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Storage stability of whole and nibbed, conventional and high oleic peanuts (*Arachis hypogeae* L.).

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Abstract

Peanuts are increasingly being used as nibbed ingredients in cereal bars, confectionery and breakfast cereals. However, studies on their oxidative stability in this format are limited. Storage trials to determine the stability to oxidation were carried out on whole and nibbed kernels of conventional (CP) and high oleic (HOP) peanuts, with respect to temperature and modified atmosphere packaging. HOP exhibited the highest oxidative stability, with a lag phase in whole kernels of 12-15 weeks before significant oxidation occurred. HOP also showed higher levels of intrinsic antioxidants, a Trolox Equivalent Antioxidant Capacity (TEAC) of 70 mMol equivalence and radical scavenging percentage (RSP) of 99.8% at the beginning of storage trials, whereas CP showed values of 40 mMol and 81.2%, respectively. The intrinsic antioxidants at the beginning of these storage trials were shown to affect the peroxide value (PV), where RSP and TEAC decreased, PV increased. Therefore in peanuts the processing format (nibbed or whole) had the highest influence on susceptibility of lipid oxidation, highest to lowest importance; processing format > temperature > atmospheric conditions.

Keywords

Antioxidants, peanut, storage, lipid oxidation,

Abbreviations used

AOAC, Association of Analytical Chemists; CP conventional peanuts; HOP, high-oleic peanuts; LDL, low density lipoprotein, MUFA, monounsaturated fatty acids; PV, peroxide value; RSP, radical scavenging percentage; TAG, triacylglycerides; TEAC, Trolox equivalent antioxidant capacity.

1. Introduction

Arachis hypogeae L. (Peanut) is an important oil seed crop, ranking fourth in world oil seed production (after soybean, oilseed rape and cotton, respectively) in 2012. The main producers are China (44%), followed by India (25%) and the US (6%) (USDA, 2012a). Along with other oilseeds peanut is being considered as a potential biofuel (Nigam and Singh, 2011) currently approx. 21.5% of the US crop is processed for oil and the remainder used for direct human consumption (USDA, 2012b). Recent intervention nutritional trials, most notably with antioxidants and polyphenols, have shown potential for peanuts to be included in many different applications within the human diet to reduce the risk of cardiovascular diseases (Kris-Etherton et al., 1999), cancer (Awad et al., 2000) and diabetes (Jiang et al., 2002), peanuts contain high levels of resveratrol, a phytoalexin, which has been reported to have anticancer, blood sugar lowering and cardiovascular protective properties (Sanders et al., 2000). Peanuts are consumed as whole kernels, in candies, peanut butter and increasingly as food ingredients, as nibbed (or sliced and diced) products incorporated into cereal bars, breakfast cereals and confectionery products.

The seed typically contains 40-50% oil by weight, the quantity and quality being dependent on the cultivar, agronomic practice and climatic conditions. The reported oil content from conventional peanuts (CP) is approximately 41-67% oleic acid (18:1), whereas those from high oleic peanuts (HOP) contain up to 80% oleic acid (Dean et al., 2011). The trait was found to be associated with two genes that increased the oleic acid content to ~80% and reduced linoleic acid contents to around 2% (Moore and Knauft, 1989). The increase in monounsaturated fatty acid and decreased in polyunsaturated fatty acids has been shown to increase the storage time of these cultivars when compared with CP. Previously reported work includes information comparing HOP and CP for storage times (Bolton & Sanders, 2002; Isleib et al., 2006; Pattee et al., 2002), but little is known about the decreases in antioxidant levels during this time, as well as the effect of further processing. It has been reported that levels of antioxidants are similar in CP and HOP (Talcot et al., 2005) whereas others have reported higher levels of antioxidants in HOP (Jonnala et al., 2006; Craft et al., 2010).

