SELECTED PHYSICOCHEMICAL AND ANTIOXIDANT PROPERTIES OF SABAH UPLAND RICE IN RAW, COOKED AND FERMENTED CONDITIONS

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2015

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THESIS SUBMITTED IN PARTIAL FULFILLMENT FOR THE DEGREE OF MASTER OF SCIENCE

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2015

DECLARATION

This thesis and the work to which it refers are the results of my own efforts. Any ideas, data, images or text resulting from the work of others are fully identified as such within the work and attributed to their original author in the text and references.

3 March 2015

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DEGREE	:	**MASTER OF SCIENCE (CHEMISTRY)**
DATE OF VIVA	:	**3 MARCH 2015**

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ACKNOWLEDGEMENT

I would like to express my deep gratitude and appreciation to my supervisor, Dr. Noumie Surugau for her patience and guidance that lead to completion of this research, from the beginning when I applying for the master in Sciences until the completion of this master programme. Her vast experience and knowledge in sciences, in addition to her good nature and humility made me fortunate enough to have an opportunity to work with her.

I also would like to thank the members of staff in industrial chemistry laboratory for the permission to use the apparatus and laboratory during and after office hours and guidance in handling chemicals and laboratory equipment especially Mr. Sanie and Mr. Racheidy whom I work with closely during my research work.

Special thanks to Mr. Prudent Sameul, Mr. Jimmy Tan Teck Chai, Ms. Jenifer and Mr. Mildred who help to gather the samples and to the donors of the rice varieties used in this research; Mr. Sebastian Thomas from Tambunan (Tadong and Poroi), Mrs. Maria (Nabawan Tadong), Mrs. Marjina Jimmi (three Telupid varieties and two Ranau varieties), Mrs. Ipin binti Kambatu (Silou) and Mrs. Kamran Mansor (two Nangoh varieties), and to the paddy team at Agricultural Research Centre at Tuaran for helping with the seed identification and information.

Lastly, to my family members who encouraged and supported me during this research and to my friends and my colleague who gave me ample of knowledge and ideas during this research.

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March 2015

ABSTRACT

Rice, Oryza sativa, is a staple food for more than half of population worldwide. Upland rice is mostly cultivated on hill terrain, because of their desirable characteristics and scarce reports on the physicochemical properties of upland rice varieties from Sabah, a research was done to uncovered more information. The objective of this study is to analyse the physicochemical properties (morphological traits, crude fat, moisture, ash and minerals content) and antioxidant properties (anthocyanin content and antioxidant power) of Sabah upland rice.For this study, eleven varieties (Tadong, Poroi, Nabawan, Silou, Baliung 2710, Telupid 2434, Bangalah 2719, Alubis 118, Ranau white, Nangoh red and Nangoh white) of upland rice varieties were collected from various districts in Sabah. Besides that, observations on the changes in these properties when the rice was cooked and fermented were also presented. Physicochemical were analysed with AOAC method, while the method for minerals were done by wet-ashing procedures prior to analysis. In term of morphological traits, the studied rice varieties were categorized as long to extra-long with length-to-width ratio of 2.0–3.0 and grain weight of 18.16–23.20 g per 1000 grains. The results for the selected physicochemical parameters in untreated (raw) rice varieties are in the range of as follows (in %, w/w): 0.83 – 1.14 ash; 1.23-1.81 crude fat and 2.24-51.12 total anthocyanin content (TAC). Meanwhile, minerals content (in mg/100g): 70.95-156.91 K, 38.72-88.81 Mg, 13.40-21.92 Ca; 3.65-7.78 Na; 1.74-4.08 Zn; 1.50-4.80 Fe; 0.88-4.24 Mn; 0.314-0.96 Cu and 0.31-1.02 Se.Antioxidant property tested using FRAP method showed values in the range of 0.154 to 1.027 mmol g^{-1}. The deeply pigmented rice varieties which were "tadong" from Tambunan (deep purple), "nangoh" from Beluran (deep red), "ragang" from Ranau (red) and "tadong" from Nabawan (red) have shown higher FRAP values compared to the non-pigmented varieties (fair or white in colour). Similarly, the pigmented rice varieties possess higher TAC; with the highest in tadong from Tambunan (51.12±1.80 mg $100g^{-1}$). The high antioxidant properties (FRAP) may be due to the high TAC in the deeply pigmented rice. Mineral contents in the pigmented rice varieties showed little differences when being compared with each other. Although the pigmented generally higher than in non-pigmented, for instance K, Ca, Na, Zn, Mn and Se were the highest in tadong rice. Cooking (boiling) had caused reduction in TAC of the rice varieties up to 73 % in tadong and a range of 16 to 68% in the rest of the rice varieties. FRAP value decreased between 40 to 73 % in the cooked rice. TAC and FRAP value decreased up to 81 % and 71 %, respectively, when the rice were fermented. As for the minerals content, the process of cooking and fermentation did not affect the content greatly. In conclusion, the physicochemical content were not affected by the type of the varieties. The pigmented varieties had a higher antioxidant properties and anthocyanin content compared to non-pigmented varieties. The process of cooking and fermentation affected the physicochemical, antioxidant activity and total anthocyanin content, however mineral contents did not affected by the type of grains and the processes.

