 'Beaumont' after roasting for 15 min. Vertical bars represent standard errors of differences of means. LSD, least significant difference; C, cultivar; RT, roasting temperatures; C*RT, cultivar and roasting temperatures.

3.6.3. Kernel taste

According to the panelists, kernels roasted at lower temperatures; 50 °C and 75 °C had a slightly nutty taste whereas increasing roasting temperatures above 75 °C significantly ($p < 0.001$) enhanced the flavour of kernels (Fig. 9). 'A4' and 'Beaumont' kernels roasted at 100 °C had a nutty taste and kernels roasted at 125 °C had a very nutty taste which could be attributed to the formation of desirable flavours through Maillard reactions during roasting (Soleimanieh et al., 2015; Taş and Gökmen, 2017). Moghaddam et al. (2016) reported that during roasting chemical changes such as the reaction of carbohydrates with proteins, fats and physiologically active substances occurs which causes the generation of flavour and aroma. Ng et al. (2014), Xiao et al. (2014) and Schlörmann et al. (2015) reported that flavour and aromatic compounds such as benzaldehyde, methylphenol and alkylbenzenes generated during roasting give nuts a more desirable, enhanced and stronger nutty-roasted flavour. Also, kernels roasted at 125 °C had the lowest PV, indicating that kernels had no noticeable off-flavours (Borompichaichartkul et al., 2009). However, 'A4' and 'Beaumont' kernels roasted at 150 °C were rated as severely bitter which is similar to Moghaddam et al. (2016) who reported that higher roasting temperatures (150 °C) caused an increase in bitterness in pistachio kernels. In high roasting temperatures carbohydrates and proteins change, fats are oxide and kernels have a bitter taste (Moghaddam et al., 2016). Özdemir (2001) reported that high roasting temperatures (> 150 °C) affect carbohydrates, proteins and oil stability of hazelnuts and ultimately decreases overall palatability of products and results in the bitterness of kernels. Our findings are also similar to Shi (2015) who reported that high roasting temperatures (149 to 204 °C) resulted to a bitter taste in peanuts due to oxidation of secondary products such as aldehydes, ethanol and ketones which are associated with off-flavours initiated at high roasting temperatures. Also, kernels roasted at 150 °C had higher levels of PV (Fig. 2), excessive crispy texture (Fig. 7) and a dark brown colour (Fig. 8) which is an indication of over roasting and may cause the development of disagreeable compounds such as 5-hydroxymethylfurfural associated with off-flavours or bitter taste (Moghaddam et al., 2016; Taş and Gökmen, 2017).
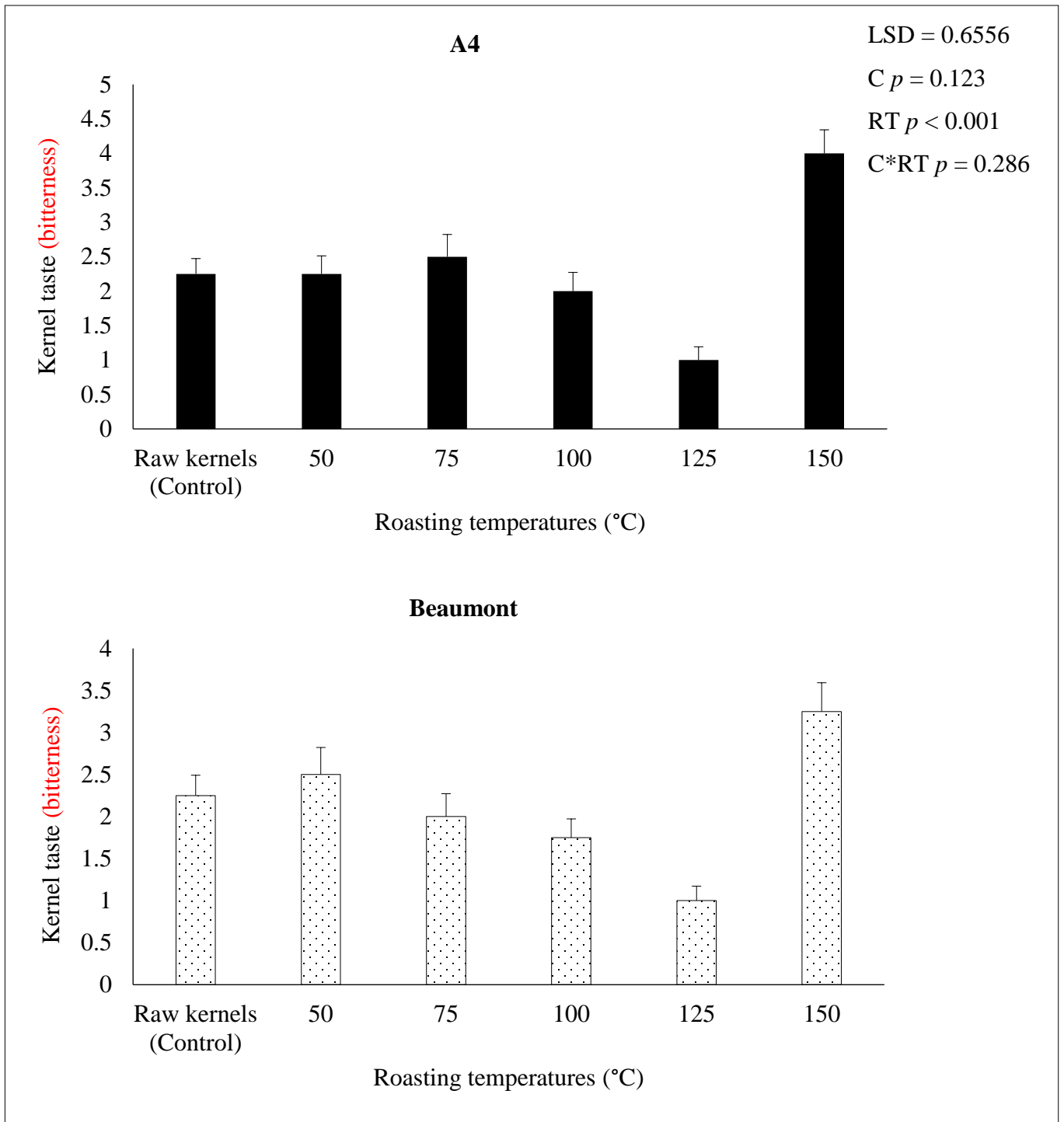
Fig. 9: Kernel taste of 'A4' and 'Beaumont' after roasting for 15 min. Vertical bars represent standard errors of differences of means. LSD, least significant difference; C, cultivar; RT, roasting temperatures; C*RT, cultivar and roasting temperatures.

4. Conclusion

The current study showed that although kernels roasted at low temperatures (50 °C, 75 °C and 100 °C) had slightly elevated levels of antioxidants, they also had higher moisture levels, promoting rancidity as indicated by higher levels of PV and poor kernel texture, colour and taste observed by trained panelists. Increasing roasting temperatures significantly affected the chemical and sensory quality of macadamia nuts. 'A4' and 'Beaumont' kernels roasted at 125 °C had lower levels of rancidity (PV) and significant concentration of flavonoids, phenols and total antioxidants. Also, according to the panelists, kernels roasted at 125 °C had an ideal crispy texture, brown colour and were very nutty. However, kernels roasted at 150 °C had high levels of rancidity, a lower concentration of antioxidants, excessive crispy texture, dark brown colour and bitter taste. Therefore, the findings of the present study suggest that 'A4' and 'Beaumont' kernels should be roasted at 125 °C to avoid quality loss due to over-roasting. It is also not recommended that macadamia kernels be kept raw due to the rapid development of rancidity.

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CHAPTER 5: ROASTING EFFECT ON STORAGE QUALITY OF 'A4' AND 'BEAUMONT' MACADAMIA NUTS (*MACADAMIA INTEGRIFOLIA*)

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Abstract

Macadamia nuts can be stored for about three months at a room temperature. Quality deterioration during the storage is a major problem for macadamia producers and suppliers. Some macadamia cultivars are more susceptible to deterioration than others. Therefore, this research was conducted to evaluate the effect of roasting on storage and postharvest quality of macadamia nuts. Two commercially important macadamia cultivars, namely, 'Beaumont' and 'A4' were used as model cultivars and kernels were roasted at 125 °C for 15 min using the hot air oven dryer. Dried kernels were used as a control. Kernels were stored in a labcon growth chamber at 20 °C for 18 weeks. Sampling for sensory and chemical analysis was done before storage and at 10 days intervals. Peroxide value (PV), acid value (AV), antioxidants (ABTS and DPPH) and phenols for both 'Beaumont' and 'A4' cultivars significantly ($p < 0.001$) increased with increasing storage. 'Beaumont' had lower PV (0.947 to 8.768 meq O_2 kg^{-1}), AV (0.3 to 0.88 %), higher concentration of phenols (0.127 to 1.159 mg GAE kg^{-1}), antioxidants ABTS (0.0145 to 0.132 mg GAE kg^{-1}) and DPPH (0.010 to 0.130 mg GAE kg^{-1}) during storage time. While 'A4' had higher PV (1.161 to 12.01), AV (0.4 to 1.6 %), lower concentration of phenols (0.083 to 0.714 mg GAE kg^{-1}) and antioxidants ABTS (0.008 to 0.075 mg GAE kg^{-1}) and DPPH (0.006 to 0.060 mg GAE kg^{-1}) during storage. The sensory assessment showed that 'Beaumont' had a nutty taste therefore, no noticeable rancid taste throughout the storage period whereas 'A4' had poor nutty taste therefore, noticeable rancid taste after week 12 of storage. In conclusion, roasting kernels at 125 °C showed that

'Beaumont' could be stored for about 18 weeks and more whereas 'A4' could be stored for about 12 weeks at 20 °C due to susceptibility to deterioration during storage.

Keywords: Peroxide value; Acid value; Phenols; Antioxidant activity; Sensory evaluation

1. Introduction

Macadamia (*Macadamia integrifolia*) is one of the most important tree nuts in the word with the annual production of about 100 000 tons (du Preez, 2015; Rengel et al., 2015). Macadamia is mainly cultivated in Australia (32 %), South Africa (30 %) and Kenya (12 %) and is highly valued by the food industry for the quality and sensory characteristics of its kernels, particularly for the use in confectionery products (Eagappan and Sasikumar, 2014; Jaskiewicz, 2015; Navarro and Rodrigues, 2016). Macadamia nuts are a rich source of oil and have a lipid content of about 80 % which is rich in monounsaturated fatty acids such as oleic (60 %), palmitoleic (20 %) and gadoleic (2.48 %) acids (Eagappan and Sasikumar, 2014; Sinanoglou et al., 2014). These fatty acids have a recognized beneficial effect on human health (Sabate and Ang, 2009; Torabian et al., 2009) and may also cause hydrolytic and oxidative rancidity which is usually indicated by acid value and peroxide value, respectively (Borompichaichartkul et al., 2013; Canneddu et al., 2016).

Rancidity leads to undesirable odours and flavours and to the reduction of nutritional value and kernel shelf life (Mencarelli et al., 2008; Tavakolipour et al., 2010). Macadamia can be stored as nut-in shell or shelled nuts (kernels) for about 3 months at room temperature, 12 months at 2 °C and 18 months at -18 °C (Fourie and Basson, 1989; Kaijser et al., 2000; Wall and Gentry, 2007) and rancidity is a major factor limiting macadamia storability (Kaijser et al., 2000; Srichamnong et al., 2010). Also, kernels are being sold as "macadamia" without distinguishing their genetic content or cultivars, which could negatively affect their composition and quality by causing rancidity therefore limiting shelf life of kernels (Gitonga et al., 2009; Hardner et al., 2009; Le Lagadec, 2009). There is limited published research studies reporting on the onset of rancidity during long term storage of macadamia nuts.

Macadamia nuts also contain significant quantities of dietary fiber, essential minerals, vitamins and antioxidants due to several groups of phytochemicals and polyphenols also present in kernels (Eagappan and Sasikumar, 2014; Rengel et al., 2015). Recently, there is much interest in the phenolic compounds due to potential health benefits related to their antioxidant and antiradical activities, anti-inflammatory properties, anticarcinogenic and antimutagenic effects and

antiproliferative potential (Alasalvar and Shahidi, 2008; Buthelezi, 2015). Previous studies report that antioxidants have the ability to scavenge reactive oxygen species, most commonly hydrogen peroxide, superoxide radical and hydroxide radical produced within the plant tissue (Franke et al., 2007; Rahman, 2016) therefore, protecting kernels from oxidation reactions during storage and marketing, thereby extending shelf life of nuts (Kornsteiner et al., 2006; Wall, 2010). However, there is limited data regarding the stability of phenolic compounds and the antioxidant activity of roasted macadamia nuts during storage. Alasalvar and Shahidi (2008) reported that macadamia nuts had a significant concentration of antioxidants activity ranging from 0.11 to 0.75 mM/ 100 g, however, little is known about the effect of antioxidants on postharvest quality and storability of macadamia nuts.

For a successfully storage, it is commercially recommended that macadamia nuts be dried immediately after harvesting and before roasting to a 1.5 % kernel moisture content to avoid quality derioration as high moisture content influences quality parameters such as mold growth and rancidity (Borompichaichartkul et al., 2009; Wang et al., 2014). Kernel moisture content of 1 % after roasting is regarded vital for maximizing sensory and chemical quality and for extending protection from the rancidification process and shelf life of macadamia nuts (Borompichaichartkul et al., 2009; Phatanayindee et al., 2012; Wang et al., 2014).

It has been previously reported that roasting nuts at mild temperatures of 100 to 130 °C and obtaining a kernel moisture content of 1 % after roasting significantly enhances flavour, aroma, colour, texture and appearance of the nuts through non-enzymatic (Maillard browning) reactions resulting from the reaction between sugars and amino acids (McDaniel et al., 2012; Schlörmann et al., 2015; Taş and Gökmen, 2017). Roasting also inactivates oxidative enzyme system (lipoxygenic enzymes), responsible for degradative reactions such as lipid oxidation or rancidity (Belviso et al., 2017; Taş and Gökmen, 2017). However, little is known about the postharvest quality and shelf life of roasted macadamia nuts, therefore, the current study evaluates the quality of mild roasted (125 °C) macadamia nuts during the accelerated storage of four and a half months (18 weeks).

2. Materials and methods

2.1. Macadamia samples

Two hybrids of Australian-bred cultivars of *Macadamia integrifolia* namely, 'Beaumont' and 'A4' were harvested from the commercial orchards of Elliot Farm in Port Shepstone, South Coast of KwaZulu-Natal, South Africa (latitude: 30°44′28″ S, longitude: 30°27′17″ E and altitude: 36 m). Nuts were harvested during the harvesting season (May to June 2017) based on industry practice. About 50 kg of nuts per cultivar were harvested and transported to Ukulinga Research Farm of the University of KwaZulu-Natal (UKZN) for further processing.

2.2. Dehusking, drying and cracking process

Dehusking (01-one-lane dehusker, Sheet Metal Works, Tzaneen, South Africa) was done on the same day of harvesting at Ukulinga Research Farm of UKZN. Following a method described by Walton et al. (2013) with slight modifications, immediately after dehusking, nut-in-shell were weighed and dried using a mechanical convection oven (RY-EB-550, Rongyao factory, Mainland, China) at Postharvest Research Laboratory of UKZN for three consecutive days, starting with 35 °C on the first day, 38 °C on the second day and 50 °C on the third day. These drying temperatures were selected according to the nut industry practice to avoid quality deterioration (Belviso et al., 2017; Walton et al., 2017). Dried nuts were checked for moisture content and were only removed from the oven when moisture content had reached 1.5 %. The moisture content of nuts was based on initial and final (dry) weight. Mass changes in nuts were used to calculate moisture content on a dry basis (d.b.) (Wang et al., 2014). Moisture content was determined according to Khir et al. (2011) as follows:

$$MC_{db} = \frac{W_i\text{-}W_d}{W_d} \times 100 \tag{1}$$

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Where MC_{db} is moisture content on a dry mass basis, W_i and W_d are the initial and the dry sample weights, respectively. Furthermore, macadamia nuts were mechanically cracked into wholes, halves and pieces using a commercial mechanical macadamia nutcracker (TZ-150 macadamia nut cracker, Alibaba Group Houlding (PTY) LTD , Hangzhou, China). The shell and kernel were separated manually or by hand and kernel recovery was calculated and expressed as a percentage weight of the nut that is kernel at 1.5 % moisture content, the rest being a shell (Eq. 2) and only full kernels were used for the experiment. Nuts that are dried to 1.5 % kernel moisture content for the purpose of dehusking and cracking are referred to as raw kernels (du Preez, 2015).

$$KR\ (\%) = \frac{NIS\ \text{-Shell}}{NIS} \times 100 \qquad\qquad (2)$$

where KR is kernel recovery and NIS is nut-in-shell.

