Effects of infrared-radiation drying on bioactive compounds and qualities of pigmented rice variaties.

Jiranan Ratseewo

A Thesis Submitted in Partial Fulfillment of Requirements for
degree of Doctor of Philosophy in Food Technology (International Program)
December 2019

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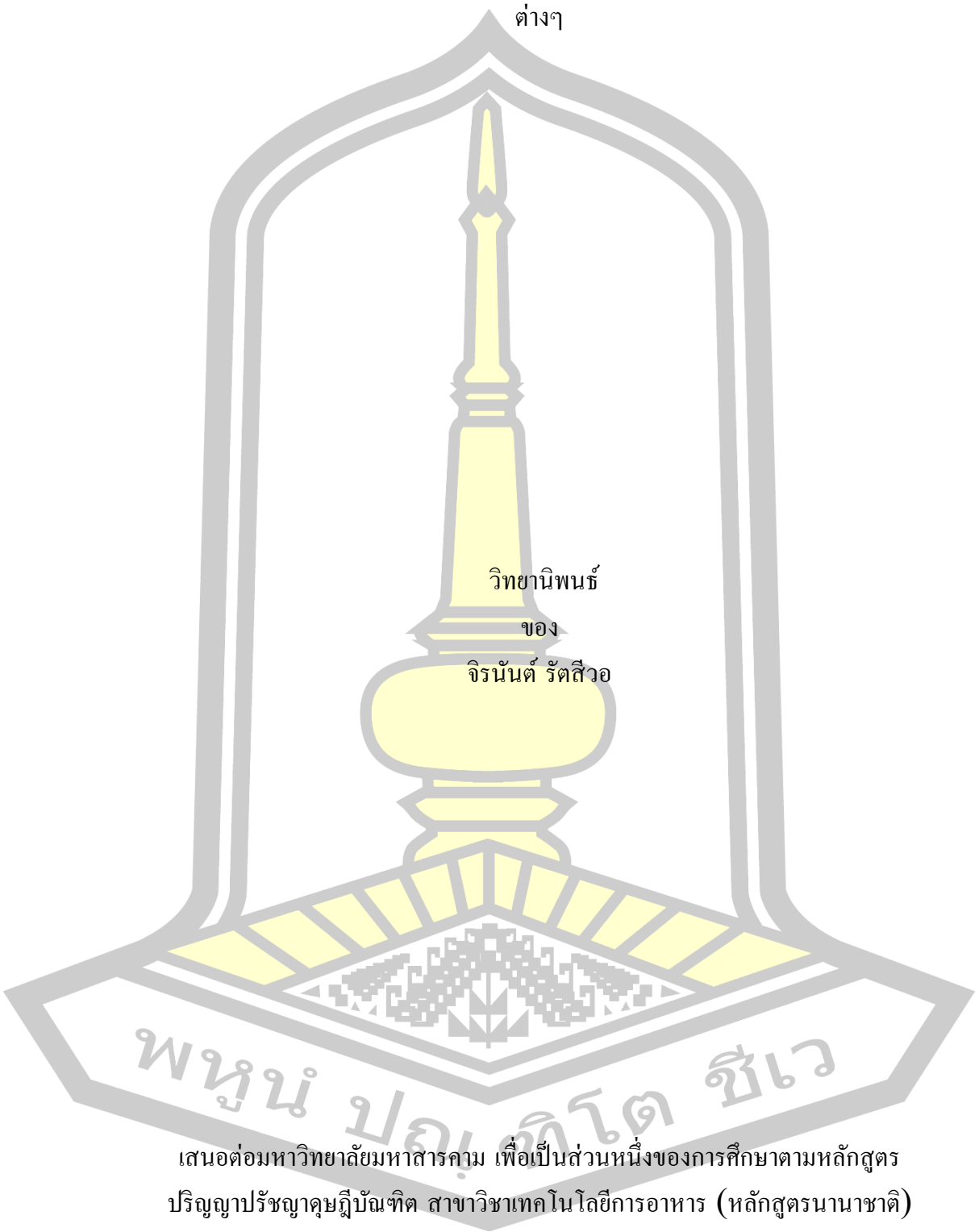

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The examining committee has unanimously approved this Thesis, submitted by Miss Jiranan Ratseewo , as a partial fulfillment of the requirements for the Doctor of Philosophy Food Technology (International Program) at Mahasarakham University

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TITLE Effects of infrared-radiation drying on bioactive compounds and qualities of pigmented rice variaties.

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ABSTRACT

Pigmented rice is a rich source of many bioactive compounds such as phenolic acids, flavonoids, anthocyanin, g-oryzanol and tocopherols that having the potential to reduce disease risk. However, these compounds can be changed by thermal drying, such as far-infrared radiation drying (FIR) and hot air (HA) drying. Recently, many studies have reported that some bioactive compounds and antioxidant activities of tomato, papaya, mulberry leaf tea and rice bran increased after treated with FIR drying. However, the knowledge regarding effect of FIR drying on bioactive compounds in pigmented Thai rice has not been reported. Therefore, the objective of the present study is to investigate the effects of infrared-radiation drying on phenolic acids, flavonoids, anthocyanins, g-oryzanol and tocopherols and antioxidant activity of pigmented rice varieties (Mali Dang, Hom Nil and Riceberry). The FIR drying conditions were set air velocity at 1.5 m/s, an intensity of FIR at 2 kW/m^2. Then the rice sample was dried at 40°C for 2 h to cut down final moisture content was 12–14% dry basis while, HA was set at 1.5 m/s, 60 40°C for 2 h. Far infrared radiation (FIR) was applied to brown and milled pigmented rice of three varieties, and their changes in bioactive compounds and antioxidant capacity were investigated, compared to hot air (HA) dried samples. The results of this study presented that free as well as bound fraction of pigmented Thai rice varieties are rich sources of phenolic components with antioxidant activity. Ferulic acid is major free and bound phenolic acids in pigmented rice. Compared to free phenolic acid, the bound phenolic content was 3 fold greater for ferulic acid. Overall, FIR increased total phenolic, flavonoid and anthocyanin contents, as well as tocopherol and antioxidant capacity in all rice varieties, whereas the opposite results were observed for HA. Gallic and ferulic acids were increased up to 75% and 31% in FIR irradiated samples, respectively, compared to HA and control. FIR also enhanced aglycone quercetin production, due to the breakage of glycosidic bonds of rutin as glycone flavonoid. Likewise, dephinidin and cyanidin anthocyanins were increased by 3.0 and 3.2 fold in FIR treated groups, respectively. The starch digestibility of different Thai rice varieties depend on varieties of rice. Pigmented Thai rice varieties (Mali Dang, Hom Nil and Riceberry) have lowered the percent of starch digested more than white rice (Hom Mali). Purified starches group were shown the lowest percent of starch digested except white rice. Riceberry jam product was

investigated in the evaluation of chemical, physical and sensory properties including analysis of bioactive compounds. The results indicated that Riceberry flour contained the highest bioactive compound and antioxidant activity, followed by the Riceberry rice jam and the stored jam and were decreased during stored time for 30 day. Similar results were found in the evaluation of chemical and physical except sensory properties that shown the same overall liking in both of fresh Riceberry jam and stored Riceberry jam. Our findings suggest that the nutritional value and health benefit of pigmented rice grains can be improved by enhancing the specific bioactive makers using FIR application.