Lipid oxidation is implicated as the primary cause of shelf life and the development of off-flavours and aromas in roasted peanuts (Bolton & Sanders, 2002; Isleib et al., 2006; Pattee et al., 2002). Oils rich in monounsaturated fatty acids (MUFAs) are associated with improved storage time as the rates of oxidation of C_{18} fatty acids are approximately 1:10:100:150 for 18:0, 18:1, 18:2 and 18:3, respectively; conjugation of double bonds in polyunsaturated fatty acids increasing the rates further (Porter et al., 1995). The complex oxidative process has been found to be accelerated by the action of light and oxygen, additionally water activity and high temperatures have shown acceleration of oxidation alongside the presence of pro-oxidants such as metal ions (Buettner, 1993; Blomhoff et al., 2006; Jensen et al., 2005; Mexis et al., 2009). Studies with walnuts found a correlation between malondialdehyde (a secondary oxidation product) concentration and peroxide value (PV), a measure of oxidation that has occurred during storage, and that the development of off-flavours and increased lipid oxidation are (high-to-low importance): temperature > concentration of O_2 > lighting intensity (Mexis et al., 2009). In other studies particularly in peanuts, oxidation has been shown primarily to be due to light intensity and the presence of oxygen (Jensen et al., 2005).

Previous studies have reported differences in the rates of lipid oxidation between the two cultivars, but little is known of the decreases in antioxidant activity during this time or the effect of increasing the surface area of the peanuts prior to storage. The objective of this study was to compare the oxidative stability of whole and nibbed, conventional and high oleic peanuts, under different temperature and atmospheric (packaging) conditions (±oxygen) to observe the decreases in intrinsic antioxidants, increases in peroxide value and concentration of pro-oxidants in both cultivars.

2. Materials and Methods

2.1. Raw materials. High oleic peanuts (HOP) were sourced from the British Peanut Council (London, UK), the American Peanut Council (Washington, DC, USA) and Sun Valley Peanuts (Wirral, UK), conventional peanuts (CP) were sourced from Imperial Snacks Ltd. (Pont-y-Clun, UK).

2.2. Chemicals. All chemicals were of analytical grade and purchased from Fischer Scientific UK (Loughborough, UK).

2.3.1 Oil content. Soxhlet extraction was carried out (in triplicate) according to AOAC Official Method 920.39C. Briefly, approximately 10.00 g of peanuts were ground and placed in a thimble and refluxed for 3 h using petroleum ether (60-80°C) as the solvent. After 3 h the solvent was evaporated under nitrogen and the residue weighed.

2.3.1. Ash content. The ash content was determined (in triplicate) using AOAC Official Method 923.03 with minor modifications. Briefly, approximately 5.00 g of ground peanuts were placed in a porcelain crucible and heated in a muffle furnace at 600°C for 3 h, after which the residue was weighed.

2.3.2. Moisture content. The moisture content was measured (in triplicate) according to AOAC Official Method 950.46B. Briefly, approximately 5.00 g of ground peanuts were placed in a porcelain crucible and heated in a vacuum oven at 105°C for 2 h, after which the residue was weighed.

2.3.3. Protein and nitrogen analysis. Protein was analysed using the combustion method for nitrogen in cereal grains according to AOAC Official Method 992.23. Approximately 25.0 mg of ground peanut (in triplicate) was encapsulated in foil and subject to pyrolysis. The protein conversion factor from nitrogen to protein is 5.46, which was used to calculate the protein content of the samples. A CE Instruments Na2100 Protein Analyser (Wigan, UK) was used and urea was used as the pure primary standard.

2.3.4. Carbohydrate analysis. The carbohydrate content was calculated using the subtraction method. The data obtained for the ash, moisture, oil and protein contents were subtracted from the initial values to give the carbohydrate value as the residue.

2.4.1. Peanut roasting. Batches of peanuts (500 g) were placed on aluminium foil covered trays and roasted at 160±1°C for 25 min, with a bed depth of 4 cm and turned twice during roasting.

2.4.2. Chopping, packaging and storage. Roast whole peanuts were nibbed using a Borrell Granule processing machine MQ-711. Rollers crushed the peanuts and then were passed through a vibrating perforated belt. The nibbed peanuts (<2 mm^3) were collected. Nibbed and whole peanuts were packed into gas (and light) impermeable foil lined polyethylene bags; either gas flushed with nitrogen, an oxygen meter (WITT Oxybaby M^+) was used to ensure the oxygen concentration was <0.2% oxygen in nitrogen or was not gas flushed. The packaged whole or nibbed peanuts, nitrogen or air flushed, were either placed in a refrigerator (4°C), at 18°C (room temperature) or in an incubator at 30°C.