2.3. Roasting process

The roasting process was carried out according to Wall and Gentry (2007) and Srichamnong and Srzednicki (2015), with slight modifications. 'Beaumont' and 'A4' were used as two distinct cultivars during the early and late harvesting seasons. Only full kernels with no visible defects were used for sampling. The kernels were roasted using convection oven (RY-EB-550, Rongyao factory, Mainland, China) at 125 °C for 15 min. This roasting temperature was selected based on the nut industry practice to avoid quality deterioration (Belviso et al., 2017; Taş and Gökmen, 2017; Tonfack Djikeng et al., 2018).

2.4. Storage conditions

Since macadamia nuts can be stored for about 18 months or more with proper storage conditions, the evaluation of kernel palatability is important (Kaijser et al., 2000; Wall and Gentry, 2007). When determining if a product is suitable for consumption, several factors including organoleptic properties such as texture, taste, odour and appearance, microbial spoilage and chemical changes

to the product during storage must be taken into consideration (Corradini and Peleg, 2007; Erten, 2016; Taş and Gökmen, 2017; Walton et al., 2017). Accelerated shelf life studies includes accelerated storage conditions such as elevated temperatures, applied to eligible product to predict product shelf life at a typical storage condition (Corradini and Peleg, 2007; Folasade and Subomi, 2016; Mereles et al., 2017; Walton et al., 2017). In the current study, roasted kernels of 'A4' and 'Beaumont' were stored in a labcon growth chamber (Labotec, Model FSIM16, Labotec (PTY) LTD, Durban, South Africa) at 20 °C for 18 weeks for the evaluation of sensory and chemical changes during the accelerated storage.

2.5. Experimental design

Roasted kernels of 'A4' and 'Beaumont' cultivars were used as two distinct treatments. Raw kernels of 'A4' and 'Beaumont' cultivars were used as a control. Only full kernels with no visible defects were used for sampling. A randomly sampled set of 15 replicates per cultivar, each weighing 2 kg were packed in commercial brown paper bags for postharvest storage trials. Kernels were stored for four and a half months (18 weeks) and were sampled before storage and every after 10 days until the end of storage. Kernels were evaluated for sensory quality: nutty taste and rancid taste, according to a visual standard scale or hedonic scale and chemical quality: peroxide value, acid value, phenols and antioxidants activity (DPPH and ABTS).

2.6. Quantification of peroxide value

After roasting, kernels were ground into fine powder using a blender (brabantia-table blender, BBEK 1051, Massdiscounter (PTY) LTD, Johannesburg, South Africa). Kernel oil content was measured from ground sample material and quantified using a method described by Meyer and Terry (2008), with slight modifications. Hexane (9.0 mL) was added into a test tube containing 3 g of ground kernel sample and the test tube was placed into an ultrasonic bath (Labotec, Model No. 132, Labotec (PTY) LTD, Johannesburg, South Africa) for 10 min. The supernatant was filtered under vacuum and another 6 mL hexane was added to the residue in the test tube. This was left for 5 min before the test tube was emptied into the Buchner funnel. After filtration, 15 mL

hexane was dried off the supernatant using a GenVac® concentrator (SPScientific, Genevac LTD., Suffolk, UK) under vacuum leaving the oil content of the sample. The residual oil was weighed and presented on dry weight basis.

Peroxide value (PV) was determined according to Walton et al. (2017), with minor modifications. A 1 g of oil sample was dissolved in 20 mL of acetic acid/chloroform (3:2 v/v) followed by adding 1 mL of a saturated potassium iodide solution by an additional burette. The reaction took place and iodine was formed. A 50 mL of deionized water was added. Iodine was titrated with $Na_2S_2O_3$ using a burette. Peroxide value (expressed as milliequivalents of peroxide per kilogram of sample) was calculated according to the following formula:

$$PV \text{ (meq per kg)} = \frac{(S - B) \times N \times 1000}{\text{Sample wt (g)} \times 1000} \tag{3}$$

where S = sample titration (µL); B = Blank titration; and N = normality of $Na_2S_2O_3$.

2.7. Quantification of Acid value

Acid value (AV) was determined according to Kardash and Tur'yan (2005) and Canneddu et al. (2016), with minor modification. A 3 g of macadamia oil was weighted in a 125 mL Erlenmeyer flask and 25 mL of ether-ethanol (2:1) solution was added. A 0.01 M of NaOH solution was used to neutralize the oil and phenolphthalein was used as an indicator. The AV was expressed as the percentage of oleic acid and was calculated according to the following formula:

$$AV \text{ (\%)} = \frac{56.1\, V \times N}{W} \times 100 \tag{4}$$

where V = volume in mL of NaOH used as the standard; N = normality of NaOH solution and W = weight in g of the sample.

2.8. Quantification of free and membrane bound phenols

Phenols were determined based on Hertog et al. (1992), with slight alterations. Roasted kernel sample (1 g each) was mixed with 10 mL 99.8 % (v/v) methanol and vortexed for 30 s. Thereafter, the mixture was shaken overnight at room temperature to extract the free phenols. Afterward, the mixture was centrifuged, and the supernatant was filtered through Whatman® no. 1 filter paper and the sample was again rinsed with 10 mL of solvent until the rinsing solvent was clear.

Then, the acid hydrolysis was also used for the remaining kernel residue to efficiently release cell wall-bound phenols. Briefly, a 10 mL portion of acidified (2 M hydrochloric acid) 60 % aqueous methanol was added to each sample and placed in a hot water bath at 90 °C for 90 min. Glass tubes were allowed to cool, and supernatants were filtered through a 0.45 µm filter.

The total phenolic concentration was determined spectrophotometrically using Folin-Ciocalteu reagent (5 mL of distilled water + 1 mL of extract + 1 mL Folin-Ciocalteu reagent + 10 mL of 7 % Na_2CO_3 + 8 mL of distilled water and left at room temperature for overnight) at 750 nm using gallic acid monohydrate as a standard and the total phenolic concentration was expressed as mg Gallic Acid Equivalents (GAE) kg^{-1} DW.

2.9. Quantification of total antioxidants activity

2.9.1. 2,2'-diphenyl-1-picrylhydrazyl (DPPH) assay

The 2,2'-diphenyl-1-picrylhydrazyl (DPPH) free radical scavenging activity was determined according to Ahmed et al. (2015), with slight modifications. The stock solution of the radical was prepared by dissolving 1.94 mg DPPH in 50 mL of methanol and was kept in a refrigerator at -20 °C until further use. The working solution of the radical was prepared by diluting the DPPH stock solution with methanol to obtain an absorbance of about 0.98 (±0.02) at 517 nm. Kernel samples (1 g) were diluted with 1.5 mL of the extraction solution, methanol: water (80:20). Thereafter, 20 µL of gallic acid or sample extract were measured into polystyrene 4.5 mL cuvette. 800 µL of

absolute methanol was added, followed by 1 mL of 0.1 mM DPPH solution which was added in the dark and covered with aluminium foil and was allowed to stand at room temperature for 60 min. The absorbance was measured at 517 nm against a blank (absolute methanol) under dim light and the results were expressed as mg DPPH GAE kg^{-1} DW.

2.9.2. 2,2'-azinobis-3-ethylbenzothiazoline-6-sulfonic acid (ABTS) assay

The 2,2'-azinobis-3-ethylbenzothiazoline-6-sulfonic acid (ABTS) was determined based on Tesfay et al. (2011), with slight alterations. 2,2'-azinobis-3-ethylbenzothiazoline-6-sulfonic acid was prepared as a 7 mM solution in water or ethanol, for measuring hydrophilic and lipophilic antioxidant fractions, respectively. The ABTS radical cation (ABTS$^{·+}$) was produced by reacting the 7 mM ABTS solution with 2.45 mM ammonium persulfate and allowing the mixture to stand in the dark at room temperature for 3 to 6 h. Kernel tissue (0.2 g) were diluted with 10 mL of acetone. Thereafter, 1.0 mL activated ABTS solution (A_{734} nm = 0.700 ± 0.5) was added to 10 μL sample solution in acetate buffer (pH 4.0). The decrease in absorbance at 734 nm was recorded after 6 min and the results were expressed as mg ABTS GAE kg^{-1} DW.

2.10. Sensory evaluation

A randomized set of macadamia kernels were examined immediately after roasting (125 °C) and at 10 days intervals of storage. Samples were given to trained panelists (5 males and 5 females) ranging from the age of 19 to 48 to assess the quality of 'A4' and 'Beaumont' kernels in terms of their taste (Kita and Figiel, 2007; Nikzadeh and Sedaghat, 2008; Sanful, 2009). Sensory quality of kernels was assessed using hedonic scale. Hedonic scale represents one of the most important sensory methods in the food industry during product development and launching of new products in the market because it informs some measure of whether products are liked or not (Nicolas et al., 2010). This further assists both marketing and Research and Development departments to reach a better product that will satisfy and be accepted by consumers (Singh-Ackbarali and Maharaj, 2014). It also provides insight about the storability of the products based on consumer preference (Singh-Ackbarali and Maharaj, 2014; Wichchukit and O'Mahony, 2015). Hedonic scale usually

ranges from 1 to 9 which represent dislike to like. Recent modifications of the hedonic scale includes the range of 5 (like or excellent) to 1 (dislike or poor) (Mademgne and Dorys, 2016). In our study, the taste of kernels was assessed according to Nikzadeh and Sedaghat (2008) and Sanful (2009) with minor modifications using a five-grade hedonic scale where nutty taste = 1: poor, 2: fair, 3: good, 4: very good and 5: excellent and rancid taste = 1: none, 2: slight, 3: moderate, 4: moderately severe and 5 severe.

2.11. Statistical analysis

The collected data was subjected to the analysis of variance (ANOVA) using GenStat statistical software (GenStat®, 18.1 edition, VSN International, UK) 18.1. Least significant difference values (LSD; $p < 0.001$) were calculated for mean separation.

3. Results and discussion

3.1. Peroxide value (PV)

The PV of 'Beaumont' and 'A4' cultivars significantly ($p < 0.001$) increased with increasing storage. Although PV increased during storage, the 'Beaumont' cultivar showed lower PV, ranging from 0.947 to 8.764 meq O_2 kg^{-1} from the beginning to the end of storage, respectively. Kernels with such low PV (0.947 meq O_2 kg^{-1}) are considered fresh and consumable and are classified at a low oxidation state (Borompichaichartkul et al., 2013). Kaijser et al. (2000), Walton (2005), Moigradean et al. (2012) and Borompichaichartkul et al. (2013) reported that kernels with PV lower 10 meq O_2 kg^{-1} are also acceptable as fresh products or high quality products although classified at moderate oxidation state. The 'A4' cultivar showed increasing PV of 1.161 to 12.01 meq O_2 kg^{-1} during week 0 to week 18 of storage, respectively. Fig. 1 also shows that PV of 'A4' were above the acceptable limit from week 14 (11.119 meq O_2 kg^{-1}) of storage. Moigradean et al. (2012) and Borompichaichartkul et al. (2013) reported that kernels with PV above 10 meq O_2 kg^{-1} are not acceptable and are associated with noticeable off-flavours. Our results are similar to Borompichaichartkul et al. (2009) who reported high PV of 13.58 meq O_2 kg^{-1} in macadamia nuts

associated with rancidity or off-flavours. Canneddu et al. (2016) reported that PV is related to lipid oxidation which constitutes a complex chain of reactions that firstly produces primary products such as peroxides that causes secondary oxidation products such as aldehydes, ketones, epoxides, hydroxy compounds, oligomers and polymers (Kanner, 2007). These compounds result in off-odours and off-flavours and are potentially toxic, which can be threatening to the health of the consumer (Moure et al., 2001). Overall, Fig. 1 demonstrates that roasting significantly ($p < 0.001$) improved shelf-life of kernels which could be attributed to the fact that roasting inactivates enzyme activity and chemical reactions such as hydrolysis of lipids into free fatty acids, often leading to the development of rancidity therefore, extending the storability of kernels (Borompichaichartkul et al., 2013; Das et al., 2014; Pannico et al., 2015).

Furthermore, control treatment showed significantly ($p < 0.001$) high PV (2.567 meq O_2 kg^{-1}) from the beginning of the storage at week 0 which could be attributed to the susceptibility of raw kernels to microbial contamination and enzyme activity associated with oxidation (Pannico et al., 2015; Tenyang et al., 2017; Tonfack Djikeng et al., 2018). Srichamnong and Srzednicki (2015) reported that when nuts or kernels contain free moisture, lipolytic enzymes are active and promotes hydrolysis of lipids into free fatty acids resulting to the development of a rancid taste (Kaleem et al., 2015).

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Fig. 1: Peroxide value of roasted kernels of 'Beaumont' and 'A4' cultivars during the accelerated postharvest storage. Vertical bars represent standard errors of differences of means. LSD, least significant difference; C, cultivar; ST, storage time; C*ST, cultivar and storage time. Raw kernels of 'A4' and 'Beaumont' were used as the control.