Keyword : Pigmented rice, Bioactive compounds, Antioxidant components, Far-infrared radiation

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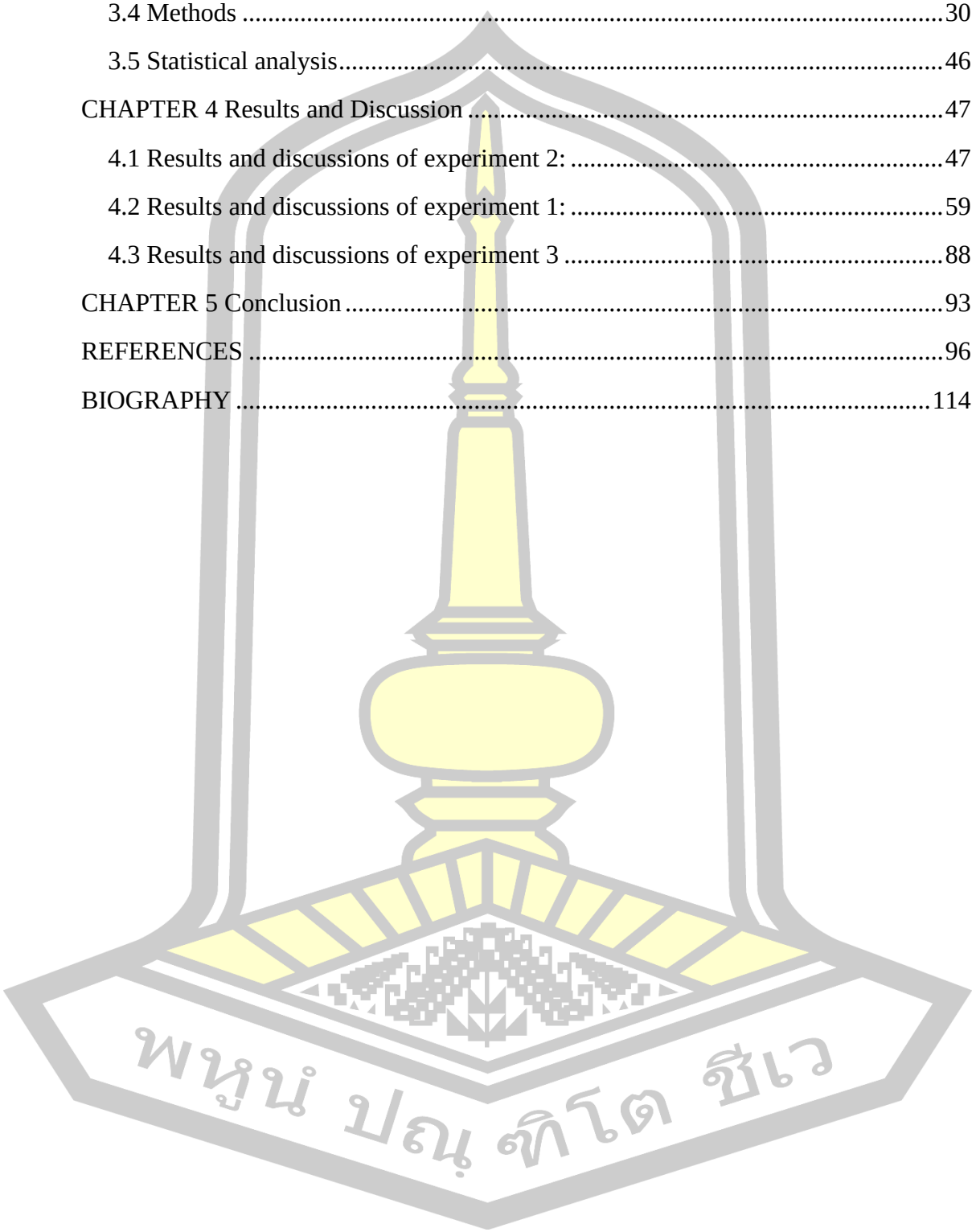

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Chapter 1
Introduction

1.1 Background

Rice is a major agricultural product and the world's major staple food. It is a rich source of essential nutrients: phytochemicals and bioactive compounds such as phenolic acids and flavonoids. These are compounds that have the potential to provide health benefits and to decrease the risk of coronary disease and cancer (Germano et al. 2006).The bioactive compounds in unpolished rice are mostly found in the outermost aleurone layers, germ and bran of the grains (Zhou, Z., Robards, K., Helliwell, S., & Blanchard 2004) The content and type of phenolics differ among varieties of rice, being related mainly to the pericarp colour. Due to the accumulation of pigments in the pericarp and seed coat of rice varying from deep-purple to brown-reddish, these varieties are referred to as "pigmented rice" grains (Zhou, Z., Robards, K., Helliwell, S., & Blanchard 2004). Pigmented rice varieties are native to Asian countries where they have been used both as foods and for therapeutic and religious purposes. Recently they have been grown widely around the world. For instance, pigmented rice varieties from Australia grains (Zhou, Z., Robards, K., Helliwell, S., & Blanchard 2004) and Brazilian rice (de Mira, Massaretto, Pascual & Marquez 2009) have been reported to possess high amounts of phenolic antioxidants including anthocyanins that have been recognized as health-enhancing cereals due to their antioxidant capability. In Thailand, three rice varieties (black, brown and red) in the northern region were also found to have high concentrations of phenolic acids, flavonoids and anthocyanins (Pengkumsri et al. 2005). However, changes in the amounts of these compounds may be affected by treatment, including thermal and non-thermal processing, during the milling and drying of the grain. In addition, besides the effect on bioactive compounds, it has been reported that milling processing decreased in essential amino acids, which are the one of important nutrients in brown rice in China (Liu, Zheng & Chen 2017). However, the effects of drying methods on amino acids of pigmented rice have not been reported.

After harvesting, paddy rice is normally dried to reduce the moisture content prior to milling. A further drying process is employed to decrease the moisture content to less than 14% for safe storage. However, the effect of the drying method can alter the antioxidant capability of the dried material (Wanyo, Siriamornpun & Meeso 2011). Hot-air (HA) drying is the most commonly used process to dehydrate vegetables and fruits; but the content of bioactive compounds and antioxidant activities decrease after hot-air drying (Wanyo, Siriamornpun & Meeso 2011).

In contrast, far-infrared radiation (FIR) has been applied for drying agricultural products, especially crops, for many years. The principal technique involves the heat of FIR rays transferring smoothly to the centre of the material being dried, without degrading molecules on the grain surface. Recent studies have reported changes in the antioxidant activity in water extracts from peanut hulls after FIR. The results showed that antioxidant activities were increased by the time of heating, either by hot air or FIR (Lee et al 2006). There were also improvements due to drying in the physical properties and antioxidant capacity of various plants, such as kaprow leaves (Raksakantong, Siriamornpun, Ratseewo & Meeso 2011). and rice bran (Wanyo, Meeso & Siriamornpun 2014). Recently, pigmented rice has been gaining popularity due to the increasing awareness of a need for healthy foods. Furthermore, several pigmented rice varieties have been grown according to organic practices by local farmers in Thailand for export, as fair-trade products. Although some researchers have reported on the bioactive compounds of pigmented rice (Pengkumsri et al. 2005). the effects of drying methods have not been reported.

Recently, the consumption of pigmented rice has increased in popularity in Thailand and in other countries such as Italy. (Melini & Acquistucci 2017). and Taiwan (Deepa, Singh & Naidu 2010). The pigmented pericarp of rice contains a high content of phenolic compounds including anthocyanins which are the major bioactive pigment component in pigmented rice (Zhou, Robards, Helliwell & Blanchard, 2004; Abdel-Aal, Young & Rabalski, 2006, Chen, Nagao, Itani & Irifune, 2012). These compounds may have anti-oxidative effects (Choi, Jeong & Lee 2007) and the capability to reduce the concentrations of reactive cell-damaging free radicals (Adom & Liu 2002). Although rice provides the daily calorie demands for many humans and animals (Ryan et al. 2011). excess consumption of boiled or steamed white rice may

be associated with some adverse health effects. Since it is an easily digestible cereal, with a high (> 71) glycemic index (GI) (Wolever et al. 1990) high levels of consumption may be associated with increased incidence of diabetes, obesity and cardiovascular complications (Jenkins et al., 2007).