2.4.3. Lipid oxidation – defatting peanuts. Peanuts were ground in a coffee grinder (Wahl Mini Grinder 150W Stainless Steel ZX595) for 30 sec. Ground peanuts (50 g) and 100 mL petroleum ether (60-80°C) were mixed together and left for 3 h in the dark at room temperature and under nitrogen, which were occasionally shaken. The mixture was filtered (Whatman No. 1 filter paper) and the petroleum ether evaporated under a stream of nitrogen. The oil was stored at 4°C under nitrogen and used within 2 h or stored at -80°C under nitrogen until required. This was repeated in triplicate.

2.4.4. Peroxide value. Peroxide value was measured using the AOAC Official Method Cd 8-53. 5.00±0.2 g of peanut oil was weighed and 30 mL chloroform:acetic acid (2:3 v/v) added. 0.5 mL saturated potassium iodide was added as an indicator and was left for one minute with occasional shaking, 30 mL of deionized water was added and titrated against 0.1 M sodium thiosulfate, whilst being vigorously shaken. 0.5 mL 1% starch solution was used as a secondary indicator to determine the end point. completed in triplicate.

2.4.5. Peanut metal chelators. Approximately 1.0 g of minced peanuts was added to 9 mL of methanol (in triplicate). The solution was vortexed and left for 24 h in the dark at 5℃. The solution was centrifuged at 1676 x g for 3 min and kept in the dark at room temperature until assayed (within 1 hour). To 0.1 mL of the solution was added to 0.6 mL deionised water and 0.1 mL of 0.2 mM ferrous chloride solution ($FeCl_2.4H_2O$). The mixture was allowed to stand at room temperature (18℃) for 30 seconds and 0.2 mL 1

mM ferrozine was added. After 10 mins the absorbance was measured at 562 nm (Jenway UV/Vis spectrophotometer 6700 series, Staffordshire, UK). Ethylene diamine tetracetate (EDTA) (0.1 mM) was used to compare the chelating activity of the peanut extracts.

2.4.6. Metal ion concentrations. Ashed samples were dissolved in 1 M nitric acid solution (in triplicate), and analyzed using a Solaar 969 AA spectrometer (TJA Solutions, Cambridge, UK). The results were gained from using Iron, copper and zinc standard solutions, which were obtained from CAMLAB, (Cambridge UK). The iron, copper and zinc lamps were from Heraeus (Cambridge, UK).

2.5.1. Scavenging activity – DPPH radical. Approximately 1.0 g of minced peanuts was placed into a centrifuge tube and 9 ml of lab grade methanol added (in triplicate). The solution was mixed using a vortex and left for 24hrs in the dark at 5℃. The solution was centrifuged at 1676 x g for 3 minutes and kept in the dark at room temperature until assayed (within 1 hour). 1 ml of this solution was added to 4 ml of 1.5 mM 2,2-diphenyl-1-picrylhydrazyl (DPPH) (Sigma-Aldrich Company Ltd, Dorset, UK) in methanol, left at room temperature for 20 minutes and then read at 517nm (Jenway UV/Vis spectrophotometer 6700 series, Staffordshire, UK) (Pellegrini et al., 2003). Results were expressed as scavenging potential (%).

2.5.2. Trolox equivalence Antioxidation capacity (TEAC). A stable stock solution of 2,2'-azino-bis(3-ethylbenzthiazoline-6-sulphonic acid) ($ABTS^+$) was produced by reacting a 7mM aqueous solution of ABTS with 2.45 mM potassium persulphate (Sigma-Aldrich Company Ltd, Dorset, UK) (1:1 v/v) (final concentration) and allowing the mixture to stand in the dark at room temperature for 12-16 hrs before use. Prior to analysis an $ABTS^+$ working solution was prepared by diluting in deionised water of the stock solution to give an absorbance of 0.70 ± 0.02 AU at 734 nm (Jenway UV/Vis spectrophotometer 6700 series, Staffordshire, UK). 0.1 mM Trolox solution in deionised water was used to construct a calibration curve. The same preparation as the scavenging assay was used for this method; briefly 0.5ml of the preparation was added to 2.5ml of $ABTS^+$ stock solution and left to react for 10 minutes in the dark and was repeated in triplicate. The results were expressed as Trolox equivalent per kg (Hwang

et al., 2001). All chemicals in this colorimetric assay were obtained from Sigma-Aldrich Company Ltd, Dorset, UK.

