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Oxidative stability and lipid composition of macadamia nuts grown in New Zealand

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Abstract

This study was undertaken to identify the parameters which might influence the stability and storage characteristics of some selected cultivars of macadamia nuts grown in New Zealand. Four cultivars of macadamia nuts (*Macadamia tetraphylla*) were harvested from the North Island of New Zealand during 1997. Total lipids, composition of fatty acids, tocopherols, sterols and stability of oils, were determined on the oil extracted from the fresh nuts. The total lipid content of the nuts ranged from 69 to 78%, while the stability of the oil measured by Rancimat test ranged from 3.6 to 19.8 h. Peroxide values of the fresh oil ranged from 0.56 to 3.61 meq O_2/kg oil. The major fatty acids were oleic acid, palmitoleic acid and palmitic acid; oleic acid accounted for 40.6 to 59% of the total fatty acids. The polyunsaturated fatty acid (18:2 + 18:3) content was low, ranging from 3.0 to 4.7%. α-Tocopherol (0.8–1.1 μg/g lipids) and δ-tocopherol (3.5–4.8 μg/g lipids) were the only two tocopherols identified in the extracted oil. The major sterols identified were sitosterol (901–1354 μg/g lipids), Δ5-avenasterol (82–207 μg/g lipids), campesterol (61–112 μg/g lipids) and stigmasterol (8–19 μg/g lipids).

1. Introduction

The macadamia is a large evergreen tree indigenous to the coastal rainforests of Australia. While 10 species have been identified only two (*Macadamia tetraphylla* and *M. integrifolia*) are grown commercially in Hawaii, Australia and New Zealand. When ripe, the nuts fall to the ground encased in a fibrous, green husk, or pericarp. When fresh, these nuts can have a moisture content of 30%; they are dried to a moisture content of ≅2% for storage.

Macadamia nuts are highly valued due to their attractive delicate taste. Very little research has been carried out on their composition but initial data on the composition of NZ-grown macadamia nuts suggest that a wide variation of the fatty acid profile exists (Dawson & Savage, 1997). Recently, macadamia nuts have generated considerable interest because they are believed to have blood cholesterol-lowering properties (Colquhoun, Humphries, Moores & Somerset, 1996). This is believed to result from the particularly high oleic acid content of the nut oil. Macadamia oil is the most highly monounsaturated oil available (Ako, Okuda & Gray, 1995), containing higher levels than olive oil, high-oleate safflower oil, rapeseed oil (Leissner et al., 1989) and walnuts (Savage, Dutta & McNeil, 1999). However, in contrast to those oils the increased level of monounsaturated fatty acid in macadamia oil was contributed by 16:1 to a considerable extent (17–34%).

The development of an unacceptable taste or rancidity is a feature of nuts that have been badly stored or stored for too long. The factors that determine the oxidative stability of macadamia nuts are still largely unknown. In storage experiments with macadamia nuts, it has been reported that the total tocopherol level (6.4–18 μg/g dry matter) is too low and differences in fatty acid composition are not great enough to contribute to differences in kernel stability (Quinn & Tang, 1996).

Macadamia nuts tend to develop rancidity rapidly during storage at room temperature (Cavaletto, Dela Cruz, Ross & Yamamoto, 1966). Cavaletto et al. stored macadamia nuts under different humidity and temperature conditions. They found that the stability of the kernels, using a trained sensory panel, decreased with increasing moisture content and increasing storage

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temperatures and concluded that the most important factor for macadamia stability is moisture content. For greatest stability, kernels must be dried to approximately 1% moisture and stored at low temperatures (preferably −18°C). Fourie and Basson (1989) showed that changes in peroxide levels can be used to predict rancidity in nuts instead of using a trained sensory panel.

The present study is a preliminary investigation of the total lipids, fatty acid composition, tocopherols, sterols and stability of four of the most commonly grown cultivars of macadamia nuts in New Zealand. These data may help in the selection of cultivars that are better suited to more extensive commercial production in the North Island of New Zealand.

2. Materials and methods

2.1. Reagents

All chemicals used in this study were supplied from Merck and Sigma Chemical companies, unless otherwise stated.

2.2. Macadamia nut samples

Four different cultivars of Macadamia nuts (*M. tetraphylla*) grown in seven different locations in the North Island in New Zealand were harvested in 1997. The nuts were dried immediately after harvest to a moisture content of 3–6% and stored uncracked in paper bags at −20°C.

2.3. Analysis

The extraction of the oil from the nuts (Hara & Radin, 1978) and analysis of the oil for peroxides [International Dairy Federation (IDF), 1991], individual fatty acids, sterols and tocopherol content followed the methods outlined by Savage et al. (1999). Total lipids were determined using duplicate Soxhlet extractions, without prior hydrolysis. Finely chopped nuts (2 g) were ground with acid washed sand (Merck) and extracted with 50 ml petroleum ether for 30 min at 100°C in a Soxtec System HT (Tecator, Sweden). The determination of the Rancimat value followed the method outlined by Savage et al., except that the oil was heated to 120°C to measure its oxidative stability.