Obesity and diabetes rates are currently increasing rapidly across the globe from 171 million in 2000 to 366 million in 2030, primarily due to environmental factors such as diet and decreased physical activity (Wild, Roglic, Green, Sicree & King 2004). The glycemic index (GI) of foods has been proposed as an important parameter of starch digestion and has been established as an indicator for the selection of carbohydrate rich foods based on their postprandial blood glucose raising potential (Jenkins 2012). Therefore, continuous consumption of high GI or high postprandial glycaemia response foods may be associated with an increased risk ofobesity, type II diabetes and cardiovascular disease (Jenkins, 2012). In vitro measurements of starch amylolysis rate, which are more convenient and avoids the ethical implications of human intervention studies, may be used as a proxy for GI testing of foods (Butterworth, Warren, Grassby, Patel & Ellis 2012). In this study, we use the recently introduced Logarithm of Slope (LOS) method (Butterworth, Warren, Grassby, Patel & Ellis 2012). which allows for rapid and accurate determinations of the rate and extent of digestion.

Pigmented rice has been reported to possess important health promoting properties such as antioxidant, antiglycation and anticancer properties (Daiponmak, Senakun & Siriamornpun 2014). Moreover, there have been a number of studies reporting starch digestibility of pigmented rice. For instance, Deepa, Singh and Naidu 2010 studied three pigmented Indian rice cultivars indicating that pigmented rice had less digestibility than normal rice. Similarly, some researchers have reported that pigmented rice had lower GI and contained much higher total phenolic content in Thai varieties from northern Thailand (Ponjanta, Chomsri & Meechoui 2016). Therefore, pigmented rice consumption may be associated with reduced disease risk, for instance, cardiovascular disease and diabetes (Choi, Jeong & Lee 2007). Recently researchers reported the phenolic compounds (Shobana, Sreerama & Malleshi 2009; McDougall et al. 2005). are potent inhibitors of two important enzymes (α-amylase and α-glucosidase). In addition, anthocyanin rich extracts from pigmented potatoes

showed high inhibitory activity towards intestinal starch digestive enzymes (Ramdath, Padhi, Hawke, Sivaramalingam & Tsao 2014). Although some GI values have been reported for northern Thai rice varieties, there is no data on the starch digestibility of flour and purified starch of pigmented Thai rice varieties.

Therefore, the objective of the present study is to investigate the effects of infrared-radiation drying on bioactive compounds and qualities of pigmented rice varieties for use as functional food. In this study, we aimed to investigate the effects of drying methods on pigmented rice, including FIR drying and hot air drying, on the content of bioactive compounds (soluble and bound phenolics, flavonoids, anthocyanins, tocopherols, etc.) along with their antioxidant activities and amino acids. Furthermore, the comparison contrasted unpolished and polished grain. The aim of this present study was also to investigate starch amylolysis of Thai rice varieties with white, red and purple pericarp color and provide an estimate of starch digestibility in purified starches and flours from rice samples. Through this approach we aim to investigate the influence of differences in starch structure (in purified starches) and polyphenol content (in flours) on the digestibility of Thai pigmented rice varieties. We thus expect to provide useful information for scientists, engineers and industrial practice.

1.2 Objectives

The objectives of the study are:

1.2.1 To investigate the effect of FIR drying on bioactive compounds and antioxidant activities in pigmented Thai rice varieties.

1.2.2 To investigate the effect of FIR drying on of bioactive compounds and antioxidant activities in processed pigmented Thai rice varieties.

1.2.3 To investigate the starch digestibility of pigmented Thai rice.

1.2.4 To develop product from selected pigmented Thai rice as functional food

1.3 Expected outcomes

1.3.1 Obtain the data appropriate application of the drying method on processed pigmented Thai rice product to improve contents of bioactive compounds and antioxidant properties

1.3.3 Obtain the starch digestibility of pigmented Thai rice.

1.3.4 Product prototype from bioactive compounds.

1.4 Hypothesis

1.4.1 FIR drying could be affected the bioactive compound and antioxidant activities changes.

1.4.2 The different of drying method for application in rice product process could be differenced the content of bioactive compound and antioxidant activities.

1.4.3 The influence of starch structure and anthocyanin content on the digestibility of Thai pigmented rice.

1.5 Scope of research

1.5.1 Study the effect of FIR drying process on bioactive compounds in pigmented Thai rice using infrared radiation.

1.5.2 Study an effect of FIR drying on marker of bioactive compounds in processed pigmented Thai rice

1.5.3 Study the starch digestibility of pigmented Thai rice affected FIR drying.

1.6 Definition of key words

1.6.1 Pigmented rice refers to rice which has a characteristic dark purple color attribute to an affecting the aleurone layer of the rice grain.

1.6.2 Bioactive compounds are extranutritional constituents that typically occur in small quantities in foods. They are being intensively studied to evaluate their effects on health (Kris-Etherton. 2002 : 71s-88s).

1.6.3 Antioxidant components are micro constituents present in the diet that can delay or inhibit lipid oxidation, by inhibiting the initiation or propagation of oxidizing chain reactions, and are also involved in scavenging free radicals. Food such as fruits, vegetables and grains are reported to contain a wide variety of antioxidant components, including phenolic compounds (Katalinic et al. 2004: 593–600)

1.6.4 The IR region is divided into three regions: the near, mid, and far IR (Figure 8). The mid IR region is of greatest practical use to the organic chemistry. This is the region of wavelengths between 3 x 10–4 and 3 x 10–3 cm. Chemists prefer to work with numbers which are easy to write; therefore IR spectra are sometimes reported in μm, although another unit, $\bar{\nu}$ (nu bar or wavenumber), is currently preferred.

1.6.5 The starch digestibility is mainly hydrolyzed starch by the enzymes for example α-amylase into maltose and glucose through several steps.

CHAPTER 2

literature review

2.1 Rice

Rice (*Oryza sativa* L.) is one of the world's most important cereal crops, and is an important staple crop, particularly in Asia. The most commonly consumed form of rice is white (milled and/or polished rice) without husk, bran and germ, while smaller, but still significant, amounts of brown rice and pigmented rice with red and black-purple pericarp are also consumed. Rice is widely consumed in the world, and the most common type (> 85%) has a white pericarp. Other types have a colored pericarp, and the most common are green, black, and red. The black and red varieties are planted mainly in South Asia and other countries (Simmons and Williams. 1997 : 5-14). A rice grain consists of the hull (including the awn, lemma and palea) and the rice caryopsis, also known as brown rice (Figure 2.1) (Juliano and Bechtel. 1985 : 17-58). The four layers of the caryopsis including pericarp, seed coat, nucellus, and aleurone, along with much of the embryo comprise the bran portion of the rice grain. We are especially interested in the antioxidative and radical-scavenging properties of rice because of their potential to provide health protection against reactive oxygen species and free radicals, which have been implicated in more than 100 diseases (Halliwell. 1992 : 33-50). Rice is a good source of calories provided by its high content of starch and high nutritional quality protein; it is hypoallergenic and easily digested (Mazza. 1998 : 71-89). . Rice is a good source of the vitamins B, thiamine, riboflavin and niacin, but contains little to no vitamin C, D or β-carotene, the precursor of vitamin A. The amino acid profile of rice is high in glutamic and aspartic acids, but low in lysine (FAO. 1993 : 162). The main antinutritional factors, most of which are concentrated in the bran, are phytate, trypsin inhibitor, oryzacystatin and haemaglutinin-lectin (FAO.1993 : 162). The rice bran oil antioxidants are very efficient in reducing low density lipoprotein and total serum cholesterol (Rukmini and Raghuram.1991 : 593-601 ; Sugano and Tsuji. 1997 : 521S-524S ; Mazza. 1998 : 71-89 ; Kim. 2005 : 286-291).. Almost all the oil of the rice grain is located in the bran and germ (Marshall. 1994 : 421-438). The different layers of rice seed (outer hull, caryopsis, aleurone, subaleurone and endosperm) and the embryo contain differ amounts of nutrients. Dietary fiber, minerals and B vitamins are highest in the bran

and lowest in the aleurone layers; the rice endosperm is rich in carbohydrate and contains a fair amount of digestible protein, with an amino acid profile which compares favorably to other grains (FAO. 1993 : 162).