2.5.3. Tocopherol analysis. This method was carried out based on method by Kornsteiner et al. (2006), briefly 50 mg of extracted oil from the peanuts was placed into a HPLC vial and 150 µl of 15:85 (v/v) dichloromethane and methanol (mobile phase) respectively was added. 20 µl was injected into an ACE 250 x 4 mm Reverse Phase C18 column, at a flow rate of 0.8 ml/min, using the same mobile phase which was isocratic in nature. The HPLC system was a 1200 series Agilent Technologies HPLC (Berkshire, UK). α-, γ- and δ-tocopherols were used as standards at 5 mM solutions and were solubilized using the mobile phase (Fisher Scientific, Leicestershire, UK) (Kornsteiner et al., 2006).

2.6. Statistical analysis. Pearson's correlation and a one-way ANOVA were used to evaluate the correlations and compare means for the rate of lipid oxidation of the two cultivar of peanut. A two-tailed paired T-test was used to compare the raw material analysis of the two cultivars of peanut, the metal ion concentrations and the peanut metal chelators. All figures and statistical data were obtained from Graph Pad Prism 5 (McCormick & O'Keefe, 2001).

3. Results and discussion

3.1. Constituent analyses. Table 1 shows the ash, carbohydrate, lipid, moisture and protein contents of the two varieties of peanut. The results show no significant differences in their compositions as determined by 2-way ANOVA between the two varieties of peanut and between each of the constituents ($p>0.01$).

The metal ion contents of the peanuts are shown in Table 2. The metal ions measured were iron (Fe), copper (Cu) and zinc (Zn) and were comparable to previous studies on the mineral composition of peanuts (Galvao et al., 1976; Jonnala et al., 2005). The table shows no statistical difference between iron concentration and cultivar ($p>0.01$) or zinc concentration ($p>0.01$), therefore, it is unlikely that iron or zinc concentrations would affect the rate of lipid oxidation for either peanut cultivar. Copper concentration showed a significant difference between the two classes of peanuts ($p<0.01$). Copper concentrations are significantly different between the two cultivars of peanut, higher in HOP than CP. Copper has been demonstrated to affect the onset of lipid oxidation in food systems and could affect storage stability of HOP, however, the concentration of copper is low (0.05-0.10 ppm) (Lloyd et al., 1997). Although significance was observed, the differences were low and, therefore, would not be expected to significantly affect the rate of lipid oxidation in the two peanut cultivars.

Table 2 shows the EDTA equivalence, the ability to bind to metal ions and reduce the rate of lipid oxidation. Chelation activity is dependent on the ability of food constituents to chelate (bind) transition metals; Ye *et al.* (2009) described ferrous ions (Fe^{2+}) as the most potent pro-oxidant in food systems. The data showed no significant differences between the two varieties ($p>0.01$) of peanut, thus the ability to bind to metals ions for either cultivate would not significantly affect the rate of lipid oxidation.

3.2. Rates of lipid oxidation. Peroxide value (PV) is a useful measure of the primary oxidation of oil, as it measures peroxides, which are important intermediates in the oxidation mechanisms in unsaturated oils (Shahidi & Wanasundara, 2002). Figures 1 and 2 show the results for PV versus storage time for whole and nibbed kernels for HOP and CP at 30℃, nitrogen gas flushed, respectively. Peanuts were packed in food grade

aluminium foil coated polyethylene packs which eliminated the risk of light induced photo-oxidation. Figures 1 and 2 show whole kernels had a lower rate of oxidation at 30℃ when compared with the nibbed kernels, nibbed kernels showed lower rates of PV. The HOP whole kernels (Fig 2) showed a lag-phase of 12-15 weeks before the PV started to increase, whereas the nibbed kernels show an increase in PV from week 1. In figures 1 and 4, similar trends are observed for CP, where higher PVs are observed for the higher temperatures, and when comparing both the nibbed to whole kernels. However, when comparing the CP to the rates of lipid oxidation with HOP, the PV in CP are considerably higher with no observable lag-phase. At 30℃ the CP whole kernels reach a PV of 20 at 6-7 weeks, (Fig. 1) compared to the HOP (Fig. 2) which did not reach a PV of 15 after 20 weeks. The whole kernel results for the CP and HOP are comparable to previous studies (Talcott et al., 2005), who reported lower rates of lipid oxidation for HOP compared to CP.