3.2. Acid value (AV)

The AV of 'Beaumont' and 'A4' cultivars significantly ($p < 0.001$) increased with increasing storage time. The 'Beaumont' cultivar showed lower AV (0.88 %) at the end of storage. According to the Southern African Macadamia Growers' Association (SAMGA), nuts with AV of less than 0.5 and 1 % are regarded as fresh and of good quality, respectively (Canneddu et al., 2016). This suggest that 'Beaumont' was of good quality and consumable throughout the storage period of 18 weeks. Our findings are similar to Canneddu et al. (2016) who reported AV of 0.7 % in fresh macadamia nuts. The 'A4' cultivar showed increasing and higher AV (1.6 %) at the end of storage. Fig. 2 also shows that AV of 'A4' became unacceptable from week 14 (1.1 %) of storage which is consistence with the results obtained for PV (Fig. 1). Canneddu et al. (2016) reported that

macadamia nuts with AV exceeding 1 % are considered to have a rancid taste. Acid value is related to the acidification of fats due to enzymatic reactions generating free fatty acids which are usually formed during decomposition of triglycerides (Buransompob et al., 2003; Walton, 2005; Walton et al., 2017). Free fatty acids are the main catalyst of hydrolytic rancidity, resulting in a progressive increase of food acidity thereby causing much stronger off-flavours (Peng, 2010; Saponaro et al., 2015; Walton et al., 2017).
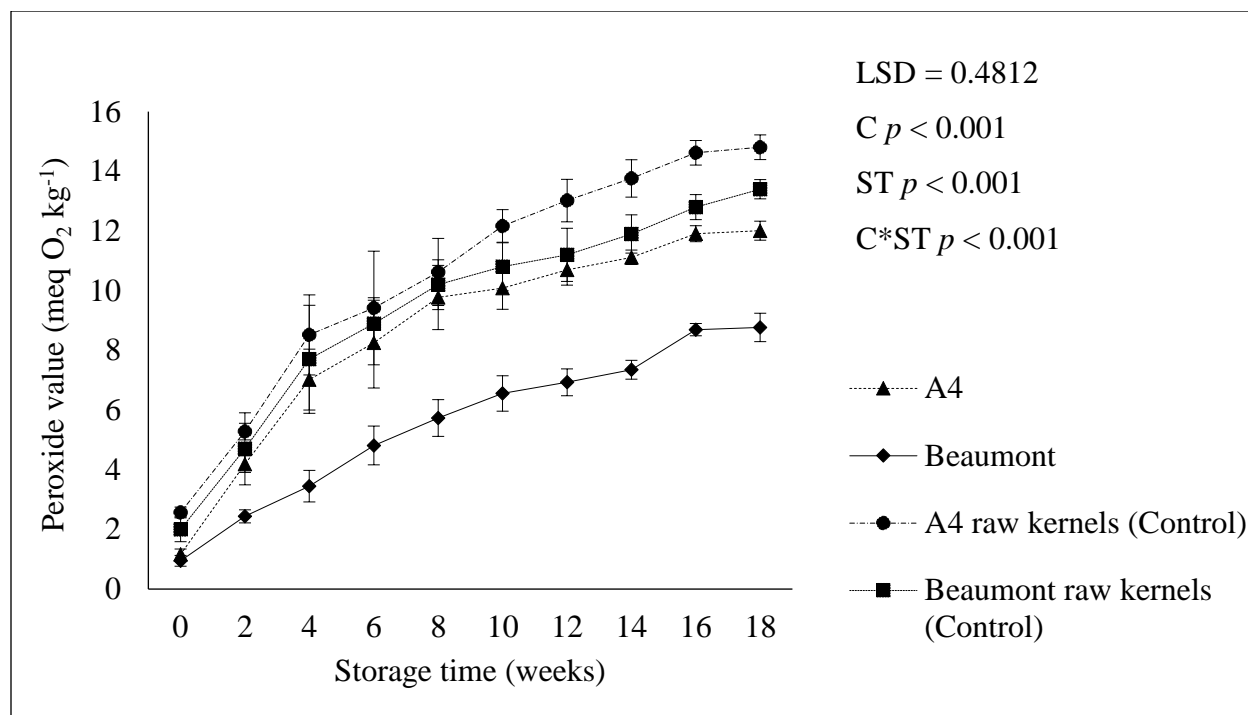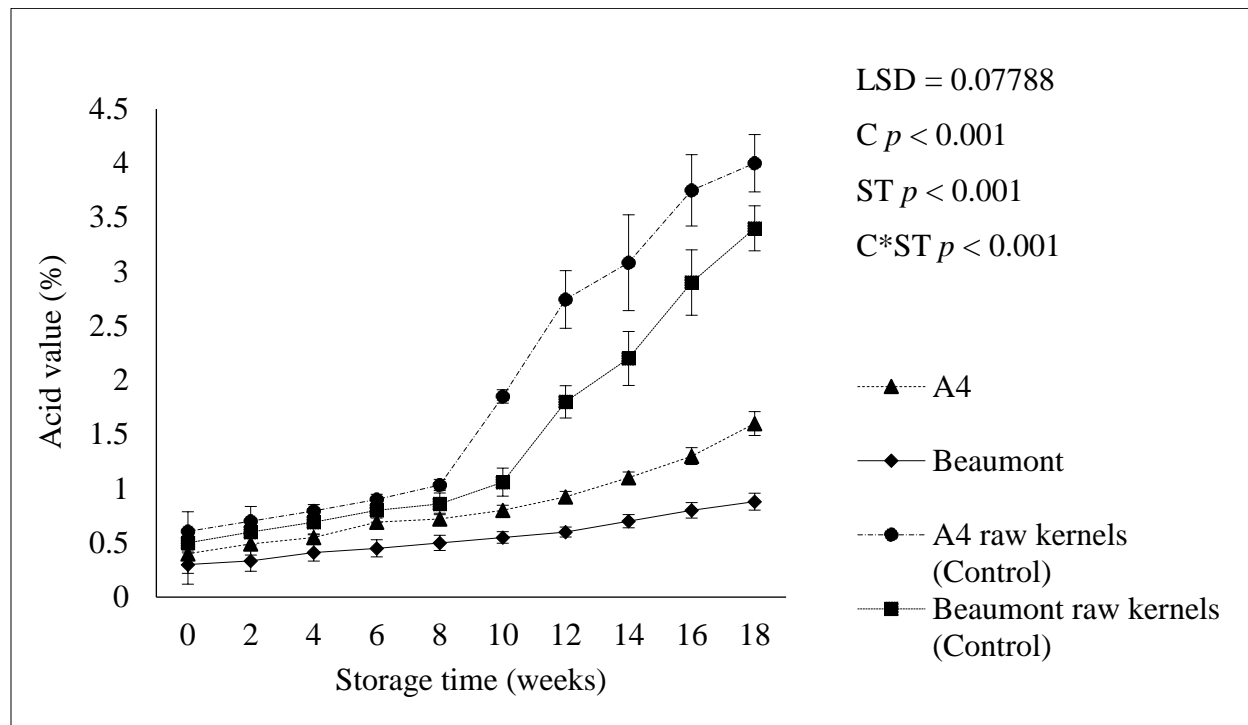

Fig. 2: Acid value of roasted kernels of 'Beaumont' and 'A4' cultivars during the accelerated postharvest storage. Vertical bars represent standard errors of differences of means. LSD, least significant difference; C, cultivar; ST, storage time; C*ST, cultivar and storage time. Raw kernels of 'A4' and 'Beaumont' were used as the control.

3.3. Phenols

The phenolic concentration of 'Beaumont' and 'A4' significantly ($p < 0.001$) increased with increasing storage (Fig. 3). The 'Beaumont' cultivar had high concentration of phenols ranging

from 0.127 to 1.159 mg GAE kg^{-1} from the beginning to the end of storage, respectively. Our findings are related to Munro (2008) who reported similar concentration of phenols (1.56 mg GAE g^{-1}) on roasted kernels of macadamia nuts. 'A4' had low phenolic concentration ranging from 0.082 to 0.714 mg GAE kg^{-1} from week 0 to week 18 of storage, respectively. 'A4' cultivar also showed a significant ($p < 0.001$) decrease of phenolic concentration from week 16 (0.782 mg GAE kg^{-1}) to week 18 (0.714 mg GAE kg^{-1}). Ioannou et al. (2012), Watson et al. (2013), Mediani et al. (2014) and Kotsiou and Tasioula-Margari (2016) reported that the degradation of phenols during processing and storage is the prime origin for the loss of quality and nutrition in many products due to oxidation and hydrolysis. Lipid oxidation and hydrolysis are the main reactions resulting in the deterioration of sensory and nutritional quality of nuts (Walton et al., 2017). Lipid oxidation is associated with unsaturated fatty acids causing off-flavours that develop as a consequence of autoxidation which is a self-sustaining free radical mechanism that produces primary products such as hydroperoxides (Phatanayindee et al., 2012). It is usually autocatalytic, with oxidation products accelerating the reaction so that the rate increases with time (Kashani et al., 2003; Nahm, 2011; Walton et al., 2017). The hydrolysis of the triglycerides which produces free fatty acids is the main catalyst of hydrolytic rancidity, resulting in a progressive increase of food acidity therefore, causing much stronger off-flavours (Saponaro et al., 2015; Walton et al., 2017). This further supports our study as Fig. 1 and 2 shows high PV and AV, respectively in 'A4' which significantly increased during storage, potentially causing degradation of phenols (Ali et al., 2018).

Fig. 3: Phenolic concentration of roasted kernels of 'Beaumont' and 'A4' cultivars during the accelerated postharvest storage. Vertical bars represent standard errors of differences of means. LSD, least significant difference; C, cultivar; ST, storage time; C*ST, cultivar and storage time. Raw kernels of 'A4' and 'Beaumont' were used as the control.

3.4. Antioxidant activity [DPPH (2,2'-diphenyl-1-picrylhydrazyl) and ABTS (2,2'-azinobis-3-ethylbenzothiazoline-6-sulfonic acid) assay]

Changes in antioxidants activity were consistent with the depletion of phenols (Fig. 3) where antioxidants activity (ABTS and DPPH) significantly ($p < 0.001$) increased with increasing storage (Fig. 4 and 5). 'Beaumont' had high concentration of antioxidants ranging from 0.015 to 0.132 ABTS mg GAE kg^{-1} and 0.009 to 0.130 DPPH mg GAE kg^{-1} from week 0 to week 18 of storage, respectively. Although very few studies report on the antioxidants activity of macadamia nuts, our findings could be related to Alasalvar and Shahidi (2008) who reported similar concentration of antioxidants (0.42 FRAP mM/ 100 g) in macadamia kernels. 'A4' had low concentration of antioxidants ranging from 0.008 to 0.075 ABTS mg GAE kg^{-1} and 0.006 to 0.060 DPPH mg GAE

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kg^{-1}) from week 0 to week 18 of storage, respectively. 'A4' also showed a significant ($p < 0.001$) decrease of antioxidants from week 16 (0.080 ABTS mg GAE kg^{-1} and 0.067 DPPH mg GAE kg^{-1}) to week 18 (0.075 ABTS mg GAE kg^{-1} and 0.060 DPPH mg GAE kg^{-1}) of storage. Ali et al. (2018) reported that the degradation of antioxidants in products could be due to oxidation of phenols. Fig. 3 shows a significant ($p < 0.001$) decrease of phenols towards the end of storage which might have caused a depletion of antioxidants (Ioannou et al., 2012; Mediani et al., 2014). Bajaj et al. (2012) and Chaaban et al. (2017) reported that the depletion of bioactive compounds such as antioxidants in products could be due to rancidity. This further supports our findings as Fig. 1 and 2 shows that 'A4' had high PV (12.01 meq O$_2$ kg^{-1}) and AV (1.3 %) at the end of storage, indicating rancid taste or off-flavours (Borompichaichartkul et al., 2013; Canneddu et al., 2016; Walton et al., 2017).

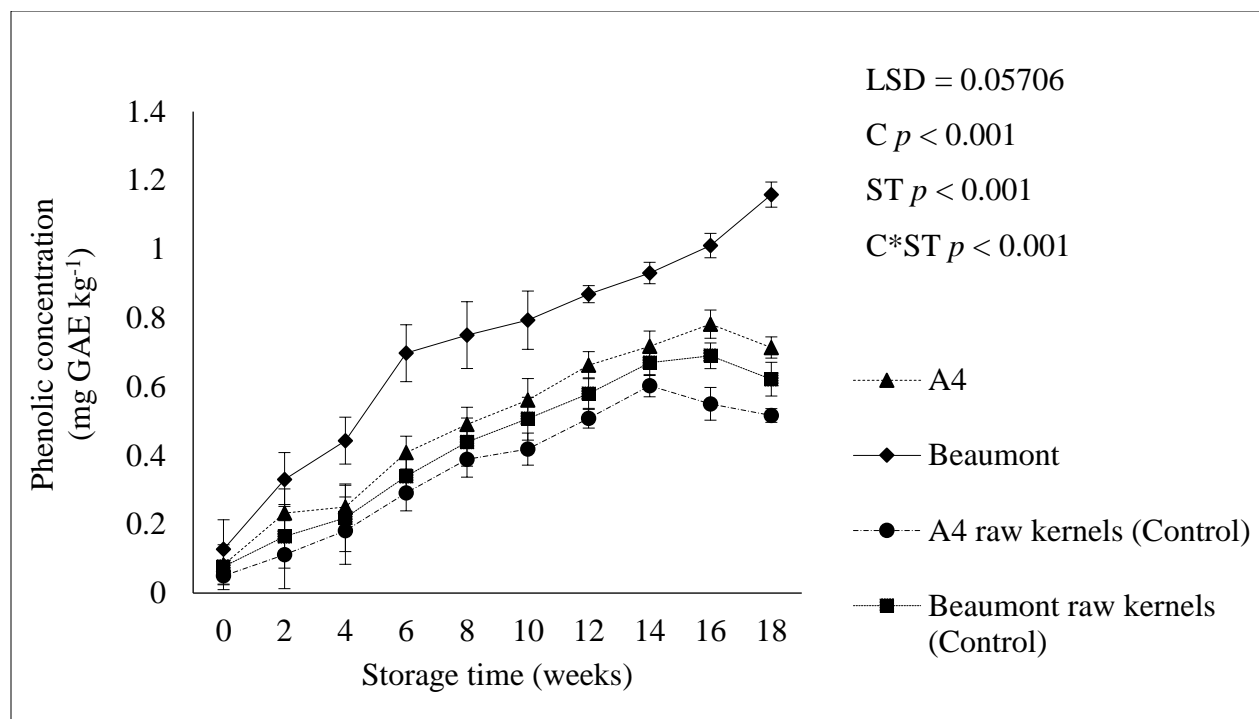Fig. 4: Antioxidants (ABTS) concentration of roasted kernels of 'Beaumont' and 'A4' cultivars during the accelerated postharvest storage. Vertical bars represent standard errors of differences of means. LSD, least significant difference; C, cultivar; ST, storage time; C*ST, cultivar and storage time. Raw kernels of 'A4' and 'Beaumont' were used as the control.
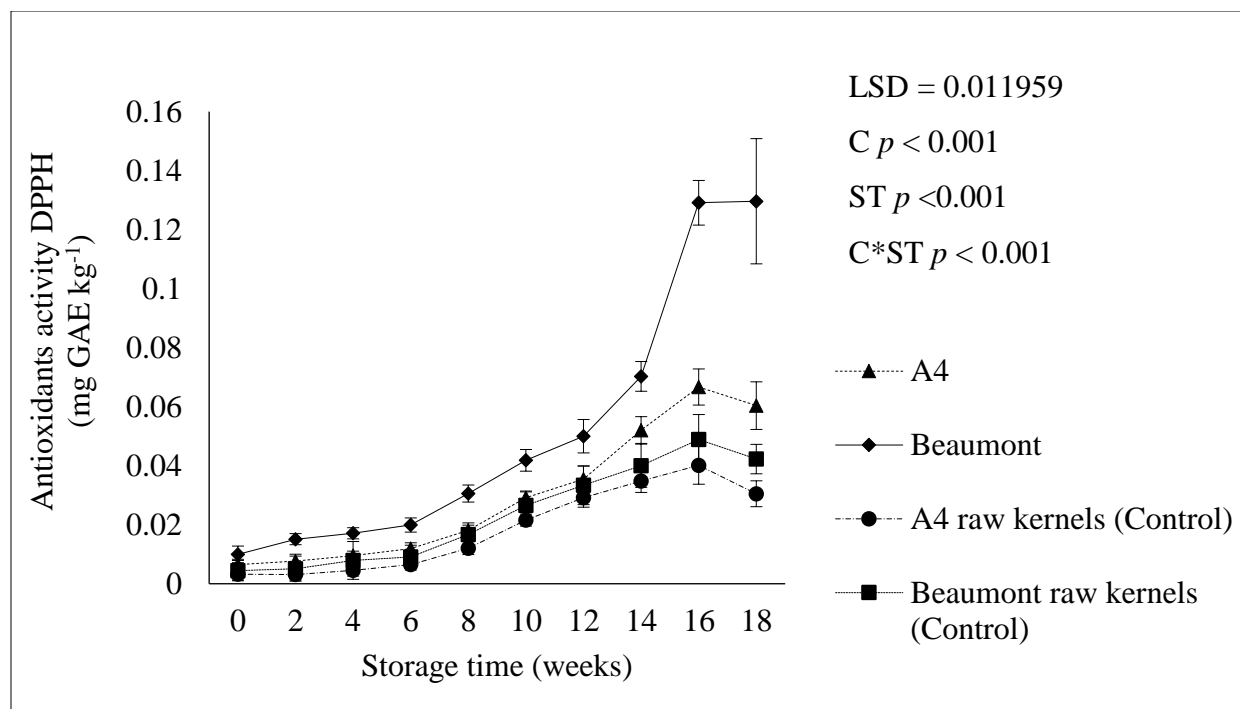
Fig. 5: Antioxidants (DPPH) concentration of roasted kernels of 'Beaumont' and 'A4' cultivars during the accelerated postharvest storage. Vertical bars represent standard errors of differences of means. LSD, least significant difference; C, cultivar; ST, storage time; C*ST, cultivar and storage time. Raw kernels of 'A4' and 'Beaumont' were used as the control.