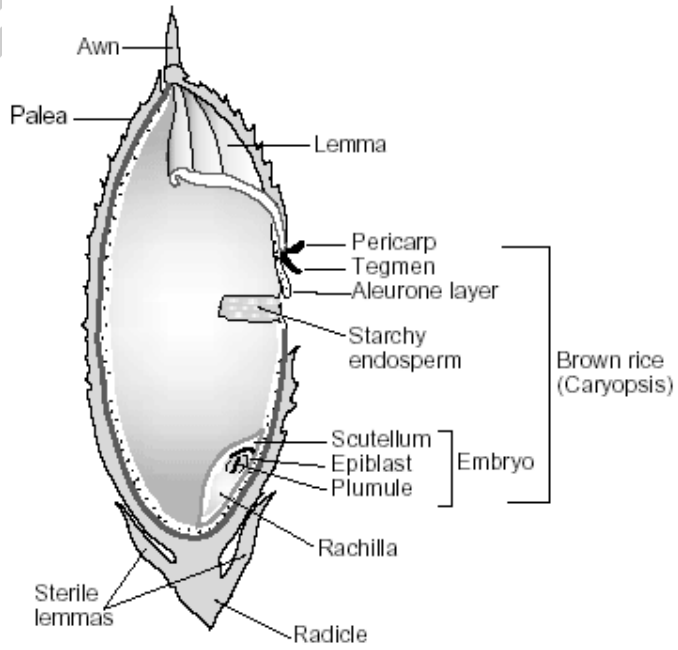


Figure 1.1 Structure of rice grain

1. Paddy rice or rough rice

Paddy rice, is also called rough rice, is used to describe the rice as it comes from the field after harvest. The rice has been threshed and each grain is separated. The grain of rice has a hard husk protecting the kernel inside. The husk (or hull) that covers rice is much thicker and tougher than most cereal grain husks. On average, paddy rice produces: 25% hulls, 10% bran and 65% white rice (Saunders and Betschart. 1979 : 191-216).

2. Brown rice

After the husk is removed the remaining product is called brown rice. Brown rice includes three components as bran, germ, and endosperm. All three are high in fiber, and contain vitamins B and E, as well as antioxidants. Brown

rice consists of an average weight of 6-7 % bran, 90% endosperm and 2-3% embryo (Chen, Siebenmorgen and Griffin.1998 : 560-565). Brown rice can reduce the blood sugar due to its low glycemic level (Meyer and others. 2000 : 921-930). Studies have also shown that cardiovascular disease is greatly reduced when consuming high levels of fiber content such as brown rice. Because obesity is the key component in heart disease, maintaining a high fiber, low fat diet can reduce the risk of heart disease and stroke (Jacob and others. 1998 : 248-257 ; Liu and others.1999 : 412-419).

3. Milled rice

Milled Rice has had the hulls and bran removed. It is also called white rice or polished rice. There are various degrees or fractions of polishing white rice imply 8-10% bran removal. In general, the more rice bran is removed from the grain during polishing, the more vitamins and minerals are lost. Protein loss due to milling is estimated at 10-15% (Malik and Chaudhary. 2002 : 207-222).

2.2 Phenolic compounds

Phenolic compounds are defined as substances possessing a benzene ring bearing one or more hydroxyl substituents, including their functional derivatives (Waterman and Mole. 1994 : 66-69). Phenols have many favourable effects on human health. They reduce the risk of heart diseases by inhibiting the oxidation of low-density lipoprotein (LDL) (Bonilla and others. 1999 : 209-215). A large range of low and high molecular weight phenols exhibiting antioxidant properties have been studied and proposed to be used as antioxidants against lipid oxidation. This is particularly true for those phenolics with multiple hydroxyl groups that are generally the most efficient for preventing lipid oxidation. Phenolic compounds are also known to posses antibacterial, antiviral, antimutagenic and anticarcinogenic properties (Moure and others. 2001 : 145-171). Phenolic compounds, ubiquitous in plants are an essential part of the human diet, and are of considerable interest due to their antioxidant properties. These compounds posses an aromatic ring bearing one or more hydroxyl groups and their structures may range from that of a simple phenolic

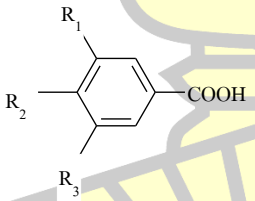
molecule to that of a complex high-molecular weight polymer. Phenolic compounds in plants may generally and conveniently be divided into three major classes based on their sizes. These are phenolic acids, flavonoids and tannins (Scalbert and others. 2002 : 262-276).

2.2.1 Phenolic acids

Phenolic acids are derivatives of benzoic acid and cinnamic acid with hydroxyl groups and methoxy groups substituted at various points on the aromatic ring (Marinova and Yanishlieva. 2003 : 301-307). Ferulic acid, p-coumaric acid, caffeic acid, vanillic acid and syringic acid are all examples of phenolic acids (Pratt and Hudson. 1990 : 171-191). Structures of some phenolic acids are shown in Figure 2.1

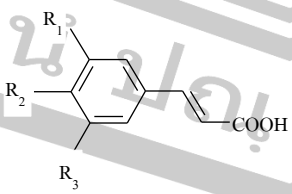
It is widely accepted that phenolic compounds significantly contribute to the overall antioxidant properties of grain. Phenolic acids have been strong inhibitors of carcinogenesis at the initiation and promotion stages induced by different compounds (Kaul and Khanduja.1998 : 81-85).

Benzoic acid derivatives



Name of acid	Position of the functional groups		
	R_1	R_2	R_3
Gallic	OH	OH	OH
p- Hydroxybenzoic	H	OH	H
Protocatechuic	OH	OH	H
Vanillic	OCH_3	OH	H
Syringic	OCH_3	OH	OCH_3

Cinnamic acid derivatives



Name of acid	Position of the functional groups		
	R_1	R_2	R_3
p-Coumaric	H	OH	H
Caffeic	OH	OH	H
Ferulic	OCH_3	OH	H
Sinapic	OCH_3	OH	OCH_3

Figure 2.2 Structures of some phenolic acids

2.2.2 Flavonoids

Flavonoids are a subset of polyphenol antioxidants, which bear the C_6–C_3–C_6 structure (Madhavi, Singhai and Kulkarni. 1996 : 159-195). The C_6-C_3 is from cinnamic acid and the other C_6 fragment is from 3 molecules of malonyl-coenzyme A (Hahn, Rooney and Earp. 1984 : 776-779) The general flavonoid structure may be described as consisting of a benzopyran nucleus with an aromatic substituent at carbon number 2 of the C ring (Waterman and Mole. 1994 : 66-69). (Figure 2.3)

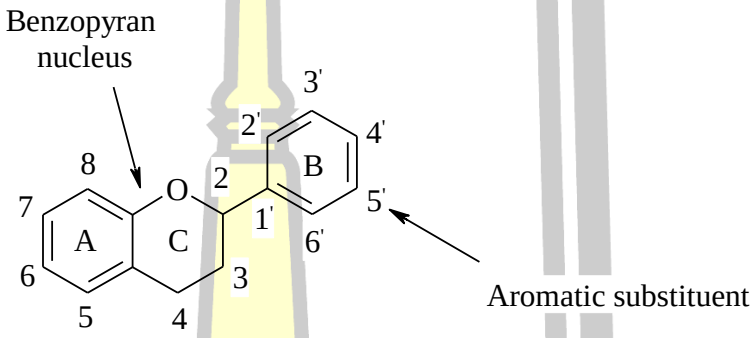


Figure 2.3 Basic structure of flavonoids

Flavonoids are commonly found in edible fruit, leaves and other parts of plant foods as either glycosides (esterified to a sugar molecule) or aglycones (not esterified to a sugar molecule). The subgroups are classified based on the substitutional pattern of the C ring and the position of the B ring. The major subgroups include flavonols, flavanones, flavanols (or flavans) and flavones (Figure 2.4). Flavonols, such as quercetin and kaempferol, have a carbonyl at C-4, double bond between C-2 and C-3, and hydroxyl at C-3; flavanones (e.g. taxifolin) have a carbonyl at C-4, no double bond between C-2 and C-3 and no hydroxyl at C-3; flavanols (e.g. catechin) have no carbonyl at C-4, no double bond between C-2 and C-3 and a hydroxyl at C-3 and flavones, such as apigenin and luteolin, have a carbonyl at C-4, a double bond between C-2 and C-3 and no hydroxyl at C-3 (Sugihara and others.1999 : 1313-1323). Flavonones give rise to other family members such as anthocyanins by undergo a series of transformation that affects the heterocyclic ring (Sofic and Prior. 1996 : 3426-3431). which are responsible for the color of fruits, legumes and vegetables (Mazza and Miniatti. 1993 : 1-28).