ABSTRAK

KAJIAN FISIKOKIMIA YANG TERPILIH DAN CIRI-CIRI ANTIOKSIDA UNTUK PADI BUKIT SABAH DALAM KEADAAN MENTAH, DIMASAK DAN DIPERAM

Padi, oryza sativa, merupakan makanan ruji bagi lebih daripada separuh penduduk dunia.Oleh kerana kajian kimia yang terhad dan ciri-ciri unik yang dimiliki oleh beras bukit Sabah, maka kajian dijalankan ke atas beras bukit Sabah yang telah dikumpulkan.Kajian ini menerangkan ciri-ciri fisikokimia dan ciri-ciri antioksidan beras bukit dari Sabah.Untuk kajian ini, sebanyak sebelas jenis beras bukit telah dikumpulkan dari pelbagai daerah di Sabah iaitu Tadong, Poroi, Nabawan, Silou, Baliung 2710, Telupid 2434, Bangalah 2719, Alubis 1118, Ranau white, Nangoh merah dan nangoh putih. Perubahan ciri-ciri di atas apabila beras tersebut dimasak dan diperam juga telah dikaji.Sampel-sampel beras telah dihadamkan dengan menggunakan kaedah pengabuan basah sebelum analisis dijalankan.Parameter-parameter kajian telah dianalisa dengan menggunakan kaedah AOAC dan kaedah-kaedah piawai yang lain.Dari segi ciri morfologi, beras-beras yang dikaji dikategorikan sebagai panjang ke amat panjang dengan nisbah panjang-ke-lebar 2.0–3.0 dan berat bijirin 18.16–23.20 g untuk setiap 1000 butir.Keputusan untuk ciri-ciri fisikokimia terpilih di dalam beras tanpa perlakuan (mentah) adalah di dalam julat berikut (dalam %, w/w): 0.83 – 1.14 kandungan abu; 1.23-1.81 lemak kasar dan 2.24-51.12 kandungan antosianin jumlah. Manakala kandungan mineral (dalam mg/100g): 70.95-156.91 K, 38.72-88.81 Mg, 13.40-21.92 Ca; 3.65-7.78 Na; 1.74-4.08 Zn; 1.50-4.80 Fe; 0.88-4.24 Mn; 0.314-0.96 Cu dan 0.31-1.02 Se. Ciri antioksidan telah diuji dengan menggunakan kaedah FRAP menunjukkan nilai-nilai dalam julat 0.154 hingga 1.027 mmolg^{-1}.Beras jenis yang berwarna pekat iaitu "tadong" dari Tambunan (ungu gelap), "nangoh" dari Beluran (merah gelap), "ragang" dari Ranau (merah) dan "tadong" dari Nabawan (merah) menunjukkan nilai-nilai kebolehan penurunan ferric dalam plasma yang lebih tinggi berbanding dengan jenis beras yang tidak berwarna (berwarna cerah atau putih).Begitu juga dengan jenis-jenis beras yang berwarna pekat mempunyai kandungan antosianin jumlah yang lebih tinggi; di mana nilai tertinggi didapati di dalam tadong dari Tambunan (51.12±1.80 mg 100g^{-1}).Kekuatan penurunan ferric oleh antioksidan yang tinggi mungkin disebabkan oleh kandungan antosianin jumlah yang tinggi di dalam beras-beras yang berwarna pekat.Secara keseluruhannya, kandungan mineral dalam sampel-sampel beras bukit tidak dipengaruhi oleh warna dan jenis beras tetapi beras Tadong dari tambunan mempunyai K, Ca, Na, Zn, Mn and Se yang tinggi.Proses memasak melalui pendidihan menyebabkan penurunan kandungan antosianin jumlah di dalam beras tersebut sehingga 73 % di dalam tadong Tambunan dan di dalam julat 16 hingga 68 % bagi jenis-jenis beras yang lain. Manakala, nilai kekuatan antioksida dalam penurunan ferric berkurang di antara 40 hingga 73 % apabila beras tersebut dimasak. Nilai-nilai kandungan antosianin jumlah dan kekuatan antioksida dalam penurunan ferric meningkat masing-masing sehingga 81 % dan 71 % apabila jenis beras tersebut diperam. Kandungan mineral tidak menunjukan perubahan ketara dalam proses pendidihan dan pemerapan. Kesimpulannya, jenis-jenis beras tidak mempengaruhi fiziokimia dan kandungan mineral tetapi mempengaruhi kandungan antisianin dan antiokidan. Proses pendidihan menyebabkan ciri fiziokimia, antisianin dan antioksidan menurun dan pemerapan menyebabkan peningkatan dalam nilai-nilai tersebut, namun proses –proses tidak mempengaruhi kandungan mineral dalam beras bukit.