The results, in agreement with previous studies (Talcott et al., 2005), indicate that whole kernels of HOP, have a higher oxidative stability compared to CP. The HOP of whole kernels show a lag-phase of 12-15 weeks before PV increased, whereas in the nibbed HOP, PVs increased from week 1 (Figs. 2 & 3), gas flushing with nitrogen did not reduce the rate of lipid oxidation, however, storage at lower temperature, 4℃ compared to 30℃,reduced oxidation. From this study the increa se in lipid oxidation are (high-to-low importance) kernel format (nibbed or whole) > storage temperature > atmospheric conditions. No differences were observed with the addition of nitrogen to the packaging, this may indicate that the oxidative processes have already started in the nibbed peanuts and that excluding oxygen at this stage did not affect the rate of oxidation. The increase in surface area for the nibbed product may account for the increase in oxidation rate, providing a higher surface area to volume ratio than the whole kernels; therefore oxygen could react and initiate the oxidative processes before packing of the products.

3.3. Lipid oxidation compared with other nut products. The air roasting of peanuts reduced their oxidative stability compared to raw unprocessed peanuts, in agreement with previous studies (Jonnala et al., 2005; Dean et al., 2011). Publications in the field

of peanut oxidative stability are limited, there are, however, studies on other nut species. Maté *et al.* (1996) reported data on both peanuts and walnuts. Changes in peanut PVs showed similar trends to the data discussed here, whereas walnuts showed a slightly longer oxidative storage time when compared to blanched and air roasted peanuts. Blanched hazelnuts also showed stability greater than peanuts, during 6 months of storage, the PV remained lower than 10 (Ebrahem et al., 1994). Blanched pistachios showed an increase of 10 in PV during 12 months storage, no data on roasted pistachios was reported (Maskan & Karataş, 1998; 1999). Although the rates of lipid oxidation for peanuts are comparable to other high lipid containing products (Jensen et al., 2005).

3.4. Radical scavenging percentage. The DPPH$^{\bullet}$ is a stable chemical radical and the DPPH$^{\bullet}$ results are expressed as the radical scavenging percentage (RSP) (Molyneux, 2004; Wu et al., 2004). Figures 2 and 4 show the differences between peanut cultivar and storage temperature on the decrease in RSP over time (weeks). HOP showed a correlation of r^2=0.80, $p<0.01$ for both processing formats, whereas CP had a stronger correlation r^2=0.93-0.97 (nibbed and whole, respectively), $p<0.01$. The statistical data shows that as PV increased, RSP decreased for both processing formats in CP, when compared with HOP. The RSP in CP decreased below 20% by week 5, whereas in HOP the RSP was at 40% by week 20. The data shows indigenous antioxidants within the HOP were more stable during storage than those associated with CP in these storage trials. Temperature was the most effective way of controlling the decrease in RSP, those stored at 4℃ showed higher RSP during s torage than those stored at 30℃.

The RSP data shows a good correlation with the rate of lipid oxidation. The increase in the rate of lipid oxidation and decrease in RSP are linked, and therefore correlations can be drawn from this data. The effect of storage conditions, in this case, temperature, impacted greatly on the rate of lipid oxidation and RSP, similarly to that of the PV, the addition of nitrogen into the packs did not affect the RSP. The increases in lipid oxidation during this study correlated well with the decrease of RSP for both processing formats, although CP showed greater reduction of RSP than HOP. The stability of HOP

may not be entirely due to indigenous antioxidants within the raw material, if this were the case expected results would show a clear difference between the whole and nibbed products. Therefore, some other property of the high oleic peanuts must be affecting the rate of lipid oxidation to a higher degree than amount and stability of indigenous antioxidants within the peanut kernel. It is most likely that the difference in the rate of lipid oxidation is the fatty acid arrangements, as those fatty acids with more double bond sites would have less oxidative stability (Porter *et al.* 1995).