3.5. Sensory evaluation

3.5.1. Nutty taste

According to the trained panelists, the nutty or sweet taste of 'Beaumont' and 'A4' significantly ($p < 0.001$) decreased during storage. The panelists rated the nutty taste of 'Beaumont' as excellent from week 0 to week 14 and very good from week 16 to week 18 of storage. Overall, 'Beaumont' had a very good taste throughout the storage. This could be attributed to high concentration of phenols (Fig. 3) and antioxidants (Fig. 4 and 5) observed in this cultivar. Kornsteiner et al. (2006), Franke et al. (2007) and Wall (2010) reported that phenols and antioxidants may protect macadamia kernels from oxidative reactions associated with off-flavours, thereby preserving

kernel quality and extending shelf life. The panelists rated the nutty taste of 'A4' as excellent from week 0 to week 6, very good from week 8 to week 10, good from week 12 to week 14 and fair from week 16 to week 18. The loss of flavour in 'A4' kernels during storage could be attributed to the low concentration and loss of phenols (Fig. 3) and antioxidants (Fig. 4 and 5) towards the end of storage (Phillips et al., 2005; Wall, 2010). Our results are also similar to Jensen et al. (2001) who reported that according to trained panelist, the nutty taste of walnut kernels significantly decreased during the storage of 25 weeks and linked this to the loss of quality due to the development of off-flavours during storage.
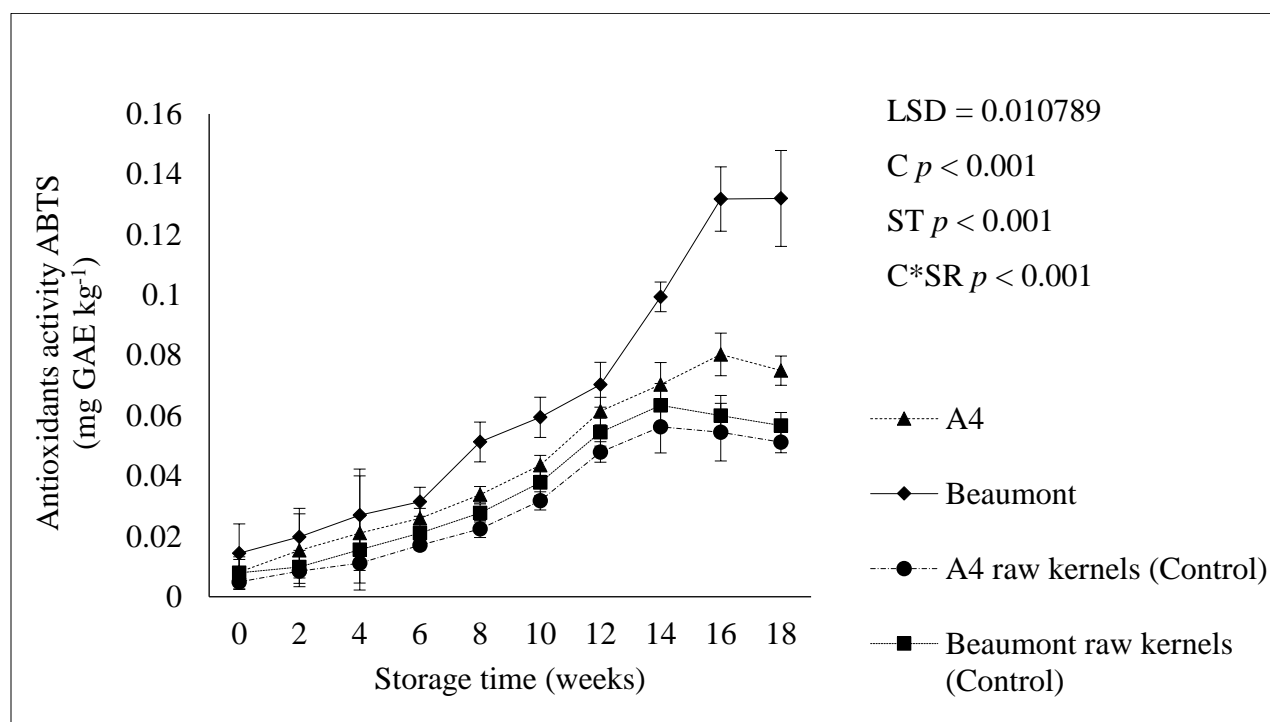

Fig. 6: Nutty taste of roasted kernels of 'Beaumont' and 'A4' cultivars during the accelerated postharvest storage. Vertical bars represent standard errors of differences of means. LSD, least significant difference; C, cultivar; ST, storage time; C*ST, cultivar and storage time. Raw kernels of 'A4' and 'Beaumont' were used as the control.

3.5.2. Rancid taste

The rancid taste of 'Beaumont' was evaluated and scored as 1 from week 0 to week 16 and 1.2 at week 18 meaning that kernels had no noticeable rancid taste throughout the storage. This is in agreement with the results obtained for PV (Fig. 1) and AV (Fig. 2) where values were below 10 meq O_2 kg^{-1} and 1 %, respectively, indicating that kernels had no rancid taste during storage (Borompichaichartkul et al., 2013; Canneddu et al., 2016), Also Fig. 6 showed that 'Beaumont' kernels had a nutty taste throughout the storage. The rancid taste of 'A4' significantly ($p < 0.001$) increased with increasing storage. Fig. 7 shows that 'A4' had no rancid taste from week 0 to week 12, slight rancid taste from week 14 to week 16 and moderate rancid taste at week 18. This is consistent with the results obtained in Fig. 1 (PV) and Fig. 2 (AV) where 'A4' had high value of above 10 meq O_2 kg^{-1} and 1 %, respectively from week 12 of the storage, suggesting that 'A4' is more prone to rancidity (Borompichaichartkul et al., 2013; Canneddu et al., 2016; Walton et al., 2017). Fig. 6 also shows 'A4' kernels had poor nutty taste towards the end of storage. Our results are also similar to Jensen et al. (2001) who reported that according to trained panelists, the rancid taste of walnut kernels significantly increased during the storage of 25 weeks and linked this to quality loss due to lipid oxidation, indicated by high PV and hexanal content during storage.
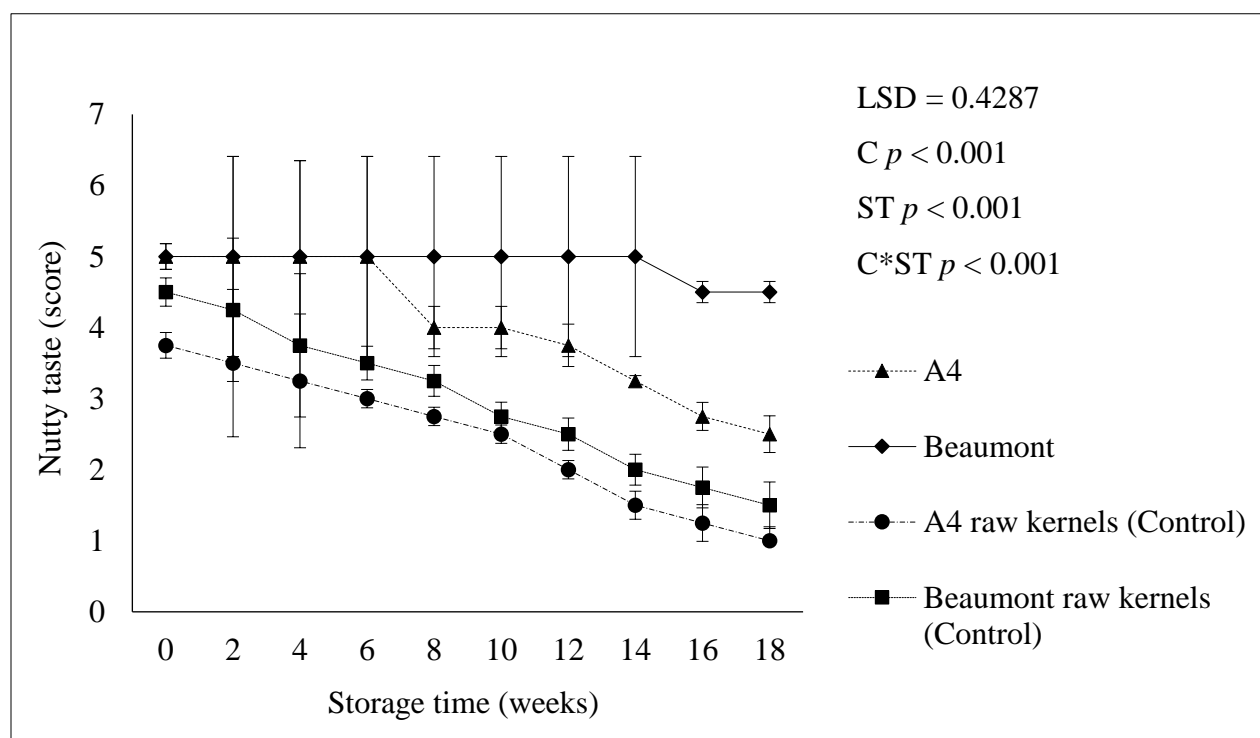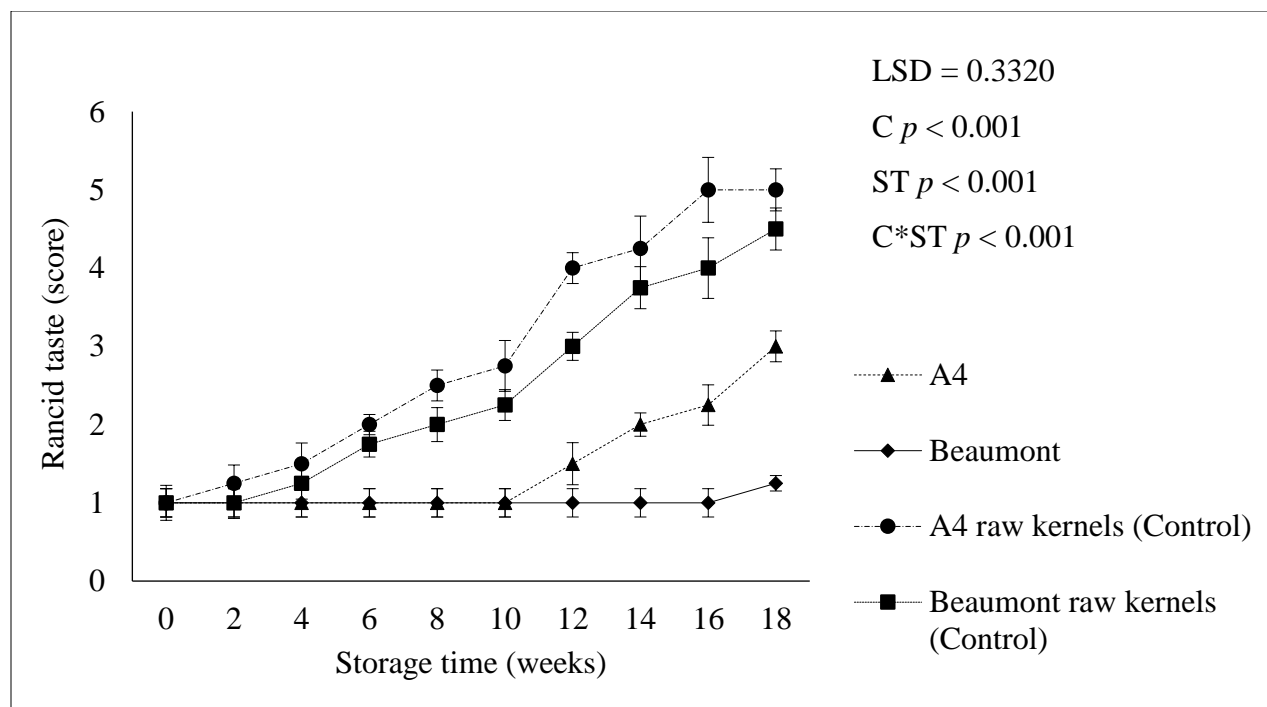
Fig. 7: Rancid taste of roasted kernels of 'Beaumont' and 'A4' cultivars during the accelerated postharvest storage. Vertical bars represent standard errors of differences of means. LSD, least significant difference; C, cultivar; ST, storage time; C*ST, cultivar and storage time. Raw kernels of 'A4' and 'Beaumont' were used as the control.

4. Conclusion

'Beaumont' had better quality which could be attributed to lower PV and AV, higher concentration of phenols and antioxidants and good sensory quality during storage while 'A4' had poor quality during storage which could be linked to higher PV and AV, lower concentration of phenols and antioxidants. Furthermore, PV is associated with the formation of peroxides in unsaturated fat, originated from the break of bounds, which generates oxidation products such as aldehydes, epoxides and polymers responsible for the rancid odour. Acid value is related to the acidification of fats due to enzymatic reactions generating free fatty acids which might have a rancid taste. As a result, nuts with high levels of PV and AV are sensitive to the development of rancidity and progressive loss of nutraceutical value, as observed in 'A4' cultivar that high PV and AV resulted

in the loss of phenols and antioxidants and limited shelf-life compared to 'Beaumont'. Future studies should consider different packaging materials which could potentially further preserve the quality of macadamia kernels and extend shelf life.

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CHAPTER 6: RAPID NON-DESTRUCTIVE VIS/NIR SPECTROSCOPIC PREDICTION OF RANCIDITY IN MACADAMIA (*MACADAMIA INTEGRIFOLIA*) NUTS

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Abstract

Rancidity is a major limiting factor affecting the postharvest quality and consequently, the storability and market value of macadamia nuts by causing disagreeable flavours and odours. Measuring rancidity is laborious, time-consuming and expensive, making it difficult to detect during grading and sorting in commercial packaging lines. In this study, visible to near infrared (Vis/NIR) spectroscopy (Vis/NIRS) and associated chemometric analytical methods were explored for non-destructive prediction of rancidity, expressed as peroxide value (PV) in 'Beaumont' and 'A4' macadamia cultivars. Reflective Vis/NIR spectral data was acquired from the total of 160 kernels of 'Beaumont' and 'A4', immediately after drying and roasting, using a laboratory bench-top monochromator NIR Systems. Reference data of rancidity (PV) was obtained on the same kernels after scanning with NIR spectroscopy. Calibration models were developed by subjecting spectral and reference data sets to partial least squares regression. Models that yielded the highest cross validation regression (R^2_{cv}), regression coefficient of prediction (R^2_p), root mean square error of prediction (RPD_p) and the lowest root mean square error of cross validation (RMSECV) and prediction (RMSEP) were selected. 'Beaumont' had the highest values of R^2_{cv} = 0.99, R^2_p = 0.94, RPD_p = 7.02, lowest values of RMSECV = 0.05 and RMSEP = 0.07. On the other hand, 'A4' had R^2_{cv} of 0.95, R^2_p = 0.88, RPD_p = 3.35, RMSECV = 0.06 and RMSEP = 0.09. Raw and roasted kernels had highest values of R^2_{cv} = 0.85 and 0.88, R^2_p = 0.91 and 0.88, RPD_p = 1.75 and 3.16, lowest RMSECV = 0.08 and 0.16 and RMSEP = 0.12 and 0.15, respectively. These

results confirmed the capability of Vis/NIRS to non-destructively predict rancidity on macadamia nuts, quickly and precisely. Therefore, the Vis/NIR spectroscopy combined with models developed in this study could be used as decision making tool for predicting the susceptibility of macadamia nuts to rancidity.