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LIST OF ABBREVIATION

IRRI	-	International Rice Research Institute
MARDI	-	Malaysian Agricultural Research and Development Institute
ARC	-	Agricultural Research Centre
FAO	-	Food and Agricultural Organization
USDA	-	United States Department of Agriculture
TAC	-	Total anthocyanin content
ROS	-	Reactive oxygen species
FRAP	-	Ferric reducing ability of plasma
RDI	-	Recommended daily intake
AOAC	-	Association of analytical communities
ICP-OES	-	Ion capture photon-omitting emission spectrometer
T	-	Tadong
P	-	Poroi
N	-	Nabawan
S	-	Silou
TBW	-	Baliung
TWR	-	Telupid
TWW	-	Bangalah
RBR	-	Ragang
RWW	-	Lanad
NW	-	Nangoh white
NR	-	Nangoh red
TPTZ	-	2,4,6-Tripridyl-s-Triazine

ACS	-	American Chemical Society
MA	-	Massachusetts
SPSS	-	Statistical package for Social Science
SD	-	Standard deviation

LIST OF SYMBOLS

Cu	-	Copper
Fe	-	Iron
Ca	-	Calcium
Mg	-	Magnesium
Ph	-	Phosphorous
Na	-	Sodium
Cl	-	Chlorine
K	-	Potassium
I	-	Iodine
Se	-	Selenium
Cr	-	Chromium
Mn	-	Manganese
Mo	-	Molybdenum
Zn	-	Zinc
ha	-	Hectare
mm	-	Millimetre
g	-	Gram
%	-	Percent
OH	-	Hydroxy
H	-	Hydrogen
OCH_3	-	Methoxy
mg	-	Milligram
A AE	-	Antioxidant activity equivalent

mmol	-	Millimole
µmol	-	Micromole
Cr	-	Chromium
I	-	Iodine
Mo	-	Molybdenum
Ph	-	Phosporous
Cl	-	Chlorin
Kg	-	Kilogram
^{0}C	-	Degree Celsius
w	-	Weight
V	-	Volume
A	-	Absorbance
pH	-	Measure of acidity and alkalinity of solution
MW	-	Molecular weight
DF	-	Dilution factor
ε	-	Molar absorptivity
nm	-	Nanometer
mM	-	Millimolar
M	-	Molar
µL	-	Microliter
ppm	-	Part per million
n	-	Sample
r^2	-	Regression