3.5. Trolox Equivalent Antioxidant Capacity (TEAC). The TEAC capacity analysis is an indicator of the potential of indigenous antioxidants to scavenge a stable radical, $ABTS^{\bullet}$, similar to that of the $DPPH^{\bullet}$. Therefore the results are discussed as TEAC, and not potential antioxidants (Molyneux, 2004; Wu et al., 2004). Figures 1 and 3 show the differences between the storage time and the decrease in TEAC for CP and HOP varieties of peanut, stored at 4℃ and 30℃, respec tively, nibbed or whole kernels. The results correlate well with the increases in peroxide value, which is attributed to the increased rate of lipid oxidation. The collected data between the two cultivars showed that as the rate of lipid oxidation increases the Trolox equivalent antioxidants decreased in both varieties and processing formats. A relationship was observed between the decrease of TEAC and storage time, r^2=0.93-0.94, p<0.01. Figure 3 showed differences in the TEAC during these storage trials, whereby HOP indigenous antioxidants slowly decreased during time, a stabilisation of TEAC was observed during weeks 16-20 for the HOP cultivar only. Figure 1 showed no differences between the processing formats, and therefore CP does not correlate well with HOP for either whole or nibbed kernels, this data is comparable to other studies (Talcott et al., 2005; Chang et al., 2006).

The differences between higher storage temperatures in both processing formats (whole or nibbed) indicates a correlation between the increase in storage time and the decrease in TEAC, r^2=0.92-0.94, p<0.01. The highly positive correlation is similar to data collected on the onset of lipid oxidation and shows a relationship between the rate of lipid oxidation and the decrease of TEAC during these storage trials. No relationships were observed for the addition of nitrogen gas flushed modified atmospheric packaging and those with air, which is similar to that of the RSP and PV. Again the data shows that

the most influential process for the control of the rate of lipid oxidation and the decreases in indigenous antioxidants is the nibbing process, followed by temperature and the addition of nitrogen.

3.6. Tocopherol analysis. Significant differences were observed between HOP and CP tocopherols (Tables 3 and 4) at the beginning of storage trials using a two-tailed T-test ($p<0.01$) for α-tocopherols, ($p<0.01$) for β/γ-tocopherols; and finally ($p<0.01$) for δ-tocopherols. Although each tocopherol showed significant differences the largest was observed in δ-tocopherol, HOP (175 µM) and CP (100 µM). The data suggests that the tocopherol concentrations of the two cultivars of peanut are significantly different at the beginning of the storage trials. Tocopherols are chain breaking antioxidants and therefore are likely to affect the rate of lipid oxidation within this study; therefore this data indicates that higher concentrations of tocopherols at the beginning of this storage trial would have a significant effect on the rate of lipid oxidation between the two cultivars of peanut.

Table 3a shows the levels of α-tocopherols in HOP at the beginning and end of the storage period for whole kernels. The data was subjected to a one-way between-subjects ANOVA and showed a significant difference between the concentration of tocopherols and storage conditions ($p<0.01$). A post hoc analysis showed that all samples, with the exception of HOP nibbed nitrogen 18℃ and HOP whole 30℃ air which showed high variance within the data, reduced significantly during storage. Contrary to other data presented in this study, the nibbed product (table 3b) stored at 18℃ showed significantly higher concentrations at the end of storage than the whole product stored at 18℃ ($p<0.01$). In addition to th is in both the nibbed and whole formats stored at 4℃ and contained air had signifi cantly higher total tocopherol concentrations than those stored under nitrogen ($p<0.01$). The differences between the whole and nibbed product in respects to slightly higher tocopherol levels at the end of the storage trials could be attributed to the production of α-tocopherols due to the oxidation of other tocopherols during this period. The data shows the addition of nitrogen to the samples did not reduce the rate of lipid oxidation and, therefore, the decrease in total tocopherols was not shown within this data. The problem may be

attributed to the low concentrations of tocopherols at the end of storage, and therefore the differences between the storage and atmospheric conditions; and the processing formats were not as large as would be expected during storage.