Keywords: Partial least square regression, peroxide value, postharvest quality, visible to near infrared spectroscopy, non-destructive technique

1. Introduction

Macadamia (*Macadamia integrifolia*) are the highest-ranking tree nuts in the word with the annual production of about 100 000 tons (du Preez, 2015; Rengel et al., 2015). They are widely consumed roasted or as an ingredient into various confectionary products (Eagappan and Sasikumar, 2014; Navarro and Rodrigues, 2016). They are a nutritious food and contribute greatly to human health by reducing the risks of cardiovascular diseases and type 2 diabetes (Jiang et al., 2005; Lovejoy, 2005; Rengel et al., 2015). These health benefits are associated with high lipid content of about 80 % which is rich in monounsaturated fatty acids such as oleic (60 %), palmitoleic (20 %) and gadoleic (2.48 %) acids (Eagappan and Sasikumar, 2014; Sinanoglou et al., 2014) and antioxidants due to several phytochemicals and polyphenols also present in kernels (Leja et al., 2001; Oboh, 2005; Rengel et al., 2015). Furthermore, unsaturated fats and oils in nuts are prone to rancidity throughout postharvest handling or processing and storage (Bai et al., 2018). Rancid nuts develop off-flavours and odours which are considered a major problem affecting the quality and storability of macadamia nuts (Srichamnong et al., 2010). Food rancidity is also associated with food-borne disease which could be threatening to the health of consumers (Bai et al., 2018).

Rancidity occurs through several mechanisms, one of which is autoxidation which generates hydroperoxides (Saponaro et al., 2015; Walton et al., 2017). Hydroperoxides can react with other nut components and decomposes to secondary oxidation products mainly, aldehydes, ketones, hydrocarbons and alcohols (Gülçin, 2012). Aldehydes are predominantly responsible for off-flavours, either directly or indirectly through their enol or tautomer forms (Macfarlane et al., 2001). Peroxide value is the most commonly used parameter and a good technique for determining the onset of oxidation as it is a measure of the hydroperoxides formed in the initial stages of oxidation (Borompichaichartkul et al., 2013). The deterioration of macadamia nuts during processing and storage can be rapidly characterized by the changes in peroxide value (Gölge and Ova, 2008). High quality macadamia product is characterized by low peroxide value of less than 1 meq O_2 kg^{-1} which is considered acceptable for freshly refined fat and is classified at low oxidation state; that between 5 and 10 meq O_2 kg^{-1} at moderate oxidation and above 10 meq O_2 kg^{-1} is classified at high oxidation state (Borompichaichartkul et al., 2013; Canneddu et al., 2016). Methods currently used to quantify

PV of the nuts are laborious, not cost effective, requires sample preparation and use expensive chemicals therefore, rapid food assessments are sought to address this issue (Bai et al., 2018).

New non-destructive technologies to assess food quality, including the use of visible to near infrared (Vis/NIR) spectroscopy (Vis/NIRS), are rapidly developing (Moscetti et al., 2015; Pannico et al., 2015). In recent years, Vis/NIRS has become one of the most evolving candidates for non-destructive prediction of kernel quality on various dry fruits, including hazelnuts, chestnuts and macadamia nuts (Guthrie et al., 2004; Moscetti et al., 2013; Moscetti et al., 2014; Pannico, 2014; Pannico et al., 2015). Although research on non-invasive techniques to measure kernel quality using Vis/NIRS are evolving, Vis/NIRS is not yet as advanced with nuts as it is with fruits such as apples and mango where spectrophotometers have been used in the pack house (Canneddu et al., 2016; dos Santos Neto et al., 2017). Therefore, there is a need for continued development of calibration models for predicting kernel quality. This should include the use of Vis/NIRS to estimate rancidity and other parameters affecting flavour of nuts such as oil quality and fatty acid composition. Recent publications by Pannico et al. (2015), Canneddu et al. (2016) and Bai et al. (2018) also suggest that further research is still necessary to investigate the use of Vis/NIRS for non-invasive prediction of rancidity on nuts. Therefore, in this study, the ability of Vis/NIRS to non-invasively quantify rancidity (peroxide value) on intact processed kernels of 'A4' and 'Beaumont' cultivars of macadamia nuts was evaluated.

2. Material and methods

2.1. Macadamia samples

Two hybrids of Australian-bred cultivars of *Macadamia integrifolia* namely, 'Beaumont' and 'A4' were harvested from the commercial orchards of Elliot Farm in Port Shepstone, South Coast of KwaZulu-Natal, South Africa (latitude: 30°44′28″ S, longitude: 30°27′17″ E and altitude: 36 m). About 50 kg of nuts per cultivar were harvested and dehusked within 24 hours after harvest using a dehusker (01-one-lane, Sheet Metal Works, Tzaneen, South Africa) at Ukulinga Research Farm of the University of KwaZulu-Natal (UKZN).

2.2. Drying and cracking process

Following a method described by Walton et al. (2013) with slight modifications, nut-in-shell (NIS) were separately placed in a mechanical convection oven (RY-EB-550, Rongyao factory, Mainland, China) at Postharvest Research Laboratory of UKZN. Dehusking and drying was started on the same day of harvesting. After dehusking, nuts were weighed and dried for three consecutive days, starting with 35 °C on the first day, 38 °C for the second day and 50 °C for the third day. These drying temperatures were selected according to the nut industry practice to avoid quality deterioration (Belviso et al., 2017; Walton et al., 2017). Dried nuts were checked for moisture content and were only removed from the oven when moisture content had reached 1.5 %. The moisture content of nuts was based on initial and final (dry) weight. Mass changes in nuts were used to calculate moisture content on a dry basis (d.b.) (Wang et al., 2014). Moisture content was determined according to Khir et al. (2011) as follows:

$$MC_{db}(\%) = \frac{W_i - W_d}{W_d} \times 100 \qquad (1)$$

where MC_{db} is moisture content on a dry mass basis, W_i and W_d are the initial and the dry sample weights, respectively. Furthermore, macadamia nuts were mechanically cracked into wholes, halve and pieces using a commercial mechanical macadamia nutcracker (TZ-150 macadamia nut cracker, Alibaba Group Houlding (PTY) LTD , Hangzhou, China). The shell and kernel were separated manual or by hand and only full kernels with no visible defects were used for the experiment. After drying, 80 kernels per cultivar were equilibrated at room temperature (20 to 21 °C) for an hour before Vis/NIR spectra were acquired. Nuts that are dried to 1.5 % kernel moisture content for the purpose of dehusking and cracking are referred to as raw kernels (du Preez, 2015).

2.3. Roasting process

Another set of dried kernels were roasted using a method described by Nikzadeh and Sedaghat (2008) and Birch et al. (2010), with slight modifications. Kernels were roasted at 150 °C for 15

min using a convection oven (RY-EB-550, Rongyao factory, Mainland, China). This roasting temperature was selected based on the nut industry practice to minimize quality deterioration (Belviso et al., 2017; Taş and Gökmen, 2017; Tonfack Djikeng et al., 2018). After roasting, 80 kernels per cultivar were equilibrated at room temperature (20 to 21 °C) for an hour before Vis/NIR spectra were acquired.

2.4. Experimental treatments

Raw and roasted kernels of 'A4' and 'Beaumont' cultivars were used as two distinct treatments. Only full kernels with no visible defects were used for sampling. A randomly sampled set of 40 kernels (20 raw and 20 roasted) per cultivar and another 40 kernels (20 kernels per cultivar) per treatment (raw and roasted) were used for NIRS scanning.

2.5. Vis/NIR spectroscopy collection

After processing, spectra of intact macadamia nuts ('Beaumont', 'A4', dried and roasted kernels) were acquired following a method described by Magwaza et al. (2014) and Pannico et al. (2015). Briefly, Vis/NIR spectral data was acquired in reflectance mode using a laboratory bench-top monochromator NIR Systems Model XDS spectrometer (FOSS NIR Systems, Inc.; Maryland, USA) equipped with a quartz halogen lamp and lead sulfide (PbS) detector. To reduce baseline shift of spectral data, the system was calibrated by scanning a 100 % white reference tile prior kernel scanning and after every 30 min of scanning kernels. The visible to near infrared reflectance spectrum ranging from 450 to 2500 nm was acquired from two opposite sides (top and bottom) of kernels and recorded as log 1/ reflectance (log 1/R). Each spectrum was the average of 32 scans recorded using Vision software (Vision TM, version 3.5.0.0, Tidestone Technologies Inc., KS, USA).

2.6. Destructive (reference) analysis

Reference measurements were taken from the same sets of kernels used for acquiring Vis/NIR spectra, using a conventional destructive method. Destructive measurements of individual kernels for PV were carried out immediately after acquiring the NIR spectral data. Kernels were ground into fine powder using pestle and mortar and stored at −20 °C for further analysis of PV.

2.6.1. Destructive analysis of PV

Kernel oil content was measured from ground sample material and quantified using a method described by Meyer and Terry (2008), with slight modifications. Hexane (9.0 mL) was added into a test tube containing 3 g of ground kernel sample and the test tube was placed into an ultrasonic bath (Labotec, Model No. 132, Labotec (PTY) LTD, Johannesburg, South Africa) for 10 min. The supernatant was filtered under vacuum and another 6 mL hexane was added to the residue in the test tube. This was left for 5 min before the test tube was emptied into the Buchner funnel. After filtration, 15 mL hexane was dried off the supernatant using a GenVac® concentrator (SPScientific, Genevac LTD., Suffolk, UK) under vacuum leaving the oil content of the sample. The residual oil was weighed and presented on dry weight basis.

Peroxide value (PV) was determined according to Walton et al. (2017), with minor modifications. A 1 g of oil sample was dissolved in 20 mL of acetic acid/chloroform (3:2 v/v) followed by adding 1 mL of saturated potassium iodide solution by an additional burette. The reaction took place and iodine was formed. A 50 mL of deionized water was added. Iodine was titrated with $Na_2S_2O_3$ using a burette. Peroxide value (expressed as milliequivalents of peroxide per kilogram of sample) was calculated according to the following formula:

$$PV \text{ (meq per kg)} = \frac{(S - B) \times N \times 1000}{\text{Sample wt (g)} \times 1000} \qquad\qquad 3$$

where S = sample titration (µL); B = Blank titration; and N = normality of $Na_2S_2O_3$.

2.7. Statistical and chemometric analysis

2.7.1. Statistical analysis

The collected data was subjected to the analysis of variance (ANOVA) using GenStat statistical software (GenStat®, 18.1 edition, VSN International, UK). Least significant difference values (LSD; $p < 0.001$) were calculated for mean separation.

2.7.2. Chemometric analysis

The chemometric analysis was performed using the Unscrambler software (The Unscrambler™ Version 10.1, CAMO, Oslo, Norway). Two individual spectra from each sample were averaged prior to calibration and validation, hence, results reported herein are based on average spectra. The spectral data were first subjected to principal component analysis (PCA) to compare spectral characteristics, using leave-out-one cross validation, to determinate effective wavelengths and detect spectral outliers (Ncama et al., 2017). The R programme was used to develop PLS models for predicting peroxide value of macadamia nuts. The models were developed categorically based on either raw or roasted kernels from 'Beaumont' or 'A4' cultivars. The "caret" library was used to cluster samples into randomly selected 70 % calibration set and 30 % independent test set. After sample clustering, the "chemometrics" library was applied to determine the possible number of principal components that can be used to omit the noisy regions of the spectral data. The maximum principal components were seventeen and therefore, the optimum number of principal components for each of the models was based on testing all seventeen components. The assessment of optimum number of components was repeated five times and the programme suggested the number to apply based on the frequency of the optimal number of components (Fig. 1).
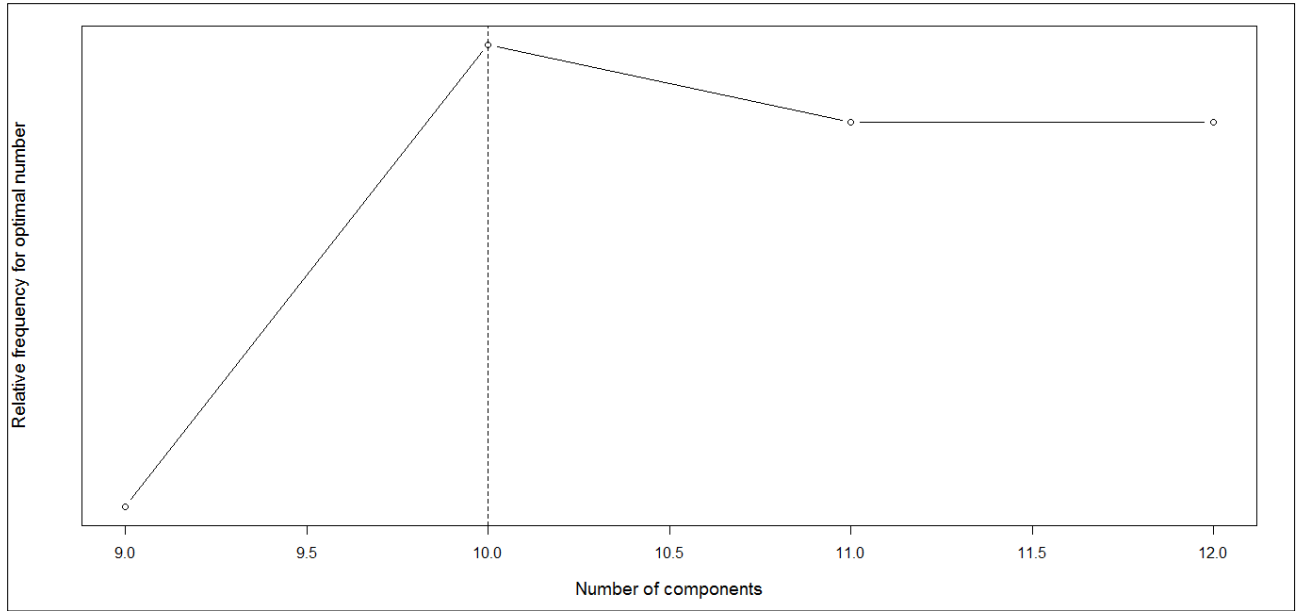
Fig. 1: Relative frequency for optimal number of components

Thereafter, the PLS library was employed to determine the optimal number of principal components based on the model root mean square error (RMSE) of prediction after cross validation (RMSEP). The PLS library displayed the reduction of root mean square error of prediction as a result of increasing the number of components (Fig. 2).
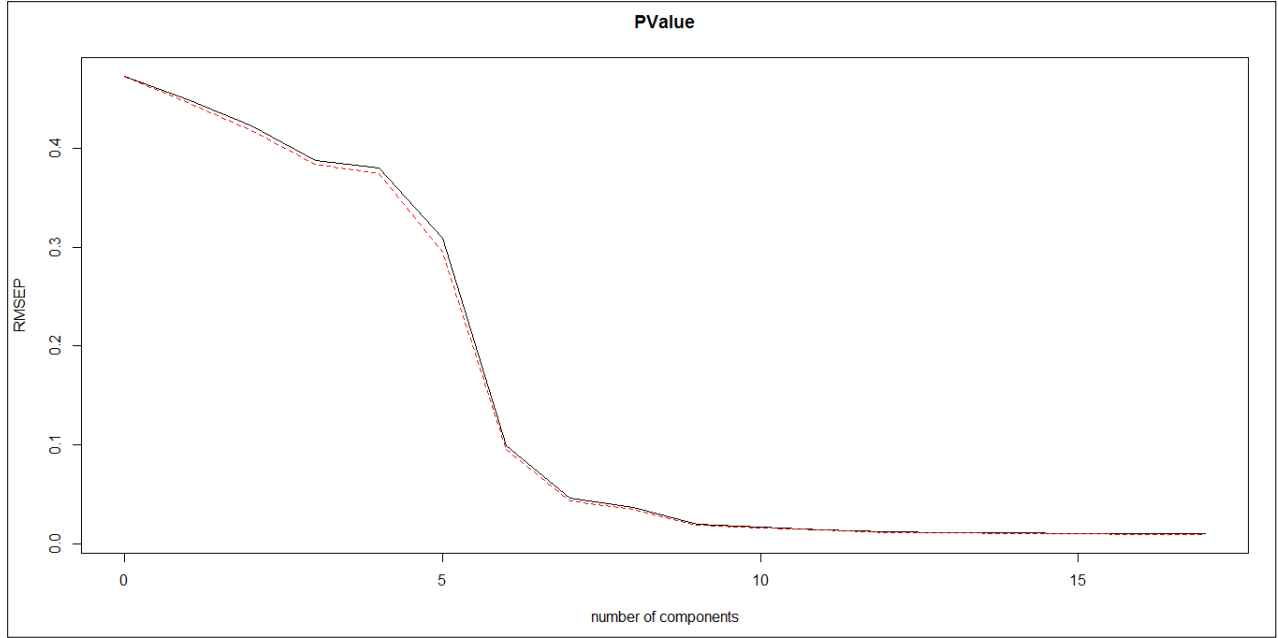
Fig. 2: Root mean square error of prediction after cross validation (RMSEP)