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CHAPTER 1

INTRODUCTION

1.1 Background

One of the most consumed foods by human population were grains. Grain was a fruit of a plant that belong to a grass family (Graminea) (Rizza *et al.,* 2002). Due to the process of spontaneous permutation, the seed of the pot stay with the grass instead of broken down by the wind, this enable people to collect and replanted the grains (Rizza *et al.,* 2002). Grains were the source of carbohydrate that provided the energy in daily diet and content less cholesterol, making it suitable to be consumed throughout a day (Rizza *et al.,* 2002). There were many types of grains that being domesticated and cultivated such as barley, wheat, and rice. There usually consumed or used as an ingredient in production of many grains related product throughout the market such as flour in bread production, cereal and alcohol.

Rice was one of the major types of grains and cereal food consumed by most of population in the world. It was mostly grown in tropical and subtropical country in the world. Rice had become a staple food for country in most parts of Asia and the Pacific, South America and the Caribbean, North African and Sub-Saharan Africa (Kennedy and Burlingame, 2003) providing half of calories in daily diet especially for the Asian population. These plants were capabled of growing in practically any climate, however hot and humid area was the best for growing (Abbas *et al.,* 2011). There were three types of rice grains characterized by the grain size that was short grain rice, medium grain rice and long grain. Each of the grain sizes had different properties when processed. For some country, rice was not only being consumed as food supplies but also as a source of income.

In Asia, local had long cultivated pigmented rice that had multiple bran colours such as purple, black and red (Ahuja *et al.,* 2007).Pigmented rice only had their hull removed, leaving the bran still intake and retained most of the nutrients

(Rizza *et al.,* 2002). Pigmented rice was tough to eat and take a longer time to cook, which makes it less favourable among consumer. Unlike pigmented rice, milled rice undergone the process of milling to remove the bran and germ to produce soft and easy grains so that was can be cooked and consumed, however milling caused loss of nutrients in the rice grains (Perera and Jansz, 2007).

In Malaysia, rice was normally cultivated either as wet paddy or upland paddy. Wet paddy was a body that being cultivated in a plateau space, with water irrigation producing higher yielding rice varieties that mostly for used to fulfil market demand. Upland paddy were cultivated on dry (high or low) land by small holder farmers in rural area for own consumption. Upland paddy was mainly cultivated in Sabah and Sarawak (165, 888 ha) where the traditional seed that were passed from older generation, was used to planted the paddy in high land or hillside (Hanafi *et al.,* 2009). In Sabah, there were various indigenous rice cultivars with different bran colour such as purple, black, red, brown but the most common type was white rice (Lum and Chong, 2012). Some examples of the widely cultivated traditional upland rice varieties in Sabah were "Tadong", "Ragang", "Tombunan", "Poroi" and "Bokilong". "Tadong" and "Ragang" were two types of pigmented rice which were deep purple (almost black) and reddish in colour, respectively. These two varieties were gaining popularity among the local consumers, because most of the research done indicating that the rice grain in bran contain more nutrition compared to the milled rice.

Rice was served as a main course because of its properties to mix well other type of food (Rizza *et al.,* 2002). Rice was prepared by boiling the rice grains in a measured amount of water (2:1). Then rice becomes soft and fluffy if it was correctly cooked. Another way to consume rice was through fermentation where it was still widely practised by the Asian population. There were three types of fermented rice product: solid, paste and liquid. The solid-state fermented products including starter types such as *pekka*, *anka* (China), *ragi* (Indonesia), *koji* (Japan), pre-digested "yellow rice" (Ecuador), and bread-like foods. Paste products including *miso* (Japan), *mocha* (Japan) and *chiang* (China). The liquid products were *shao-hsing* wine (China), *sake* (Japan), and rice vinegar (Panmei *et al.,* 2003). The fermented food was known for its great value of benefit to health and was one way for the people to gain nutrient (Nicolau *et al.,* 2011). In Sabah, the fermented

upland rice were widely popular among the Kadazans, Dusuns and Muruts communities especially during Harvest Festival as snacks and alcoholic beverages (Suhaimi, 2010).