The data was subjected to a one-way between-subjects ANOVA which showed significant differences between the storage conditions and shelf life of β/γ-tocopherol ($p<0.01$) and δ-tocopherol levels ($p<0.01$) (Table 3a and 3b) for HOP. The order of tocopherol oxidation observed during this experiment shows δ-tocopherol as the least stable, at the beginning of storage the δ-tocopherol concentration was 170 μM, during the 20 weeks of storage the tocopherol concentration reduction ranged from 60-99% (53.36-7.56 μm), depending on storage conditions. Similarly the reduction of β/γ-tocopherols during storage ranged between 45-72% (14.83-7.24 μm) reduction, and a 5-65% (17.68-7.38 μm) reduction for α-tocopherols. The data indicates that the oxidative stability of tocopherols is similar to that reported in previous studies (Hashim et al., 1993; Kulås & Ackman, 2001), showing that α-tocopherol has higher oxidative stability than other tocopherols, the resistance to oxidation is $\alpha > \beta/\gamma > \delta$.

Table 4 shows the tocopherol contents at the start (0 week) and end (7 weeks) of storage for both processing formats of CP, stored in nitrogen at 18℃. The whole and nibbed tocopherol data was subjected to a one-way between-subjects ANOVA and significant differences were observed between weeks 0 to 7 (whole and nibbed) ($p<0.01$). A *post hoc* analysis revealed that at the start of storage (0 weeks) for whole and nibbed peanuts the β/γ-tocopherols were significantly higher than at the end of storage trials (7 weeks) ($p<0.01$). δ-tocopherol contents for the whole peanut were significantly higher than for the nibbed format and at the end of this storage ($p<0.01$). An interesting observation during this study was the increase in α-tocopherol levels at the end of storage when compared with those at the beginning of storage, this was significant ($p<0.01$). Goffman & Möller (2000) reported a 20% increase in tocopherol concentration in whole rape oilseeds during storage, which is similar to the increase observed in table 4, which shows an increase in α-tocopherol in 7 week stored whole peanuts compared to the nibbed samples or those peanuts at the beginning of storage. No other significant differences were observed. The data indicates that α-tocopherols

are more stable to oxidation, and may not be the main source of chain breaking antioxidants in peanuts. However, significant differences were observed between α-tocopherol contents for nibbed peanuts. This data correlates well with previous studies (Goffman & Möller, 2000; Kulås & Ackman, 2001) and the HOP data, which suggest δ-tocopherols oxidative stability, is lower than β/γ- and α-tocopherols, respectively.

The nibbing process reduces the stability of peanuts, but increases the potential of inclusion into a wide variety of products. Antioxidant decreases were observed in both varieties of peanut, although at a faster rate in CP, and in both processing formats (whole or nibbed kernels). Peanuts are well positioned to fulfil the requirements set out by consumers for a healthy stable product, the high oleic breeding lines show increased stability during processing as well as providing health promoting benefits (Jang et al., 1997; Kris-Etherton et al., 1999; Sanders et al., 2000; Blomhoff et al., 2006). This stability could be attributed to the increase in monounsaturated fatty acids in HOP when compare with CP, but this study suggests that other factors (intrinsic antioxidants) may increase HOP's oxidative stability. It is likely that other nuts would follow this trend; therefore the incorporation of nibbing to other roasted nuts, most notably pecans, walnuts, cashew and almonds would increase their susceptibility to lipid oxidation. The evaluation of the nibbing process on other roasted nuts would be beneficial to the nut industry and would provide the consumer with a saleable and healthy product.

4. Conclusions

In summary, the rates of lipid oxidation are higher for the nibbed peanuts than the whole kernels, as would be expected. Controlling the temperature of nibbed peanuts appears to be the most effective method for reducing the rate of oxidation. The lag-phase observed in the development of PVs for the HOP merits further study. This study showed a significant difference in TEAC and total tocopherols between the two cultivars of peanut, HOP and CP, which showed significantly higher concentrations in HOP cultivar. The RSP showed a good correlation with the peroxide value and the rate of lipid oxidation in these storage trials. The use of both TEAC and RSP, alongside PV and total tocopherol analyses showed that the storage of conventional and high oleic

peanuts were determined by the following (highest to lowest importance) surface area > temperature > addition of nitrogen.