Based on the RMSE value as determined in Fig. 2, the optimal number of components was detected to be higher than 5 but less than 10. The maximum of 10 was due to 10 being the suggested number based on frequency. However, reducing the RMSE of calibration to values below 0.05 lowered the performance of the models in the independent test set. Therefore, the number of components used was selected as a number between 5 and 10, because it was hypothesised that 5 components was the most likely to yield the most robust model. The accuracy of the selected number was confirmed by higher regression coefficient(R^2p) and cross validation regression (R^2_{cv}) (Eq. 3) after predicting the independent test set lower RMSE (Eq. 4) of predicting the independent test set (RMSEP) (Eq. 4) and higher ratio of predictive deviation (RPDp) (Eq. 5)

$$R^2 = 1 - \frac{\Sigma(y_{cal} - y_{act})^2}{\Sigma(y_{cal} - y_{mean})^2} \tag{3}$$

$$RMSEC/RMSEP/RMSECV = \sqrt{\Sigma(y_{pred} - y_{act})^2 / n} \tag{4}$$

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$$RPD_P = \frac{SD}{RMSEP} \tag{5}$$

2.8. Results and discussion

2.8.1. Developing Vis/NIRS-based models for predicting rancidity

Good prediction of rancidity was obtained in roasted (R^2_{cv} = 0.88, R^2_p = 0.88, RMSECV = 0.16 and RMSEP = 0.15) and dried (R^2_{cv} = 0.85, R^2_p = 0.91, RMSECV = 0.08 and RMSEP = 0.12) kernels of macadamia nuts. The models developed for roasted and dried kernels presented very similar RMSECV and RMSEP of 0.16 and 0.15 for roasted kernels and 0.08 and 0.12 for dried kernels, respectively, indicating robust fitting (Magwaza et al., 2016). The calibration models for 'Beaumont' and 'A4' were accurate with higher R^2_{cv} of 0.99 and 0.95 and lower RMSECV of 0.05 and 0.06, respectively. The validation models for 'Beaumont' and 'A4' had higher R^2_p of 0.94 and 0.88 and lower RMSEP of 0.07 and 0.09, respectively (Table 1). This study findings were similar to Jensen et al. (2001) and Canneddu et al. (2016) who reported accurate models for predicting rancidity in walnuts (R^2 = 0.82 and RMSECV = 7.7) and macadamia nuts (R^2p = 0.80 and RMSEP = 0.14), respectively.

Different studies recommended that it is very important to verify the accuracy of a model by checking its RPD values even though highly significant correlation exists between the NIR predicted and actual laboratory values (Davey et al., 2009; Magwaza et al., 2012; Pannico et al., 2015; Wang et al., 2015). The RPD values less than 1.5 are considered unsuitable, those between 1.5 and 2.0 are suitable for rough predictions, those between 2.0 and 2.5 are fit for quantitative predictions, those between 2.5 and 3.0 are respectively considered good and excellent models while those above 3.0 are regarded as satisfactory prediction models (Bellon-Maurel et al., 2010; Magwaza et al., 2012; Olarewaju et al., 2016). The RPD value of 1.75 for raw kernels clearly indicate a suitable model for rough prediction of rancidity. The RPD values, 3.16, 3.35 and 7.02 for roasted kernels, 'A4' and 'Beaumont' respectively, indicates a satisfactory model for prediction of rancidity (Table 1). Similar findings were reported by Pannico et al. (2015) who demonstrated

that lipid oxidation which is a measure of rancidity could be measured accurately (RPD = 2.58) in hazelnuts.

In the current study, the accuracy and precision of Vis/NIRS was suitable and satisfactory for rapid quantification of rancidity in dried and roasted kernels and in 'Beaumont' and 'A4' cultivars of macadamia nuts. Therefore, the NIR analysis in combination with models developed in the current study is sufficiently accurate for the route screening of processed macadamia nuts. The NIRS techniques with its low operating costs can be accurately used in the macadamia industry to assess rancidity in kernels (Canneddu et al., 2016).

Table 1: Partial least square regression models for assessing peroxide quantity of macadamia nuts

Calibration set (70 %)					Validation set (30 %)			
Samples source	No. of samples	No. of components	R2cv	RMSECV	R2p	RMSEP	RPDp	Wavelength
'A4'	40	7	0.95	0.06	0.88	0.09	3.35	400-2500
'Beaumont'	40	6	0.99	0.05	0.94	0.07	7.02	400-2500
Raw	40	5	0.85	0.08	0.91	0.12	1.75	400-2500
Roasted	40	5	0.88	0.16	0.88	0.15	3.16	400-2500

R^2_{cv}, cross validation regression; RMSECV, root mean square error of cross validation; R^2_p, regression coefficient of prediction; RMSEP, root mean square error of prediction; RPD_p, ratio of predictive deviation on predicting test set.

The peroxide values for 'Beaumont', 'A4', roasted and dried kernels of macadamia nuts predicted using Vis/NIRS were plotted against the destructively analyzed peroxide values in Figure 3. The prediction statistics of macadamia nuts showed that PV of 'Beaumont' ($R^2 = 0.94$), 'A4' ($R^2 = 0.88$), roasted ($R^2 = 0.88$) and raw ($R^2 = 0.91$) kernels were successfully predicted. Our results are in agreement with Bai et al. (2018) who reported a good prediction of PV ($R^2 = 0.72$) on galip nuts roasted at 150 °C. This could be due to the decomposition and polymerization of the peroxide into a range of secondary products such as aldehydes and ketones during roasting (Makeri et al., 2011). In summary, satisfactory models should be developed with data that cover a wide range of thermal

processing treatments such as different roasting temperatures, duration (time) of roasting and large number of nuts or kernels. This is to ensure wider levels of PV to avoid low predictability by the model (Bai et al., 2018).
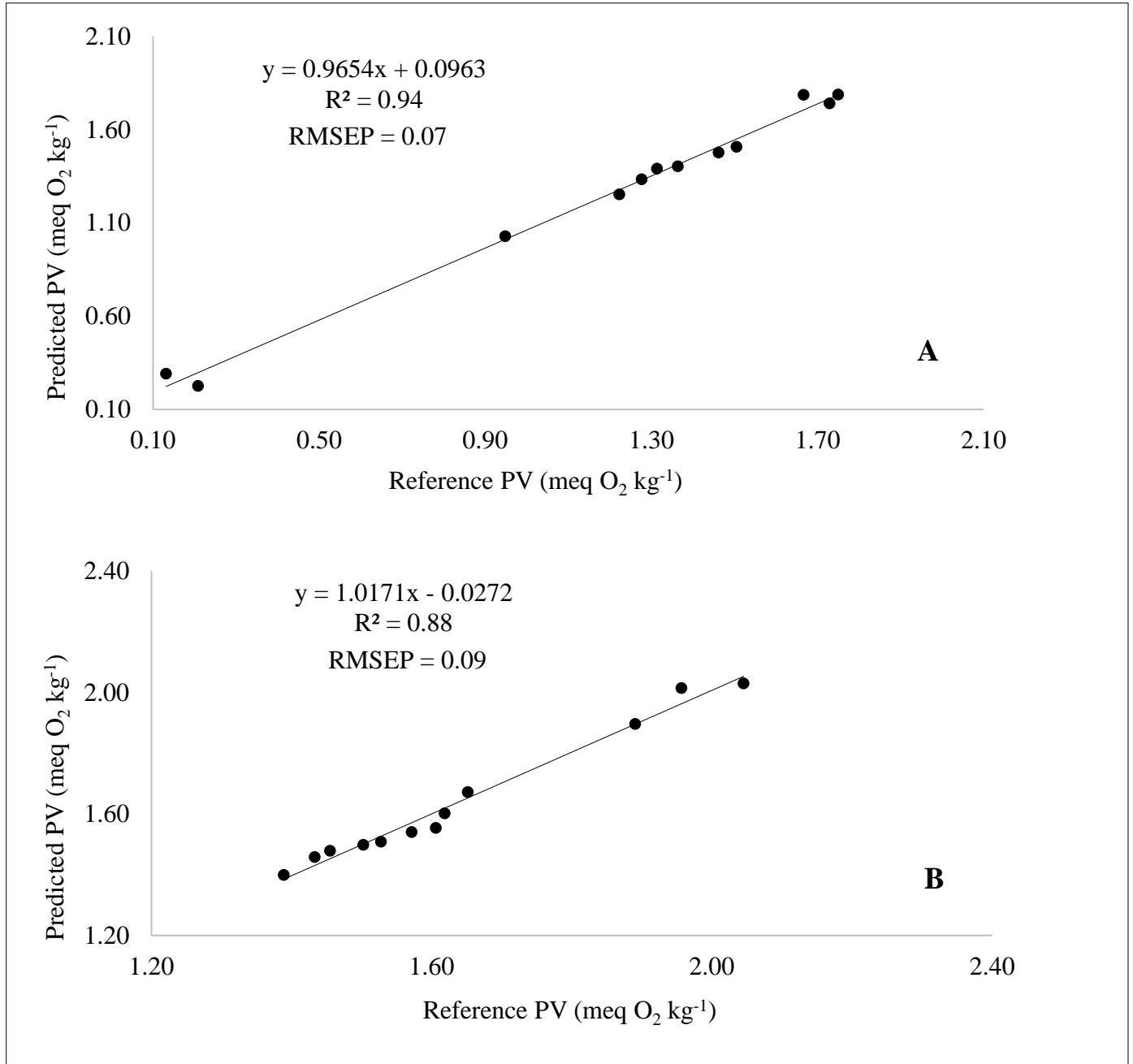

Fig. 3a: Scatter plots of NIR predicted against reference values for PV of 'Beaumont' (A) and 'A4' (B) kernels.
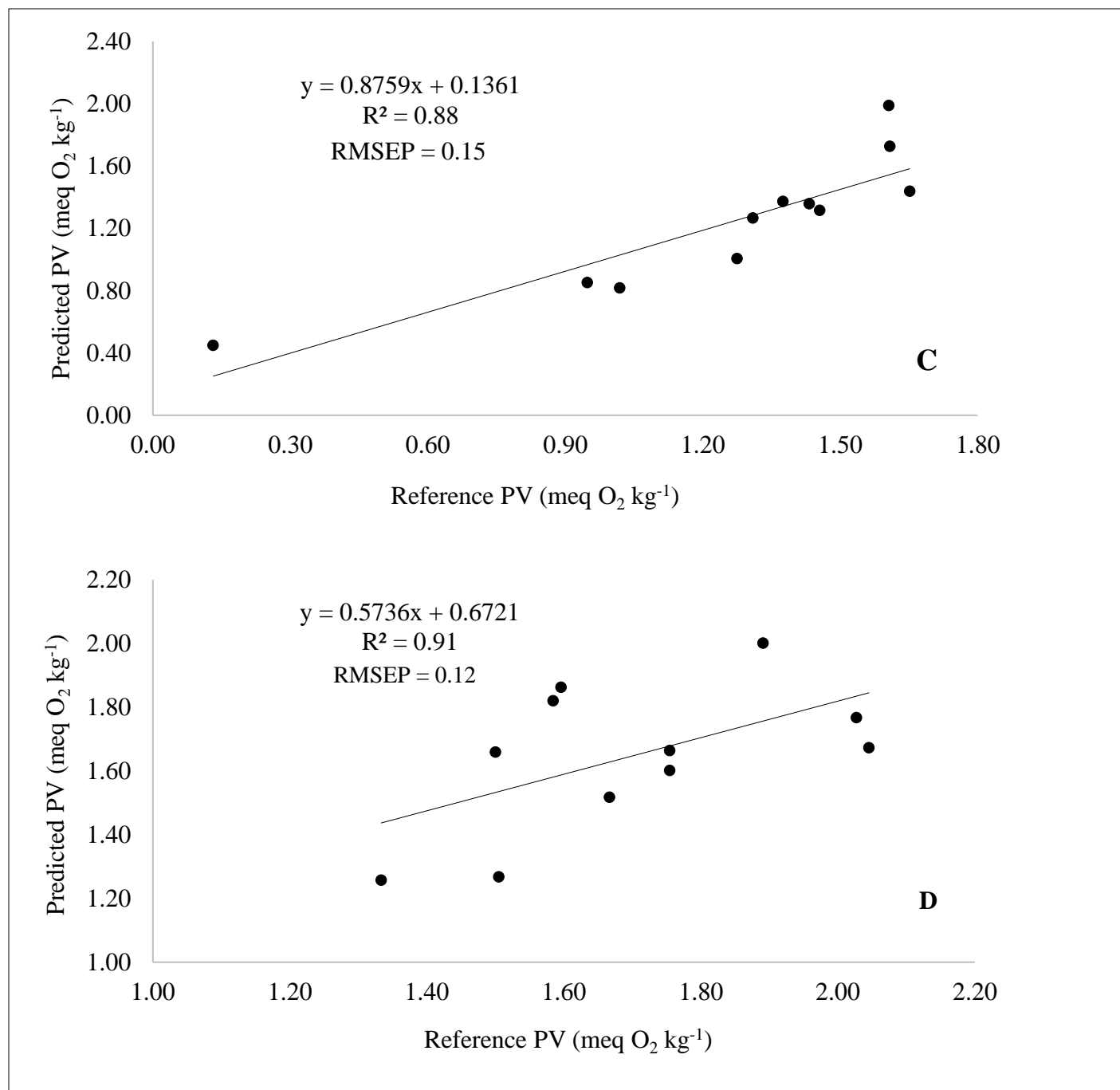
Fig. 3b: Scatter plots of NIR predicted against reference values for PV of roasted (C) and raw (D) kernels.

2.8.2. The comparison between chemically analyzed and predicted peroxide value

Table 2 shows a brief summary of predicted and chemically analyzed peroxide values for individual kernels of macadamia nuts ('A4', 'Beaumont', raw and roasted kernels). The predicted peroxide values were consistent with analyzed peroxide values for 'A4', 'Beaumont', raw and roasted individual kernels. For example, the predicted and chemically analyzed peroxide value for kernels were: A4 (1.635 and 1.636 meq O_2 kg^{-1}), 'Beaumont' (1.271 and 1.214 meq O_2 kg^{-1}), raw (1.645 and 1.696 meq O_2 kg^{-1}) and roasted (1.236 and 1.256 meq O_2 kg^{-1}), respectively. This clearly indicates the capability of Vis/NIRS to accurately predict PV on macadamia nuts. The accuracy of the predictive ability of calibration can be further justified from the minor squared differences of the RMSEP or higher R^2_{cv}, R^2_p, RPDp and the lower RMSECV and RMSEP between the chemical and NIR values (Table 1). Furthermore, PV observed for 'A4', 'Beaumont', raw and roasted kernels of macadamia nuts were lower than 3 meq O_2 kg^{-1} which is within the acceptable limit (Bai et al., 2018). A high-quality macadamia product is characterized by low peroxide value of less than 1 meq O_2 kg^{-1} which is considered acceptable for freshly refined fat and is classified at low oxidation state; that below10 meq O_2 kg^{-1} at moderate oxidation state and above 10 meq O_2 kg^{-1} is classified at high oxidation state (Borompichaichartkul et al., 2009; Moigradean et al., 2012). Future studies should include a wide range of drying or roasting temperatures to obtain a wide variability of PV in nuts.