1.2 Problem statement

Despite the increasing interest on the Sabah's upland rice, there were still limited reports on their nutrients content and physicochemical characteristics. Studies had been reported by several researchers (Hanafi *et al.,* 2009; Mariam *et al.,* 1991; Ramli *et al.,* 2012 and Shorabi *et al.,* 2012), however most research were done only on the agronomic studies and some microbial studies on fermented rice (Chiang *et al.,* 2006) but very few on nutritional research (Lum and Chong, 2012). Therefore, it was essential to carry out baseline study on the nutrients content of the traditional upland rice varieties. Lately in Sabah, the farmers in the rural prefer to cultivate their land with a more profitable crop such as oil palm and rubber or developed their land further to tourism and real estate purpose, thus reducing the land for upland rice cultivation. With this impending "threat" to upland rice cultivation, there was a valid concern that the traditional rice varieties that had been in their possession for generations will extinct one day. The cultivation of upland paddy only produce lesser yield compared to the wet paddy, in addition to that the modern paddies were much more resistance to environment challenges such as drought and diseases. So the modern paddies were more preferable as it was profitable and able to fulfil the demand in market, thus the low-yielding upland paddy only being cultivated in small amounts. Therefore, studies on the chemical content on the traditional rice varieties were important to provide ample knowledge on the beneficial aspect of the upland rice that was the chemical studies to the people, so that upland rice in Sabah can continue to be cultivated.

1.3 Significance of studies

The growing interest on upland rice was largely due to their desirable characteristics, particularly in terms of their fragrance, colour, size, and shape where they were mostly sold with their bran still intake. The unique characteristic might be an indication that the upland rice different chemical composition that potentially become beneficial in our daily diet. The pigmented rice had attracted much interest because of its bran contained many phytochemicals with potential health benefit. Previous studies showed that red rice had gained popularity in Japan

as a functional food due to its high polyphenols and anthocyanin content (Itani and Ogawa, 2004). Nowadays people were much concern of the health, one of the ways they can maintain the healthy were through their diet. Upland rice was known for their health benefit properties, Sabah upland rice might be able to be introduce to the market as health food. Another aspect that was being studied was the effect of food processing such as cooking and fermenting on the nutrients content in the rice. It was scientifically known that nutrients such as vitamins and phytochemical contents in fruits, vegetables and grains were easily destroyed through heating and other treatments. The Sabah upland rice especially the darker colour pigment would had a higher concentration of chemical content compared to the lighter colour pigment because it have more functioning compound that contributed to intensity of colour and fragrance of the rice grains. Thus the previous studies would provide guidance to parameter which was yet to be done by other researchers and this research would illuminate and promoting more studies on Sabah upland rice.

1.4 Research objectives

The overall objective of this research was to further the knowledge on Sabah's upland rice in three different conditions in term of their nutrients. In order to know the peoples' health beneficial factors in Sabah's upland rice, the important nutritional value was uncovered and analysed to give additional information to the current knowledge of upland rice. Further this research can showed the changes of nutrient contents in three conditions of interested conditions; two of them were in a consumable condition.

Specifically, the objectives of this research were:

1. To study the morphological properties of the Sabah's upland rice grain from various locations.
2. To study physicochemical contents (moisture, ash, crude fat and mineral) and antioxidant properties (antioxidant power and anthocyanin content) of the collected Sabah's upland rice in three conditions raw, cooked and fermented.
3. To analyse the changes of the selected physicochemical content and antioxidant properties in cooked and fermented rice.

Objective 1 was focused on physical properties, the appearance and locations where it was collected of the sample. In objective 2, data was gathered from various research methods that show the interested parameter data and comparing the highest value in each circumstance. Thus in objective 3, the data collected was used to determine how the data changes if the same process were being involved that was the process of cooking and fermentation.