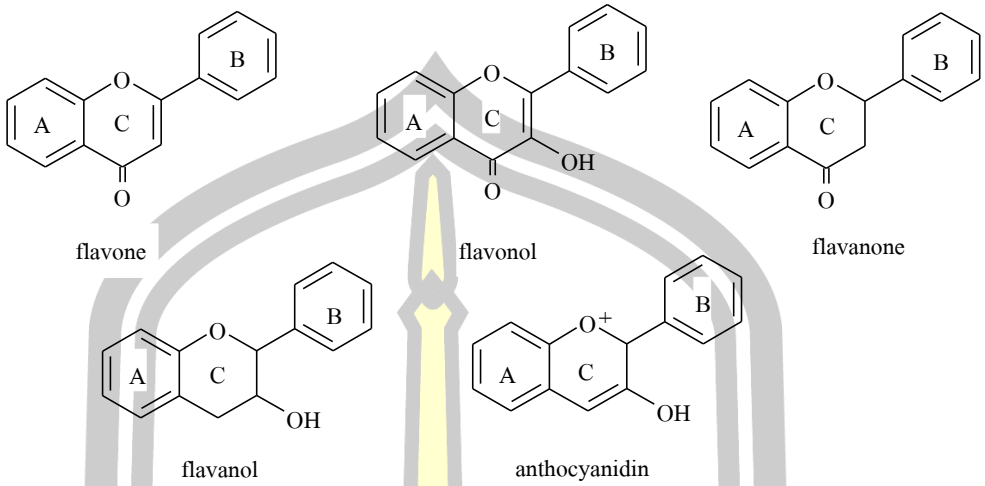


Figure 2.4 Structure of major flavonoid sub-groups

2.2.3 Tannins

Tannins are substances of vegetable origin capable of transforming fresh hide into leather (Hahn, Rooney and Earp. 1984 : 776-779). Tannins are rich in phenolic hydroxyl groups. They are divided into two classes, namely hydrolysable tannins and condensed tannins (Waterman and Mole.1994 : 66-69). Hydrolysable tannins are phenolic carboxylic acids esterified to sugars such as glucose. They are called hydrolysable tannic since they break down into sugars and a phenolic acid (gallic or ellagic acid) upon hydrolysis with acid, alkali or hydrolytic enzymes (tannase) (Hahn, Rooney and Earp. 1984 : 776-779). (Condensed tannins are polymers of flavan-3-ol units and are also known as proanthocyanins (or proanthocyanidins) because they yield anthocyanins upon heating in acidic media (Santos-Buelga and Scalbert. 2000 : 1094-1117).The structures of condensed tannins and hydrolysable tannins are shown in Figure 2.5 (Krause and others. 2005 : 59-75).

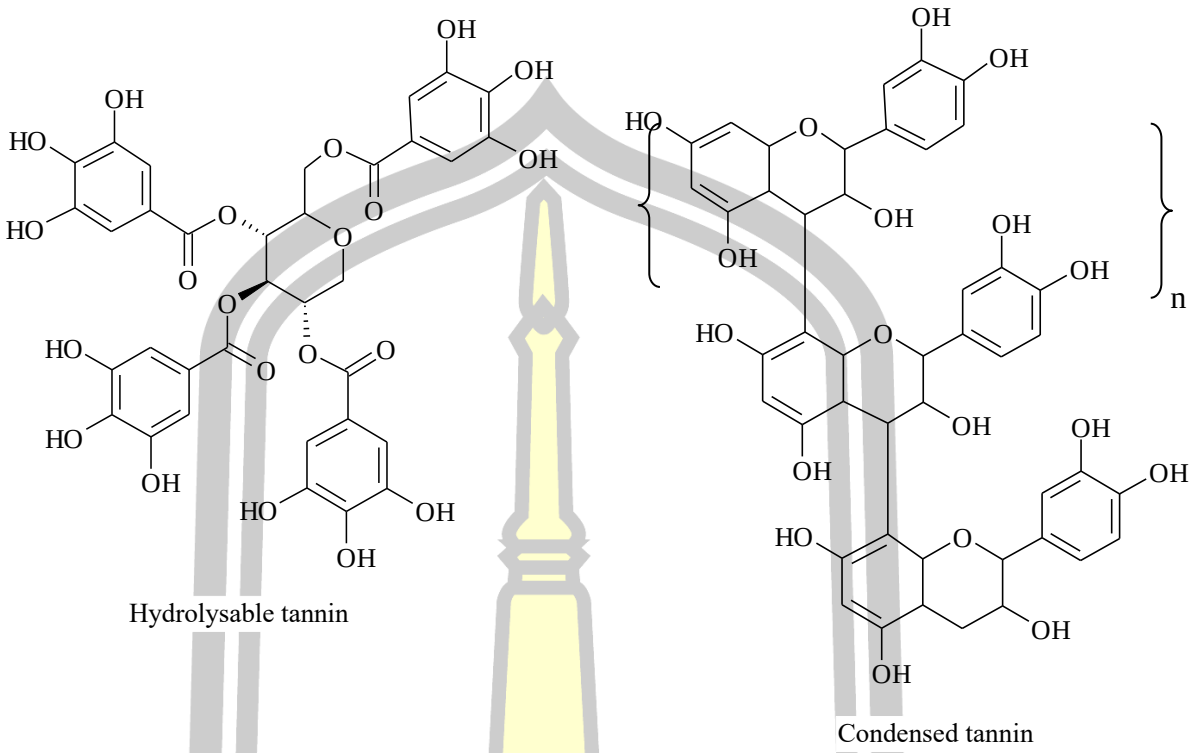


Figure 2.5 Structures of hydrolysable tannins and condensed tannins

2.2.4 Biosynthesis of phenolic compounds in plants

Phenolics display a wide variety of structures, ranging from simple moieties containing a single hydroxylated aromatic ring to highly complex polymeric substances (Strube et al. 1993, Harborne 1994). The biosynthetic pathways of phenolic compounds in plants are quite well known (Haddock et al. 1982, Harborne 1988, Macheix et al. 1990, Dixon and Paiva 1995, Strack 1997). The biosynthetic pathways of some flavonols and phenolic acids are shown in Figure 6. The biosynthesis and accumulation of secondary compounds can be an endogenously controlled process during developmental differentiation (Macheix et al. 1990, Strack 1997). or it can be regulated by exogenous factors such as light, temperature and wounding (Bennet and Wallsgrove 1994, Dixon and Paiva 1995). Phenylalanine, produced in plants via the shikimate pathway, is a common precursor for most phenolic compounds in higher plants (Macheix et al. 1990, Strack et al. 1997). Similarly, hydroxycinnamic acids, and particularly their coenzyme A esters, are common structural elements of phenolic compounds, such as cinnamate esters and amides, lignin, flavonoids and condensed