Table 2: Predicted and chemically analyzed peroxide values

'A4'		'Beaumont'		Raw		Roasted	
Pred	Analy	Pred	Analy	Pred	Analy	Pred	Analy
1.635	1.636	1.271	1.214	1.645	10696	1.236	1.256

Pred: LSD = 0.3322, treatments $p < 0.001$

Analy: LSD = 0.3369, treatments $p < 0.001$

Pred, predicted; Analy, chemically analyzed; LSD, least significant difference

2.8.3. The typical spectra collected from raw and roasted nuts

The average spectra from raw and roasted kernels of macadamia nuts showed a high similarity (Fig. 4). Both spectra are characterized by a gradual increase in absorbance at 458 to 2437 nm having significant absorbance peaks at 935, 1234, 1462, 1718, 1940 and small peaks at 2314 and 2354 nm. Pannico et al. (2015) and Canneddu et al. (2016) reported similar absorbance peaks in hazelnuts and macadamia nuts. The peaks at 1700 to 1800 nm correspond to the CH bond of the CH_2 group first overtone stretching band and mostly related to kernel defects in nuts (Moscetti et al., 2014; Pannico et al., 2015). Two small peaks observed around 1300 to 1500 nm and around 2300 to 2350 nm are the first OH overtone and HO combinations, respectively and both associated with moisture content in macadamia nuts (Canneddu et al., 2016). In a study by Pannico et al. (2015), flawed kernels of hazelnuts and lipid oxidation were characterized by the absorbance peak 2300 nm which is related to the double C bond (C=C) stretching and deformation bands of lipids (Pannico, 2014). In the current study, a predominant absorption peak was observed at 1718 nm which correspond to the C-H bond of the -CH_2 group first overtone stretching band (Canneddu et al., 2016). This could be due to the fact that thermal processing changes the internal microstructure of kernels, resulting in a texture that is typically more brittle, crispy, and or crunchy which could potentially lead to changes in PV (Boge et al., 2009; Borompichaichartkul et al., 2009; Le Lagadec, 2009). This study findings were similar to Yildiz et al. (2001) who reported that lipid peroxide in soybeans were characterized by a predominant peak around 1700 nm.
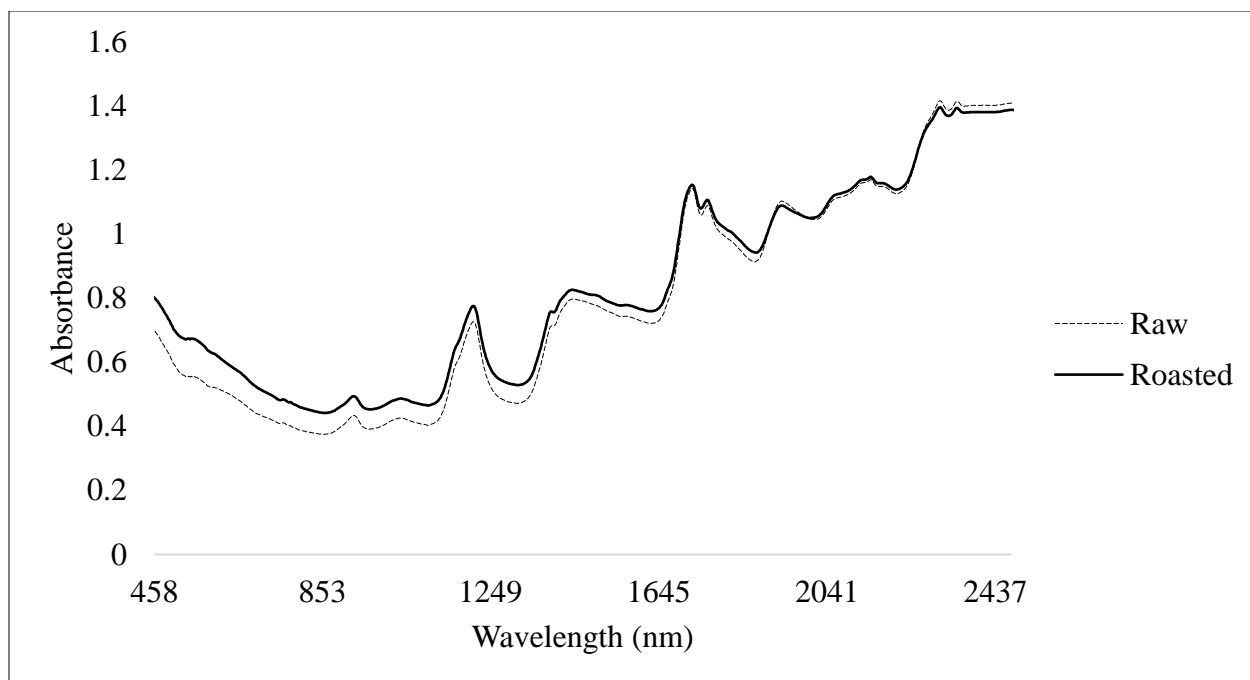
Fig.4: The average spectra of intact raw and roasted kernels of macadamia nuts.

3. Conclusion

Overall, the calibration or validation and prediction model results in this current study confirmed that Vis/NIRS in reflective mode has the capability to quantify PV on intact kernels of processed macadamia nuts with significant reliability. Therefore, this technique can be used as a rapid non-destructive decision making tool to predict rancidity of macadamia nuts. By using this rapid technique, quality control costs of monitoring macadamia nuts' quality will be reduced. More experiments are recommended which will include more data variability in order to improve robustness and increase the classification accuracy to 100 %. The latter results would be useful to the processing industry in establishing ideal thermal processing treatments to avoid quality loss or development of rancidity as a consequence of over-roasting.

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CHAPTER 7: GENERAL DISCUSSION, CONCLUSIONS AND RECOMMENDATIONS

7.1. Introduction

Macadamia (*Macadamia integrifolia*) is one of the most important tree nuts in the world with the annual production of about 100 000 tons (du Preez, 2015; Rengel et al., 2015). Macadamia is mainly cultivated in Australia (32 %), South Africa (30 %) and Kenya (12 %) (Eagappan and Sasikumar, 2014; Jaskiewicz, 2015; Navarro and Rodrigues, 2016). South Africa is the world's largest exporter of macadamia nuts (36.37 %) followed by Australia (14.6 %), Kenya (12.1 %), Hong Kong (9.7 %), the Netherlands (4.5 %) and China (3.8 %) (DAFF, 2015b; Manenzhe, 2015). More than 95 % of South African annual production is shipped to international markets, mainly in the United States, Europe and Asia (DAFF, 2016). Research studies have mainly focused on improving the kernel quality due to increasing global production and market competition of macadamia nuts (du Preez, 2015; Walton and Wallace, 2015).

Rancidity is one of the major problems affecting quality, storability and market value of macadamia nuts (Canneddu et al., 2016). Oxidative rancidity constitute a complex chain of reactions that firstly produce primary products such as peroxides that cause secondary oxidation products such as aldehydes, ketones, epoxides, hydroxy compounds, oligomers and polymers (Kanner, 2007; Tenyang et al., 2017). These compounds result in off-odours and off-flavours and are potentially toxic and threatening to the health of the consumer (Kaleem et al., 2015; Tonfack Djikeng et al., 2018). Hydrolysis is another form of rancidity which occurs as a result of lipolysis or hydrolysis of triglycerides in the presence of micro-organisms or enzyme action, moisture and heat and is the initial step in the deteriorative rancidity pathway, leading to the liberation of free fatty acids (FFAs) which then leads to hydrolytic rancidity (Walton, 2005; Walton et al., 2017). The liberated FFAs such as capric, lauric, and myristic acid have stronger off-flavour or distinctly soapy flavour, which is the main reason hydrolytic rancidity is often referred to as soapy rancidity (Peng, 2010; Saponaro et al., 2015).

Rancidity can also occur as a consequence of high initial moisture content (> 30 %) in macadamia nuts after harvest (Borompichaichartkul et al., 2009; Wang et al., 2014). Such high moisture content promotes the growth of microbes such as fungi, which produce specific enzymes that break down carbohydrates and accelerate the hydrolysis of lipids into free fatty acids, leading to the development of rancidity (Borompichaichartkul et al., 2009; Pannico, 2014; Wang et al., 2014). Since macadamia nuts contain high amount of unsaturated fatty acids they are prone to hydrolytic and oxidative rancidity when they contain high levels of free moisture (Borompichaichartkul et al., 2009). Furthermore, rancidity has been reported to also result from prolonged storage or improper storage conditions (Kaijser et al., 2000). Rancidity may also result to the loss of other quality attributes such as antioxidants (Bajaj et al., 2012). Detecting rancidity in macadamia nuts is extremely difficult since the kernel is covered by a shell (DAFF, 2015b; du Preez, 2015) and rancidity does not show any visual symptoms and can develop during harvesting, processing and storage (Bai et al., 2018; Tonfack Djikeng et al., 2018).

Pannico et al. (2015) and Canneddu et al. (2016) evaluated lipid oxidation and peroxide value in fresh and flawed kernels of hazelnuts and macadamia nuts, respectively and reported that flawed kernels had high levels of lipid oxidation and peroxide value, respectively. These findings suggested that the levels of lipid oxidation and peroxide value could be used as potential biochemical indicators of kernel quality. Moigradean et al. (2012) and Borompichaichartkul et al. (2013) reported that a high-quality macadamia product is characterized by low peroxide value of less than 1 meq O_2 kg^{-1} which is considered acceptable for freshly refined fat and is classified at low oxidation state; that between 5 and 10 meq O_2 kg^{-1} at moderate oxidation state and above 10 meq O_2 kg^{-1} is classified at high oxidation state and is unacceptable.

Also, thermal processing such as drying and roasting has been proposed by previous studies as primary preservation techniques of nuts (Borompichaichartkul et al., 2013; Soleimanieh et al., 2015; Taş and Gökmen, 2017). Moisture content essential for microbial growth, enzyme activity, and chemical reactions is reduced in dried nuts (Wall and Gentry, 2007; Wang et al., 2014). Roasting enhances flavour, aroma, colour and texture of the nuts through non-enzymatic (Maillard browning) reactions, resulting from the reaction between sugars and amino acids (McDaniel et al.,

2012; Schlörmann et al., 2015; Taş and Gökmen, 2017). It also inactivates oxidative enzyme system (lipoxygenic enzymes), reduces moisture content, eliminates microorganisms and minimizes deteriorative reactions such as lipid oxidation which exhibit antioxidant activity (Belviso et al., 2017; Taş and Gökmen, 2017). A study by Borompichaichartkul et al. (2013), Tenyang et al. (2017), Tonfack Djikeng et al. (2018) and Bai et al. (2018) demonstrated that roasted kernels of macadamia, sesame, walnuts and galip nuts had low peroxide value or rancidity compared to raw and boiled kernels. These findings suggested that peroxide value could be used as potential biochemical indicator for processed kernel quality.

A major challenge in nut industry is that nuts are processed at any temperature from 30 to 200 °C for about 15 to 60 min which could cause reactions leading to the loss of nutritional quality or development of disagreeable compounds such as 5-hydroxymethylfurfural (Borompichaichartkul et al., 2013; Srichamnong and Srzednicki, 2015; Stuetz et al., 2017; Süvari et al., 2017a; Tonfack Djikeng et al., 2018). Several physical and chemical changes such as microstructural and lipid modifications may enhance the susceptibility of roasted nuts to oxidation thus, reducing its shelf life (Belviso et al., 2017). Therefore, the aim of this study was to evaluate and compare quality parameters of raw and roasted macadamia kernels and the impact of different roasting temperatures on sensory and nutritional quality during storage. Another major challenge facing the macadamia industry and researchers alike, is to develop non-invasive technology such as visible to near infrared (Vis/NIR) spectroscopy (Vis/NIRS) to rapidly assess quality of nuts.

The existing analytical methods for the quantification of rancidity are time-consuming, use chemicals, and are costly to be used for evaluating nut quality in industrial scale (Canneddu et al., 2016). Furthermore, destructive analysis of rancidity require precise sample preparation from a batch of representative samples on which quality analysis of nuts from an entire orchard could be based on (Guthrie et al., 2004; Canneddu et al., 2016). Aside from their hard-labor and invasive nature, the disadvantage of traditional analytical methods is that growers are likely to deliver nuts of poor quality to the market because of quality variation within a consignment (Guthrie et al., 2004; Moscetti et al., 2015; Pannico et al., 2015). Increasing demands of the export market for assurance of good quality has spurred investigations into the potential use of NIRS as a tool to

non-destructively grade the quality of nuts on-line (Moscetti et al., 2014; Pannico, 2014). Near infrared spectroscopy can be used in postharvest quality control and real-time quality evaluation during processing and storage (Singh et al., 2006). This may greatly benefit the South African macadamia industry since it is export oriented. Packers could segregate nuts based on susceptibility to rancidity and nuts that are more prone to rancidity could then be exported as processed products since those products will have extended shelf life. Although Vis/NIRS has become one of the frequently used technologies for non-destructive evaluation of a wide range of postharvest quality assessments of fruits and vegetables (Magwaza and Tesfay, 2015), it is not yet as advanced with nuts as it is with fruits such as mango and apples where spectrophotometers have been applied in the pack house (dos Santos Neto et al., 2017). Also, very limited research has been conducted to evaluate the potential of Vis/NIRS to predict rancidity on macadamia nuts (Canneddu et al., 2016). Therefore, another aim of this study was to investigate the feasibility of Vis/NIRS to predict rancidity on intact kernels of macadamia nuts.

7.2. Postharvest quality of raw and roasted macadamia nuts

The study findings demonstrated that roasting significantly improved the sensory and chemical quality of macadamia nuts. In Chapter 3, kernels of both 'A4' and 'Beaumont' roasted at 125 °C had better quality compared to raw kernels. This could be due to the fact that roasting improves flavour, aroma, colour, texture and appearance of the nuts through non-enzymatic (Maillard browning) reactions (McDaniel et al., 2012; Schlörmann et al., 2015; Taş and Gökmen, 2017). It also inactivates enzymes that accelerates nutrient deterioration and reduces degradative reactions such as lipid oxidation and rancidity therefore, extends shelf-life of nuts (Birch et al., 2010; Marzocchi et al., 2017). Roasted kernels of 'A4' and 'Beaumont' had lower PV (10.597 and 5.139 meq O_2 kg^{-1}, respectively) at the end of storage. This suggested that 'A4' kernels were still consumable and 'Beaumont' kernels were classified as fresh at the end of the accelerated storage of 70 days. The results of the current study were similar to those reported by Borompichaichartkul et al. (2013), Tenyang et al. (2017), Tonfack Djikeng et al. (2018) and Bai et al. (2018), who observed lower levels of rancidity in roasted kernels of macadamia, sesame, walnuts and galip nuts. In the current study, roasted kernels of 'A4' and 'Beaumont' had higher concentration of

flavonoids (0.030 and 0.063 mg quercetin GAE kg^{-1}), phenols (0.508 and 0.521 mg GAE kg^{-1}) and antioxidants: ABTS (0.029 and 0.032 mg GAE kg^{-1}) and DPPH (0.019 and 0.020 mg GAE kg^{-1}) at the end of storage. Similar results were reported by McDaniel et al. (2012), Srichamnong and Srzednicki (2015) and Lin et al. (2016) who observed higher antioxidants and phenolic concentration in roasted kernels of peanuts, macadamia and almond nuts, respectively. This could be due to the release of some bound antioxidant phenolic compounds acting as free radical scavengers from the cell matrix and increase phenolic extractability upon roasting (Kumar and Pandey, 2013). Roasting may cause complex physical and chemical reactions on phenolics, including leaching of water soluble phenolics, freeing phenolics from bond forms, degradation of polyphenols, breakdown and the transformation of phenolics, such as the formation of complex products from phenolics and proteins, and the formation of Maillard reaction products having antioxidative activity (Belviso et al., 2017; Taş and Gökmen, 2017). Also, according to the panelists roasted kernels had enhanced crispy texture, aroma, flavour, appearance and good marketability throughout the storage period. This could be due to Maillard browning and caramelization reactions during roasting (Purlis, 2010; Shi, 2015; Srichamnong and Srzednicki, 2015). The results of the PCA scores (Chapter 3, Fig. 12 and 13) showed that quality parameters of raw kernels were positively affected by the storage whereas roasted kernels were only positively affected by storage from day 50 to 70, confirming that roasting does enhance quality and storability of nuts. These results demonstrated that roasting 'A4' and 'Beaumont' kernels improved most of chemical and sensory quality and storability of kernels.

