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Characterization of micro-components of avocado oil extracted with supercritical carbon dioxide and their effect on its oxidative stability

by

Mathilda Elizabeth Mostert

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DECLARATION

I declare that the thesis which I herewith submit at the University of Pretoria for the award of the degree of PhD (Food Science) is my research and has not been submitted by me for a degree to any other University or institution of higher education.

Mathilda Elizabeth Mostert
August 2007

Our life is an apprenticeship to the truth that around every circle another can be drawn; that there is no end in nature, but every end is a beginning, and under every deep a lower deep opens.

RALPH WALDO EMERSON

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ABSTRACT

Characterization of micro-components of avocado oil extracted with supercritical carbon dioxide and their effect on its oxidative stability

By

Mathilda Elizabeth Mostert

Promotor: Dr K.G. Duodu
Co-promoters: Dr L. M. du Plessis
Prof B.M. Botha
Department: Food Science
Degree: PhD (Food Science)

The main objective of this study was to determine the effect of fruit ripeness and drying method on the oxidative stability and micro-component content of avocado oil extracted with supercritical carbon dioxide (SC-CO_2). A secondary objective was to determine the effect of fruit ripeness, method of fruit drying and extraction method on the extractability of avocado oil with hexane and SC-CO_2.

For the oil extractability study, unripe and ripe avocado fruit pieces were either freeze-dried or oven-dried (80^{o}C) and extracted with hexane or SC-CO_2. For both extraction methods, oil yield was higher from ripe fruit than from unripe fruit. Scanning electron microscopy (SEM) indicated structural degradation during ripening, making the oil more available for extraction in ripe fruit. Oil from freeze-dried samples was in most cases more extractable than from oven-dried samples possibly through formation of rigid structures due to starch gelatinisation and dehydration and protein crosslinking around the oil cells during oven drying. Oil yield was higher with hexane than with SC-CO_2 extraction because hexane is less selective, permeates the whole plant material and leads to a more complete extraction, while SC-CO_2 may create paths of least resistance in the plant material where it moves preferentially, thus leading to a less complete extraction.

For oxidative stability studies and micro-component characterisation, oil extractions were performed on an industrial scale SC-CO_2 extractor. For all treatments (unripe freeze-dried, ripe freeze-dried, unripe oven-dried, ripe oven-dried), oil was divided into four fractions and analysed for fatty acid profile, peroxide value (PV), anisidine value (AV), free fatty acids (FFA), oxidative stability index (OSI), colour, tocopherol, sterol, chlorophyll, carotenoid and total unsaponifiable content.

Oil from ripe, freeze-dried avocado had relatively lower levels of chlorophyll, carotenoids and tocopherols, than oil samples from the other treatments. This may be due to relatively higher lipoxygenase levels in ripe fruit which may bring about higher oxidative breakdown of these components. Also, the activity of lipoxygenase may be preserved under the lower temperature conditions of freeze-drying, but inactivated at high temperature during oven-drying.

Intensity of blue and red on the Lovibond colour scale of all oil samples as well as chlorophyll and carotenoid content increased with progressive extraction. These pigments are presumably extracted in the latter stages of extraction because they are located in chloroplasts, chromoplasts and idioblast cells with thicker membranes than the parenchyma cells where triglycerides are located. Levels of total sterols, total tocopherols and their isomers did not show any specific trends with progressive extraction, which could be related to their location in cell membranes where they would be extracted concurrently with the triglycerides. Levels of total unsaponifiables were mostly higher in the first than the latter fractions. This could be due to the early elution of non-polar waxes which are highly soluble in SC-CO_2 and highly available due to their location on the surface of the avocado skin.

The fatty acid profile of the avocado oil was not influenced by the degree of ripeness or drying method and therefore did not affect the OSI. Oleic acid increased while linoleic acid decreased with progressive extraction. Compared to the changes observed in levels of some of the micro-components, the changes in fatty acid levels with progressive extraction were

relatively small and the fatty acid profile alone could not explain the OSI of the oil. Oil from oven-dried avocado had lower PVs but higher AVs than oil from freeze-dried fruit indicating more advanced oxidative deterioration in oil from oven-dried samples than from freeze-dried samples. FFA levels were higher in oil from ripe, freeze-dried fruit. Levels of hydrolytic enzymes increase during fruit ripening and are preserved during freeze-drying while they are inactivated during oven-drying. FFA levels decreased with progressive extraction. Free fatty acids are very soluble in the SC-CO_2 and due to their location on the surface of the plant material, they could be extracted early in the extraction.

Oil from oven-dried fruit had relatively higher OSI compared to the other treatments. The OSI of all samples increased with progressive extraction. There was a significant negative correlation between FFA and OSI for both drying methods. AV correlated positively with OSI for oil from oven-dried fruit and negatively for oil from freeze-dried fruit. AV contributed the most to the prediction of OSI in oven-dried fruit, while FFA contributed the most in freeze-dried fruit. It was suggested that the high OSI of oil from oven-dried fruit, despite its high AV, may be due to the presence of compounds with high antioxidant activity in the oil formed through the high temperatures of the oven-drying process. Therefore, using multiple regression techniques, predictive models were developed to determine the effect of the micro-components on the oxidative stability of the oil.

The OSI correlated positively with chlorophyll (0.83) and carotenoids (0.80). The models indicated that chlorophyll and carotenoids were the most important variables in predicting the oxidative stability of avocado oil extracted with SC-CO_2. This might be due to the antioxidant effect of carotenoids and the possible formation of pheophytin and pyropheophytin, thermal breakdown products of chlorophyll, which exert antioxidant effects in oil.

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