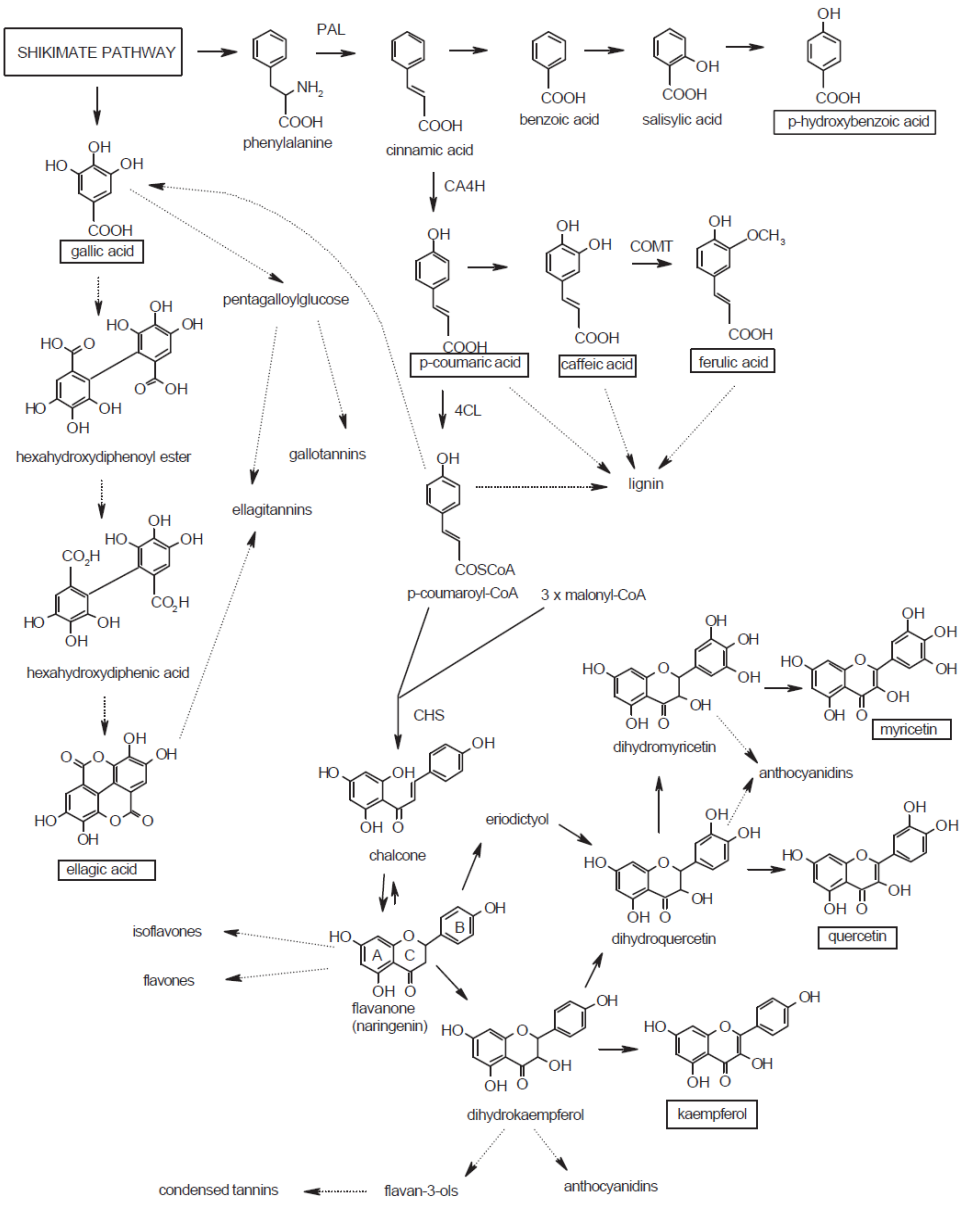


Figure 2.6 Biosynthetic pathways of phenolic compounds

tannins (Macheix et al. 1990). The phenylalanine/hydroxycinnamate pathway is defined as general phenylpropanoid metabolism. It includes reactions leading from L-phenylalanine to the hydroxycinnamates and their activated forms (Strack 1997). The enzymes catalysing the individual steps in general phenylpropanoid metabolism are phenylalanine ammonialyase (PAL), cinnamic acid 4-hydroxylase (CA4H), and hydroxycinnamate: coenzyme A ligase (C4L). These three steps are necessary for the biosynthesis of phenolic compounds (Macheix et al. 1990, Strack 1997). growing body of evidence indicates that phenylpropanoid and flavonoid pathways are

catalysed by several membrane-associated multienzyme complexes (Dixon and Paiva 1995, Winkel-Shirley 1999).

2.3 Phenolic compounds as antioxidants

Recent epidemiological studies have suggested that increased consumption of whole grains, fruits and vegetables is associated with reduced risks of chronic diseases (Hu.2002 : 3-9). Grains and their products are one of the most commonly consumed food items and a staple in Thailand diet. Grains are important sources of energy, protein, dietary fiber, minerals, vitamins and phytochemicals such as phenolic acid, phytic acids, lignans and phytoestrogens (Slavin and others. 1999 : 459s-463s). Phenolic acids, particularly ferulic acid, p-coumaric acid and vanillic acids, are predominant in bran layer of grains and are mainly present as a covalently bound form with insoluble polymers. Phenolic acids are known to act as antioxidants not only because of their ability to donate hydrogen or electrons but also because of their stable radical intermediates, which prevent the oxidation of various food ingredients, particularly fatty acids and oils (Cuvelier, Richard and Berset. 1992 : 645-652 ; Maillard and others. 1996 : 238-244). Recent studies have reported the antioxidant activities of black rice(Hu and others. 2003 : 5277-5371). sorghum (Awika and others.2003 : 6657-6662). buckwheat (Holasova and others. 2002 : 207-211).oat (Handelman and others. 1999 : 4888-4893). and cereal bran products (Yu and others.2002 :2600-2603). The antioxidant activity of phenolics is mainly due to their redox properties, which allow them to act as reducing agents, hydrogen donators, and singlet oxygen quenchers. In addition, they have a metal chelation potential (Rice-Evans and others. 1995 : 375-383). All polyphenols are capable of scavenging singlet oxygen and alkyl radical through electron donating properties, thus generating a relative stable phenoxyl radical (Santos-Buelga and Scalbert. 2000 : 1094-1117).

Generally the efficacy of phenolic compounds as antioxidants depends on the structure, a number of factors such as the number of hydroxyl groups bonded to the aromatic ring, the site of bonding, matual position of hydroxyls in the aromatic ring (Sroka and Cisowski. 2003 : 753-758). and their ability to act as hydrogen or electron donating agents and free radical scavengers.

A relationship exists between the efficacy of phenolic compounds as antioxidants and their chemical structure. The configuration and total number of hydroxyl groups substantially influence the mechanism of antioxidant activity (Heim and others. 2002 : 572-584). The phenolic ring with hydroxyl groups are the main structural features required for antioxidant activity. In order for phenolic compounds to act as antioxidants, their hydroxyl groups have to be in free form. This is because the attachment of an external groups reduces the antioxidant power of the phenolic compounds as they lack hydrogen atom for donation (Farag, El-Baroty and Basuny. 2003 : 81-87).