In accordance with literature (Borompichaichartkul et al., 2009; Moigradean et al., 2012; Pannico, 2014; Tonfack Djikeng et al., 2018), changes in peroxide value was one of the major factors contributing to the loss of quality attributes in macadamia nuts. For example, raw kernels of 'A4' cultivars had high peroxide value of 10 meq O$_2$ kg^{-1} from week 50 of storage which is classified at high oxidation state and associated with noticeable rancid taste and is unacceptable (Borompichaichartkul et al., 2009; Moigradean et al., 2012). Also, raw kernels of 'A4' had high levels of PPO activity (5.003 U kg^{-1}), low concentration of flavonoids (0.036 mg quercetin GAE kg^{-1}), phenols (0.4791 mg GAE kg^{-1}), antioxidants; ABTS (0.024 mg GAE kg^{-1}) and DPPH (0.0171 mg GAE kg^{-1}) at the end of storage and poor sensory quality; texture, aroma, bitterness,

overall appearance and marketability during storage. The results of the PCA correlation loadings (Chapter 3, Fig. 12) showed that the ratio of peroxide value, polyphenol oxidase, kernel appearance, bitterness, aroma and marketability were positively correlated with each other and with storage time. Srichamnong and Srzednicki (2015) reported that in the presence of free moisture in raw kernels, lipolytic enzymes are active and promote hydrolysis of lipids into free fatty acids resulting to the development of a rancid taste (Kaleem et al., 2015). Hence roasting improved the quality of kernels as mentioned earlier.

The findings discussed above, support the hypothesis that roasting reduced quality deterioration in macadamia nuts by reducing levels of rancidity and the deterioration of other chemical and sensory quality attributes. In conclusion, the quality and storability of macadamia nuts can be enhanced through the application of thermal processing techniques such as roasting.

7.3. Quality of macadamia nuts roasted at different temperatures

Different roasting temperatures; 50 °C, 75 °C, 100 °C, 125 °C and 150 °C significantly affected quality parameters of 'A4' and 'Beaumont' kernels of macadamia nuts. Sensory quality was assessed according to Nikzadeh and Sedaghat (2008) and Sanful (2009) with minor modifications using a five-grade hedonic scale where texture was evaluated as 1: very hard, 2: hard, 3: slightly crispy, 4: crispy and 5: very crispy; colour where 1: very light, 2: light, 3: slightly brown, 4: brown and 5: extremely brown and taste where 1: very nutty, 2: nutty, 3: lightly bitter, 4: bitter and 5: extremely bitter. In Chapter 4, the moisture content of 'A4' and 'Beaumont' significantly ($p <$ 0.001) decreased with increasing roasting temperatures; 50 °C (1.474 and 1.432 %), 75 °C (1.429 and 1.4 %), 100 °C (1.393 and 1.318 %), 125 °C (1.319 and 1.211 %) and 150 °C (1.218 and 1.025 %), respectively. The significant decrease of kernel moisture content at 150 °C could be due to dehydration and loss of volatile compounds such as reaction of free amino acids and short-chained peptides with free mono- and disaccharides during nonenzymatic browning and protein denaturation and degradation that might occur upon roasting nuts at higher temperatures above 130 °C (García-Alamilla et al., 2017; Marzocchi et al., 2017; Süvari et al., 2017a).

Although kernels of 'A4' and 'Beaumont' roasted at 50, 75 and 100 °C had high concentration of flavonoids, phenols and antioxidants (Chapter 4, Fig 3, 4 and 5), they were more prone to deterioration as shown by high PV (2.203, 1.72 and 1.569 meq O_2 kg^{-1} and 1.303, 1.232 and 1.011 meq O_2 kg^{-1}), respectively. Moigradean et al. (2012) reported that a high-quality macadamia product is characterized by low PV of less than 1 meq O_2 kg^{-1} which is considered acceptable for freshly refined fat and is classified at low oxidation state. These kernels had poor sensory quality according to panelists; hard texture, light colour and slightly to nutty taste. These results suggested that roasting temperatures between 50 to 100 °C do not effectively enhance quality of nuts. 'A4' and 'Beaumont' kernels roasted at 125 °C had the lowest PV (1.161 and 0.947 meq O_2 kg^{-1}), high concentration of flavonoids (0.066 and 0.071 quercetin mg GAE kg^{-1}) phenols (0.082 and 0.127 mg GAE kg^{-1}) and antioxidants; ABTS (0.007 and 0.008 mg GAE kg^{-1}) and DPPH (0.003 and 0.006 mg GAE kg^{-1}) and good sensory quality; crispy texture, brown colour and nutty taste. These results suggested that roasting kernels at 125 °C significantly enhanced kernel quality. Peroxide value lower that 1 meq O_2 kg^{-1} is associated with fresh kernels with no detectable rancid taste (Borompichaichartkul et al., 2009; Moigradean et al., 2012).

The results of this study are similar to Bai et al. (2018) and Tonfack Djikeng et al. (2018) who reported a lower PV in galip nuts and walnuts roasted at 120 °C. The enhancement of flavonoids, phenols, antioxidants and sensory quality may be due to the increase in extractable phenolic compounds after roasting with the formation of Maillard products (McDaniel et al., 2012; Srichamnong and Srzednicki, 2015). The findings of this study were also in agreement with Lin et al. (2016) who suggested that antioxidant activity of almond kernels increased upon roasting due to Maillard reaction products, resulting from the reaction between sugars and amino acids (McDaniel et al., 2012; Schlörmann et al., 2015; Taş and Gökmen, 2017). Kernels roasted at 150 °C showed high PV (1.727 and 1.682 meq O_2 kg^{-1}) which could be due to the decomposition and polymerization of the peroxide into a range of secondary products such as aldehydes and ketones, promoted by higher temperatures (Bai et al., 2017; Tenyang et al., 2017). Tenyang et al. (2017) and Tonfack Djikeng et al. (2018) reported that the increase of PV in sesame and walnuts, respectively, due to thermal processing could be attributed to the increase of hydroperoxides as a result of free radicals attacking the unsaturated fatty acids of oil. The results in the current study

suggested that roasting 'A4' and 'Beaumont' kernels at 150 °C promoted quality deterioration as shown by the decrease and lower concentration of flavonoids (0.053 and 0.067 mg quercetin kg^{-1}), phenols (0.038 and 0.087 mg GAE kg^{-1}), antioxidants ABTS (0.003 and 0.005 mg GAE kg^{-1}) and DPPH (0.001 and 0.006 mg GAE kg^{-1}), respectively, and poor sensory quality, excessive crispy texture, dark brown colour and rancid taste, which is an indication of over roasting and may cause the development of disagreeable compounds such as 5-hydroxymethylfurfural associated with off-flavours or bitter taste (Moghaddam et al., 2016; Taş and Gökmen, 2017). Furthermore, Kotsiou and Tasioula-Margari (2016) reported that the degradation of phenols at high roasting temperatures could be due to oxidation and hydrolysis or rancidity.

The findings discussed above support the hypothesis that higher roasting temperatures promote quality deterioration in macadamia nuts. Therefore, to avoid quality deterioration as a consequence of over-roasting, macadamia nuts should be roasted at 125 °C for 15 min. The shortcomings of the studies in Chapter 3 and 4 are that only two cultivars were used for the experiments, kernels were only roasted for 15 min and in Chapter 4 the data was only taken after processing therefore, the effect of roasting temperatures on the shelf life of 'A4' and 'Beaumont' kernels was not reported.

7.3. Storage and postharvest quality of 'A4' and 'Beaumont'

Two commercially important macadamia cultivars, namely, 'Beaumont' and 'A4' were used as model cultivars and kernels were roasted at 125 °C for 15 min using the hot air oven dryer. In Chapter 5, the 'Beaumont' cultivar had better quality compared to 'A4' during the accelerated storage of 18 weeks. Although peroxide value (PV) and acid value (AV) significantly increased during storage, the 'Beaumont' cultivar shower lower PV (0.947 and 8.764 meq O$_2$ kg^{-1}) and AV (0.3 to 0.88 %), respectively during the storage of 18 weeks. These results suggested that the kernels of 'Beaumont' were of good quality without any detectable rancid taste (Borompichaichartkul et al., 2013; Canneddu et al., 2016). This is further supported by high concentration of phenols (0.127 to 1.159 mg GAE kg^{-1}), antioxidants, ABTS (0.014 to 0.132 mg GAE kg^{-1}) and DPPH (0.010 to 0.130 mg GAE kg^{-1}) and good sensory quality; nutty taste without any noticeable rancid taste during the storage. These results suggested that the 'Beaumont' cultivar

could be stored for 18 weeks or more due to its preserved quality during storage. 'A4' cultivar showed higher PV (1.161 to 12.01 meq O_2 kg^{-1}) and AV (0.4 to 1.6 %) during storage. Moigradean et al. (2012) and Borompichaichartkul et al. (2013) reported that kernels with PV above 10 meq O_2 kg^{-1} are not acceptable and are associated with noticeable off-flavours. Canneddu et al. (2016) reported that macadamia nuts with AV exceeding 1 % are considered to have a rancid taste. The results of the current study suggest that the 'A4' cultivar is more prone to deterioration during storage and can only be stored for 12 weeks (PV =10.692 meq O_2 kg-1, AV = 0.925 %). The findings of the current study are similar to Borompichaichartkul et al. (2009) who reported the high PV of 13.58 meq O_2 kg^{-1} in macadamia nuts associated with rancidity or off-flavours. The susceptibility to deterioration of 'A4' cultivar is also demonstrated by low concentration of phenols (0.082 to 0.714 mg GAE kg^{-1}) and antioxidants; ABTS (0.008 to 0.075 mg GAE kg^{-1}) and DPPH (0.006 to 0.060 mg GAE kg^{-1}) and poor sensory quality indicated by poor nutty taste and rancid taste during storage. Ioannou et al. (2012), Watson et al. (2013), Mediani et al. (2014) and Kotsiou and Tasioula-Margari (2016) reported that the degradation of phenols during processing and storage is the prime cause of the loss of quality and nutrition in many products due to oxidation and hydrolysis.

These findings support the hypothesis that the quality and storability of macadamia nuts is largely influenced by cultivar. 'Beaumont' cultivar showed good quality during the storage of 18 weeks compared to 'A4' cultivar, therefore, would be preferred for long term storage. The shortcomings of the study in Chapter 5 is that the experiment was based on two commercial cultivars and the storage trials were only conducted at 20 °C.

7.4. Non-destructive evaluation of peroxide value (PV)

Peroxide value (PV) is the most frequently used technique for determining the onset of oxidation as it is a measure of the hydroperoxides formed in the initial stages of oxidation (Das et al., 2014; Tenyang et al., 2017; Tonfack Djikeng et al., 2018). Peroxide value could be measured using instrumental techniques such as gas chromatography (GC), gas chromatography-mass spectrometry (GC-MS), high-performance liquid chromatography (HPLC) and titrating using

burette (Fard et al., 2003; Walton, 2005; Walton et al., 2017). Although these methods are commercially effective, they are currently not used by the macadamia industry because it is slow, difficult, time-consuming, use chemicals, not a representative of entire samples and costly to be used for assessing PV in an industrial scale (Burdurlu and Karadeniz, 2003; Canneddu et al., 2016). Hence the objective of the research conducted in Chapter 6 was to investigate the feasibility of visible and near infrared (Vis/NIR) spectroscopy (Vis/NIRS) to predict PV on intact kernels of macadamia nuts.

Vis/NIRS is a non-destructive technique capable of providing non-visible information about comparative proportions of C–H, O–H, and N–H bonds in nuts (Guthrie et al., 2004; Moscetti et al., 2014; Pannico et al., 2015). Predictive model statistics showing the accuracy of prediction developed for PV has been proposed in Chapter 6 (Table 1). Good prediction of rancidity was obtained in roasted kernels (R^2_p = 0.88, RMSECV = 0.16 and RMSEP = 0.15), raw kernels (R^2_p = 0.91, RMSECV = 0.08 and RMSEP = 0.12), 'Beaumont' (R^2_p = 0.94, RMSECV = 0.05 and RMSEP = 0.07) and 'A4' (R^2_p = 0.88, RMSECV = 0.06 and RMSEP = 0.09). This study findings were similar to Jensen et al. (2001) and Canneddu et al. (2016) who reported accurate models for predicting rancidity in walnuts (R^2 = 0.82 and RMSECV = 7.7) and macadamia nuts (R^2p = 0.80 and RMSEP = 0.14), respectively. These results suggested that NIR analysis in combination with models developed in the current study is sufficiently accurate for the route screening of processed macadamia nuts. This will greatly benefit the South African macadamia industry since it is export oriented, packers could segregate nuts based on susceptibility to rancidity and nuts that are more susceptible to rancidity could then be exported as processed products since those products will have extended shelf life.

These findings support the hypothesis that NIRS is a potential tool for non-destructive prediction of rancidity in macadamia kernels. The predicted peroxide values were consistence with analyzed peroxide values for 'A4', 'Beaumont', raw and roasted individual kernels (Chapter 6, Table 2).

7.4. Conclusions

Chapter 3 showed that roasting significantly improved kernel quality and storability of 'A4' and 'Beaumont' cultivars indicated by lower PV, high concentration of flavonoids, phenols, antioxidants, confirming the vital role of antioxidant activity in delaying lipid oxidation or rancidity. Also, according to the panelists, roasted kernels had enhanced crispy texture, aroma, flavour, appearance and good marketability throughout the storage period. For this reason, it can be recommended that macadamia kernels be roasted for improved quality and longer storability or shelf life. Chapter 4 demonstrated that different roasting temperatures significantly affected the quality of macadamia nuts. 'A4' and 'Beaumont' kernels roasted at 125 °C had lower PV, higher concentration of phenols and antioxidants and enhanced sensory quality; crispy texture, brown colour and nutty taste. Although kernels roasted at 50 to 100 °C had high phenols and antioxidants, kernels were more prone to rancidity indicated by high PV and had poor sensory quality; hard texture, light colour and slightly nutty taste whereas kernels roasted at 150 °C had high levels of rancidity, a lower concentration of flavonoids, phenols, antioxidants, excessive crispy texture, dark brown colour and bitter taste. Therefore, the findings of the current study suggested that 'A4' and 'Beaumont' kernels should be roasted at 125 °C to avoid quality loss due to over roasting. Chapter 5 showed that the 'Beaumont' cultivar had lower PV, AV, high phenols and antioxidants and good sensory quality; nutty taste with no noticeable rancid taste during the accelerated storage of 18 weeks compared to 'A4' cultivar which had poor quality during storage due to higher PV and AV, lower concentration of phenols and antioxidants and poor sensory quality; poor nutty taste and rancid taste. The results from the study in Chapter 6 indicated that Vis/NIRS is a useful technique for measuring PV on macadamia nuts. The total analysis takes less than 5 min once the spectrometer is pre-calibrated. In comparison to the conventional wet chemical analysis, Vis/NIRS can measure a large number of samples in a day and yet still meets the trading specification. Furthermore, by applying this technique, the amount of hazardous solvents can be reduced dramatically as well as the cost of labor.

7.5. Recommendations

Roasted kernels had good quality during storage, therefore, it can be recommended that macadamia kernels be roasted for improved quality and longer storability or shelf life. To avoid quality deterioration as a consequence of over-roasting, macadamia kernels should be roasted at 125 °C. The 'Beaumont' cultivar had good quality during the storage of 18 weeks and can be recommended for long-terms storage. Future studies should include various cultivars, processing treatments, storage conditions and packaging materials to obtain wider differences in quality parameters and storability of macadamia nuts. Also, more experimentation is needed to include more data variability in order to improve robustness and increase the classification accuracy to 100 %. Future studies should also include a wide range of drying or roasting temperatures to obtain a wide variability of PV in nuts.

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