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Conflict of interest

There are no conflicts of interest in this research paper.

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Figure 1: Represents the peroxide value and TEAC of conventional peanuts (CP) over 12 weeks. The CP was either nibbed (Nib) or whole (W) kernels and stored at either 30℃ undergoing gas flushing (N_2).

Figure 2: Shows the peroxide and RSP values of HOP over 19 weeks. Peanuts were whole (W) or nibbed (N) and stored at 30℃ undergoi ng gas flushing (N_2).

Figure 3: The change of peroxide value and TEAC of HOP over 19 weeks. The HOP was either nibbed or whole kernels and stored at 4°C undergoing gas flushing (N_2).

Figure 4: Shows the peroxide and RSP values of HOP over 12 weeks. The peanuts were either nibbed (Nib) or whole (W) kernels stored at 4℃ undergoing gas flushing (N_2).

Constituents	CP (%)	HOP (%)
Lipid	52.18 ± 0.41	53.04 ± 0.05
Protein	26.89 ± 1.50	25.91 ± 1.31
Carbohydrate	13.90 ± 2.36	14.34 ± 1.99
Moisture	4.78 ± 0.58	4.47 ± 0.75
Ash	2.26 ± 0.07	2.24 ± 0.19

Table 1: The main macro-nutrients of both varieties of peanuts ± indicate the standard deviation.

	HOP	**CP**
Fe	0.71 ± 0.04 [ppm]	0.74 ± 0.01 [ppm]
Cu	0.36 ± 0.02 [ppm]	0.64 ± 0.02 [ppm]
Zn	1.06 ± 0.09 [ppm]	1.02 ± 0.01 [ppm]
Chelation	0.10 ± 0.00 [M]	0.07 ± 0.02 [M]

Table 2: The concentrations of metal ions (Fe, Cu, Zn) and chelating potential (1M EDTA equivalence) for CP and HOP. ± indicate the standard deviation.

	α-tocopherol	β/γ-tocopherol	δ-tocopherol
Initial conc.	18.89±0.60	29.33±0.0.05	175.00±0.0.14
Air:4℃	8.14±0.10	11.99±0.25	53.26±0.63
Air:18℃	8.13±0.87	7.24±0.46	24.28±0.04
Air:30℃	15.83±1.15	9.86±0.76	9.86±1.18
N_2: 4℃	7.38±0.76	9.49±0.10	27.18±0.20
N_2: 18℃	13.27±0.22	14.38±0.26	22.29±0.89
N_2: 30℃	9.46±0.13	9.77±0.97	9.77±0.43

Table 3a: Reduction in α-, β/γ- and δ-tocopherol concentrations (μMol) for HOP whole kernels.

	α-tocopherol	β/γ-tocopherol	δ-tocopherol
Initial conc.	18.89±0.60	29.33±0.05	175.00±0.14
Air:4℃	11.30±0.26	13.79±0.46	37.76±1.22
Air:18℃	13.32±0.17	16.40±0.23	40.66±0.27
Air:30℃	9.23±0.33	9.63±0.30	3.18±0.06
N_2: 4℃	9.32±0.08	9.91±0.24	24.99±0.59
N_2: 18℃	17.68±0.90	14.83±0.69	7.56±0.26
N_2: 30℃	12.32±0.29	11.76±0.35	9.04±0.47

Table 3b: Reduction in α-, β/γ- and δ-tocopherol concentrations (μMol) for HOP nibbed kernels.

Storage weeks	α-tocopherol [μmol]	β/γ-tocopherol [μmol]	δ-tocopherol [μmol]	Total tocopherol [μmol]
0	39.01±0.32	39.45 ±0.01	100.14±0.51	178.60±0.84
7 (*1)	46.05±0.80	11.68±0.10	10.24±0.75	67.97±1.65
7 (*2)	36.24±0.64	7.24±0.14	6.45±0.60	49.93±1.38

Table 4: Tocopherol contents of whole (*1) and nibbed (*2) CP after 7 weeks of storage at 18℃ in nitrogen