3. Results and discussion

The total amount of extracted lipids (Table 1) in the kernels ranged from 69 to 78 g/100 g dry matter (DM); this was slightly higher than the results reported by Dawson and Savage (1997) which ranged from 60 to 73% in 100 g/DM. The oxidative stability determined by the Rancimat technique showed a wide variation between the different cultivars ranging from 3.6 to 19.8 h (Table 1). The cultivar Jordan was the most stable oil, even when heated to 120°C, while the two cultivars of PA 39, grown at different locations, showed values ranging from 6.6 to 7.3 h, suggesting that this cultivar may be less stable during long-term storage. Cultivar GT 207 appears to have a very unstable oil. It is interesting to note that this cultivar also had the highest level of peroxides compared to the other nuts and in addition it had the highest level of fatty acid 18:2 (Table 2) of all the macadamia nuts analysed. In a recent study by Quinn and Tang (1996), the Rancimat induction time of commercially refined macadamia nut oil was 0.5 h at 130°C, while the oils in this study were unrefined and were only heated to 120°C. The standard temperature used in the Rancimat method is 110°C. In this study, the macadamia oils were heated to 120°C as the induction point at 110°C was very long and only reached after heating for 36 h (results not shown). In contrast to macadamia nut oils, other common nut oils heated to 110°C have induction times ranging from 3.9 to 7.8 h (for walnut oils) (Savage et al., 1999) and 15.6 to 25.3 h (for hazelnut oils) (Savage, McNeil & Dutta, 1997).

The fatty acid content of the macadamia nut oil is shown in Table 2; the mean monounsaturated fatty acid content was 80% while the total saturated fatty acids ranged from 13.2 to 17.8%. The polyunsaturated fatty acid content (18:2 + 18:3) was relatively low and ranged from 2.8 to 4.7% (mean 3.6±0.7). These data are comparable to data previously reported in the literature (Dawson & Savage, 1997; Mason & McConachie, 1994), except that this is the first study to report the presence of *cis*-vaccenic acid ($18{:}1^{\Delta 11}$) in oil extracted from macadamia nuts. The composition of the fatty acids varied substantially between the different cultivars, particularly the oleic acid content. The mean oleic acid content of PA 39 was 42% while Beaumont had a mean value of 53%.

The peroxide values ranged from 0.56 to 3.61 meq O_2/kg oil (Table 1). One cultivar (GT 207 from New Plymouth) showed a peroxide value much higher than the other samples analysed. This cultivar also appeared to have the highest content of linoleic acid (18:2) of all samples, and had a relatively low content of total tocopherols and tocotrienols. Overall peroxide formation is generally low in whole macadamia nuts as the kernel is protected by a thick pericarp.

The levels of tocopherol in New Zealand-grown macadamia nuts were low and only α-tocopherol and δ-tocopherol were identified in the oil extracted from the four different cultivars (Table 3). The total values observed in this study are a little higher than that reported by Quinn and Tang (1996), who reported a total content of tocopherol of 9–25 μg/g lipids for macadamia nuts grown in Hawaii. In other nut species, e.g. hazelnuts (Savage et al., 1997) and walnuts (Savage et al., 1999), tocopherols have been proved to contribute to kernel stability. In macadamia nuts it appears that the α- and δ-tocopherol contents are too low to influence the kernel stability. On the other hand, considerably large amounts of α-tocotrienol were tentatively identified in the samples, ranging from 13 to 48 μg/g lipids. α-Tocotrienol was identified by comparing retention time

Table 1
Total oil (g/100 g DM), peroxide value (meq O_2/kg oil) and Rancimat value (h) of the four different cultivars of nuts harvested in 1997

Cultivar	Harvest location	Total oil (±S.E.)	Peroxide value (±S.E.)	Rancimat value (±S.E.)
Jordan	Auckland	69.1 (1.3)	1.13 (0.01)	19.75 (0.75)
PA 39	Manakau	76.4 (0.1)	2.89 (0.34)	7.34 (0.24)
PA 39	Whangarei	73.6 (0.4)	1.10 (0.19)	6.57 (0.15)
Beaumont	Pukekohe	73.4 (1.9)	1.35 (0.18)	8.15 (0.17)
Beaumont	Great Barrier Island	78.4 (2.4)	0.56 (0.00)	8.29 (0.09)
Beaumont	Kerikeri	–[a]	0.72 (0.06)	9.94 (0.87)
GT 207	New Plymouth	71.6 (1.8)	3.61 (0.05)	3.59 (0.02)

[a] Insufficient sample for analysis.