Phenolic acids are known to be scavengers of oxygen species. The position of the hydroxyl groups in the aromatic ring is important in the efficiency of phenolic acids as antioxidants (Sroka and Cisowski. 2003 : 753-758) For instance, the presence of hydroxyl group in the para position of phenolic acid is important for high antioxidant activity (Pannala and others. 1998 : 594-606 ; Pannala and others. 2001 : -1168) Phenolic acids have been shown to be strong inhibitors of carcinogenesis at the initiation and promotion stages induced by different compounds (Kaul and Khanduja. 1998 : 81-85)

The antioxidant activity of phenolic acids depends on the degree of hydroxylation. The derivatives of cinnamic acids are generally more effective than the derivatives of benzoic acid (Marinova and Yanishlieva. 2003 : 301-307) The presence of the CH=CH-COOH group in cinnamic acid derivatives ensures greater efficiency than the COOH group in benzoic acids (Madhavi, Singhai and Kulkarni. 1996 : 159-195) The double bond has been reported to participate in stabilizing the phenolxyl radical by resonance (Cuvelier, Richard and Berset. 1992 : 645-652) according to(Marinova and Yanishlieva. 2003 : 301-307) Hydroxycinnamic acid ester serve as antioxidants *in vitro*, and it has been suggested that they may serve as natural antioxidants for lipids *in vivo* (Daniels and Martin. 1967 : 589-595 ; Daniel and others. 1999 : 109-114 ; Rice-Evans and others. 1997 : 152-159) Although more attention has been paid to flavonoids as potential natural antioxidants. Phenolic acid esters, such as chlorogenic acid, also perform well as antioxidant, particulary in protecting lipids from peroxidation (Rice-Evans and others. 1997 : 152-159)

2.4 Phenolic compounds found in rice bran and rice hull

Phenolic compounds in rice can be found in the free, soluble conjugate or esterified, and insoluble-bound forms. It is reported that 74 % of total phenolics present in rice, are in the insoluble-bound form (Adom and Liu. 2002 : 6182-6187). Most of the studies found in the literature so far have not looked into insoluble-bound phenolic compounds, hence results reported are often underestimated.

Rice contains a wide range of phenolic acids, belonging mainly to the benzoic acid and cinnamic acid groups. Phenolic acids are different from other phenolic compounds by bearing acidic properties due to the presence of a carboxylic acid group. Ferulic acid and p-coumaric acid are the major phenolic acids found in many cereals, including rice (Adom and Liu. 2002 : 6182-6187 ; Liyana-Pathirana and Shahidi. 2006 : 1256-1264). A significant proportion of these phenolic acids are linked to lignans and arabinoxylans (Nordkvist and others. 1984 : 657-661). Ferulic acid is highly concentrated in the cell walls of aleurone layer that is rich in arabinoxylan.

The primary phenols in cereals are flavonoids and phenolic acid (Adom and Liu. 2002 : 6182-6187 ; Adom and others. 2003 : 7825-7834). which are found predominantly in the bran (Slavin and others. 1999 : 459s-463s). Rice bran polyphenols are *p*-hydroxycinnamic acid derivatives such as *p*-coumaric acid, ferulic acid and *p*-sinapic acid. Tricin, a flavone derivative, has been isolated from rice bran.

In general, seeds contain a great variety of natural antioxidants, such as tocopherols, carotenoids, and many other phenolic compounds. (Graf. 1992 : 435-448 ; Adom and Liu. 2002 : 6182-6187 ; Kikuzaki and others. 2002 : 2161-2168 ; Kim and others. 2006 : 466-473). It is well known that the antioxdants in rice bran, namely tocopherol, tocotrienol and oryzanol (a ferulate ester of triterpene alcohols), are isolated from the lipid-soluble extracts of the bran (Saunders. 1990 : 632-636) and have potent hypocholesterolaemic and anti-tumor activities (Seetharamaiah and Chandrasekhara. 1988 : 927-935 ; Qureshi and others. 2000 : 3130-3140S) The antioxidative activity of cereal extracts is very different and depends on the extraction agent, the kind of cereals and, to a certain extent, also on the cultivar and the morphological fraction (Zielinski and Kozlowska. 2000 : 2008-2016). Adom and Liu

2002 : 6182-6187 analyzed a number of cereals, namely corn, wheat, oat and rice and reported that corn had the highest free phenolic content (0.411 mg/g of grain), followed by rice (0.407 mg/g of grain), then wheat (0.368 mg/g of grain), and oat (0.343 mg/g of grain). The content of insoluble-bound phenolic was significantly higher among all of the above cereals that are expected to inhibit lipid peroxidation and protect against damage to membrane functions. Recently, Zhou and others 2004 : 401-406. determined the quantity of phenolic acid in three cultivars of fresh and aged rice. The results showed the higher levels of ferulic acid (255–362 mg/kg of grain) and p-coumaric acid (70–152 mg/kg of grain) in brown rice than those in milled rice (ferulic acid 61–84 mg/kg of grain). In addition, bound phenolic acids comprised 80–90% w/w of the total phenolic acids for brown rice and 53–74% w/w for milled rice. Osawa and others 1985 : 3085-3087 indicated the extracts of hull fractions of Kusabue and Katakutara rice seeds were more active than other fractions. The far infrared-treated rice hull (FRH) extracts significantly decreased thiobarbituric acid-reactive substances values and volatile aldehydes and was effective in reducing the production of dimethy- disulfide responsible for irradiation off-odor in irradiated raw and cooked turkey meat during aerobic storage (Lee and others. 2003 : 1904-1909).

Olofsdotter and others 1995 : 543-560 and Geally and others 2000 : 33-34 reported that allelopathic chemicals, including ferulic acid, are abundant in rice straw. (Chung and others 2001a : 815-819). also isolated phenolic acids, including o-hydroxyphenylacetic acid, from rice straw and nine phenolic acids from rice hulls. These chemicals inhibited seed germination and seedling growth of barnyardgrass at concentrations of 1x 10^{-3} M and sometimes even lower Chung and others. 2003 : 1063-1070. Hudson and others 2000 : 1163-1170. has demonstrated the presence of eight polyphenols in rice bran, including protocatechuic acid, *p*-coumaric acid, ferulic acid, sinapic acid, vanillic acid, caffeic acid, which is a methoxycinnamic acid derivative, and tricin. Phenolics mainly found in the bran are made up of different types of compounds, free, soluble conjugates and bound phenolics. The major portion of phenolics in grains existed in the bound form. Ferulic acid was the major phenolic compound, with free, soluble-conjugated and bound ferulic acids present in the ratio of 0.1:1:100. About 74% of the total phenolics present in rice is in the insoluble bound forms, with ferulic acid being the major phenolic compound present. isolated

compound from black colored rice bran of *Oryza sativa* cv. Heugjinjubyeo showed strong antioxidative activity in DPPH radical scavenging assay. Shih and Daigle 2003 : 2672-2675. found that methanolic extracts of rice seeds, milled-rice co-products, and other selected plant seeds, including cottonseed, soybean, and corn. The order of antioxidant values in relative effectiveness are rice hull > rice bran > brown rice.

Several phenolic compounds, such as *p*-hydroxybenzoic acid, vanillic acid, p-coumaric acid and ferulic acid were found in aqueous extracts of rice residues and straw Rimando and others. 2001 : 16-20 ; Chung and others. 2003 : 1063-1070. In addition, Nam and others 2006 : 613-620. demonstrated that extracts from the pigmented rice seeds had higher antioxidative activity than did the non-pigmented variety. Recently, (Finocchiaro and others 2007 : 1006-1019). found that dehulled red rice show a total antioxidant capacity more than three times greater than dehulled white rice and its high total antioxidant capacity was essentially characterized by the presence of proanthocyanidins (PA) and associated phenolics. In addition, (Jeon and others 2004 : 92-97). investigated that rice hull supplementation to human lymphocytes followed by H_2O_2 treatment inhibited damage to cellular DNA, supporting a protective effect of rice hull against oxidative damage.

2.5 Analytical methods for total phenolic content

Different methods for analysis and quantification of phenolic compounds have been developed. They may be classified into two groups: those that analyse total phenol content and those that target a specific group of phenolic compounds. Methods such as the Folin-Ciocalteu phenol assay (Singleton and Rossi. 1965 : 144-158). and the ferric ammonium citrate method (ISO. 1988 : 9648). are employed in quantification of total phenol content (as total reducing phenolic groups) whereas methods such as the vanillin-HCl assay (Price and others. 1978 : 1214-1218). are specific for catechins and proanthocyanidins. A number of factors are known to influence analysis of phenolic compounds. These factors include the chemical nature of the phenolic compounds, extraction methods, sample particle size and the assay method itself (Naczk and Shahidi. 2004 : 95-111).