Table 2
Fatty acid composition (% of total) of oil extracted from macadamia nut cultivars grown in New Zealand

Cultivar (location)	14:0	16:0	16:1	18:0	$18:1^{\Delta 9}$	$18:1^{\Delta 11}$	18:2	18:3	20:0	20:1	22:0	22:1	24:0	Others
Jordan (Auckland)	1.84	8.41	29.65	1.72	47.34	3.05	2.99	0.17	1.23	2.13	0.39	0.19	0.12	0.77
PA 39 (Manakau)	1.11	11.13	30.39	2.84	43.18	3.62	2.83	0.17	2.06	1.40	0.56	0.10	0.11	0.49
PA 39 (Whangarei)	1.30	10.56	33.75	3.19	40.55	3.29	2.63	0.20	2.02	1.36	0.45	0.07	0.14	0.50
Beaumont (Pukekohe)	0.96	8.50	21.50	1.49	54.48	2.69	3.96	0.16	1.55	2.55	0.54	0.24	0.19	1.19
Beaumont (Great Barrier Island)	1.13	9.85	29.25	2.01	46.14	3.37	3.13	0.18	1.65	1.83	0.49	0.15	0.17	0.66
Beaumont (Kerikeri)	0.97	8.54	16.86	2.02	59.01	2.65	3.81	0.18	1.81	2.63	0.61	0.23	0.18	0.48
GT 207 (New Plymouth)	1.68	10.54	25.78	1.64	48.29	2.64	4.47	0.20	1.31	2.14	0.41	0.16	0.14	0.60

Table 3
The tocopherol content (μg/g lipids) of oil extracted from macadamia nuts

Cultivar (location)	α-Tocopherol	δ-Tocopherol	α-Tocotrienol
Jordan (Auckland)	1.1	4.5	48.4
PA 39 (Manakau)	1.0	4.2	17.2
PA 39 (Whangarei)	0.8	4.8	23.8
Beaumont (Pukekohe)	0.9	3.5	12.5
Beaumont (Great Barrier Island)	0.9	4.3	33.5
Beaumont (Kerikeri)	0.9	4.7	30.6
GT 207 (New Plymouth)	0.8	4.2	28.3

Table 4
Composition of desmethylsterols (μg/g lipids) of oil of extracted from macadamia nut cultivars

Cultivar (location)	Campesterol	Stigmasterol	Sitosterol	Δ5-Avenasterol	Total
Jordan (Auckland)	92	15	1354	88	1549
PA 39 (Manakau)	112	10	916	82	1120
PA 39 (Whangarei)	93	15	901	145	1154
Beaumont (Pukekohe)	61	8	947	101	1117
Beaumont (Great Barrier Island)	73	11	1058	156	1298
Beaumont (Kerikeri)	109	17	1069	207	1402
GT 207 (New Plymouth)	72	19	1079	150	1320

with the standard sample. No further attempt was made, however, to confirm the structure of this compound. A few other unidentified peaks were also present; the identification of these compounds needs to be studied. Furthermore, the total content of tocopherols and tocotrienols in the samples analysed might be linked with the oxidative stability, since, the cultivar Jordan which showed the highest oxidative stability in the Rancimat test, also appeared to have the highest content of total tocopherols and tocotrienols, 54.0 μg/g lipids, and, the two cultivars of PA 39 that showed the lowest resistance to oxidative stability likewise appeared to contain lower amounts of total tocopherols and tocotrienols.

The major sterols identified (Table 4) were sitosterol, ranging from 901 to 1354 μg/g lipids, Δ5-avenasterol, ranging from 82 to 207 μg/g lipids, campesterol, ranging from 61 to 112 μg/g lipids and stigmasterol, ranging from 8 to 19 μg/g lipids. Traces of cholesterol were also found in all samples (results not shown). The content of total desmethylsterols ranged from 1117 to 1549 μg/g lipids (Table 4). Δ5-Avenasterol has an additional double bond on its side-chain which gives it an antioxidative property in frying oil (Gordon & Magos, 1983).

The cultivar Jordan appeared to have the highest oxidative stability, as measured by the Rancimat technique, but it did not show a Δ5-avenasterol content higher than other cultivars. The total desmethylsterol content appeared to be slightly higher in cultivar Jordan than in the rest of the cultivars analysed. In addition, the two cultivars of PA 39 that were shown to have the lowest resistance to oxidative stability belonged to the group of samples containing the lowest amount of total desmethylsterols.

4. Conclusions

In this study, no clear relationship existed between the stability of the oil and the content of polyunsaturated fatty acids. It is more likely that the stability of the oil is influenced by factors such as the positions of the individual fatty acids within the triacylglycerol molecule and the presence of tocopherols, carotenoids, free fatty acids and sterols as suggested by Neff, Mounts, Rinsch, Konishi & El-Agaimy, 1994.

Macadamia nuts have very low concentrations of polyunsaturated fatty acids and this explains why the level of peroxides in the oil is quite low. The cultivar Jordan had a very high Rancimat value compared to all the other cultivars and this suggests that this cultivar will be more stable to long term storage.

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