2.5.1 Folin-Ciocalteu method

The Folin-Ciocalteu method (Singleton and Rossi. 1965 : 144-158). quantifies the total concentration of phenolic hydroxyl groups present in the sample being assayed (Waterman and Mole. 1994 : 66-69). The assay is based on a reduction-oxidation reaction during which the phenolate ion is oxidized under alkaline conditions while reducing the phosphotungstic-phospho-molybdic complexs in the reagent to a blue colored solution. The method is simple however, it is not specific and it detects all phenolic groups in extracts including those found in extractable proteins. Moreover, it is susceptible to interference with reducing substances such as ascorbic acid (Naczk and Shahidi. 2004 : 95-111). Notwithstanding these demerits, the Folin-Ciocalteu method is widely used and provides a reasonably good and reliable estimate of the concentration of total reducing phenolic groups.

2.5.2 Ferric ammonium citrate method

The ferric ammonium citrate method (ISO. 1988 : 9648). is based on the ability of phenolic compounds in alkaline conditions to reduce ferric ion to ferrous. Under these conditions the reaction results in the formation of a blue-green colour. The absorbance of the reaction products at 525 nm is linearly related to concentration of the phenolic compounds (Daiber. 1975 : 1399-1411). The ferric ammonium citrate method is not specific as it not only responds to phenols but also other reducing agents such as ascorbate (Beta and others. 1999 : 1003-1010). It is also not very sensitive especially at low tannin concentrations (Deshpande and others. 1986 : 401-409). However, it is simple and offers advantages for samples such as sorghum where it distinguishes between condensed-tannin containing and condensed-tannin free sorghum types (Daiber. 1975 : 1399-1411). The method also gives a reasonably good estimation of total reducing phenolic groups and exhibits similar trends in values as the Folin-Ciocalteu method.

2.6 Antioxidant capacity assays

Most natural antioxidants are multifunctional in complex heterogeneous foods; their activity cannot be assessed by any one method (Frankel and Meyer. 2000 : 1925-1941 ; Sanchez-Moreno. 2000 : 121-137). No single assay will accurately reflect all of the radical foundations or all antioxidants in a mixed or complex system, and it must be appreciated at the outset that there are no simple universal methods by which antioxidant capacity can be measured accurately and quantitatively (Prior, Wu and Schaich. 2005 : 4290-4302). also too many analytical methods result in inconsistent results, inappropriate application and interpretation of assays, and improper specifications of antioxidant capacities. There are two reaction mechanisms in which antioxidants can deactivate radicals. The first of these methods is the single electron transfer assay (SET) which detects the ability of a potential antioxidant to transfer one electron to reduce any compound, including metals, carbonyls and radicals (Wright and others. 2001 : 1173-1183). According to (Prior and others 2005 : 4290-4302)., SET reactions are usually slow and require a lengthy time to reach completion, so the antioxidant capacity calculations are based on percent decrease in product rather than kinetics. The second method is the hydrogen atom transfer (HAT), which measures the antioxidant's ability to quench free radicals by hydrogen donation. HAT reaction is solvent and pH dependent and is usually quite rapid. The presence of reducing agents, including metals, is a complication in HAT assays and can lead to erroneously high apparent reactivity (Prior, Wu and Schaich. 2005 : 4290-4302).

2.6.1 The 2, 2- diphenyl-1-picryhydrazyl (DPPH) method

A rapid, simple and inexpensive method that has been developed to determine the antioxidant activity of foods utilizes the stable 2, 2-diphenyl-1-picryhydrazyl (DPPH) radical. The structure of DPPH and its reduction by and antioxidant are shown below. The odd electron in the DPPH free radical gives a strong absorption maximum at 517 nm and is purple in color. The color turns from purple to yellow as the molar absorptivity of the DPPH radical at 517 nm reduces from 9660 to 1640 when the odd electron of DPPH radical becomes paired with a

hydrogen from a free radical scavenging antioxidant to form the reduced DPPH-H. The resulting decolorization is stochiometric with respect to number of electron captured (Miller and others. 2000 : 312S-319S).

2.6.2 Ferric reducing ability of plasma (FRAP) assay

In FRAP assay, ferric ions (Fe^{3+}) are reduced to ferrous (Fe^{2+}) ions by antioxidants (Benzie and Strain. 1996 : 70-76). In this context, antioxidants are considered as reductant and the oxidant is modified by Fe^{3+}. The oxidizing species react with the antioxidant instead of the possible substrate and is reduced to a harmless species. Different mixtures and solutions of antioxidants can be investigated. In the reduction, an intensely colored ferrous-tripyridyltriazine complex is formed and the absorbance of the solution is measured. The values of absorbance of the test mixture are compared to the values of solutions of known concentration of Fe^{2+} in control samples.

2.7 Stability of bioactive compounds during food processing

Under difference food processing conditions, bioactive compounds undergo degration via isomerization and oxidation, which impact its bioactivity and reduce the functionality for health benefits. The degradation reactions of bioactive compounds are influenced by factors such as reaction medium, temperature , physical state, and environmental conditions. The most important factors during processing are heat, light and oxygen. The stability of lycopene during heating and illumination has been controversial. Pesek and Warthesen 1987. reported that the degradation rate of lycopene was lower than b-carotene when a vegetable juice containing lycopene was exposed to light at 4 °C for 8 days. In contrast, Henry, Catignani, and Schwartz 1998. found that the degradation rate of lycopene was higher than beta-carotene when safflower oil was heated at 75, 85 or 95 °C. Obviously the stability of lycopene may be variable in different food systems because of the complex nature of food components.

de Torres, Maroto, Gutiérrez, and Coello 2010. studied Effect of freeze-drying and oven-drying on volatiles and phenolics composition of grape skin compare two

drying methods, freeze-drying and oven-drying, at 60 ˚C, as skin preservation methods. Many volatile compounds, which are of interest in the aroma profile, were identified in varieties as terpenes (linalool, etc.), sesquiterpenes (farnesol), norisoprenoids (vitispirane, etc.), C6 alcohols (1-hexanol, etc.), etc., and their amount decreased significantly with the oven-drying method, in contrast to the freeze-drying method. Both phenolic compounds, anthocyanins and flavonols, were identified in fresh and dehydrated samples, thus resulting in the freeze-drying method being less aggressive than oven-drying methods.

Capecka , Mareczek, and Leja 2005. studied The herbs of lemon balm, oregano, and peppermint were analysed immediately after harvest and after drying to determine their antioxidant activity and content of total phenolics, L-ascorbic acid, and carotenoids. The strongest inhibition of linoleic acid (LA) peroxidation was found for fresh and dried oregano. For peppermint and lemon balm it was significantly lower and decreased after drying. The ability to scavenge the free radical DPPH (2, 2-diphenyl-1-picrylhydrazyl) was very high in almost all tested samples, exceeding 90%. The three species tested had a very high content of total phenolics and drying of oregano and peppermint resulted in their considerable increase. The highest content of ascorbic acid was determined in fresh peppermint and lemon balm and carotenoid content was at a similar level in all the species tested. Drying caused great losses of these compounds.

Wanyo, Siriamornpun, and Meeso (2010) studied combined far-infrared radiation with hot-air convection (FIR–HA) drying was used for improving colour and antioxidant properties of mulberry leaf tea. Antioxidant properties and phenolic compounds of FIR–HA dried mulberry tea were determined and compared with the commercial product and with fresh leaves. We found that a smaller decrease in *L* and *b* values of the FIR–HA dried tea than those of commercial tea was observed. FIR–HA tea was found to have similar colour to fresh leaf while the commercial tea had darker colour. A significant decrease in total phenolic acid content (TPC) and total flavonoid content (TFC) was found in hot-air (HA) dried commercial tea compared to fresh leaves, while TPC in FIR–HA dried tea was significantly increased. Similar results were found in 1, 1-diphenyl-2-picrylhydrazyl (DPPH) radical activities. However, the results were different for ferric reducing antioxidant power (FRAP).

Both teas had lower FRAP values compared to fresh leaves. Eleven phenolic compounds were identified in fresh leaf and in mulberry tea, namely *p*-coumaric acid, benzoic acid, (+)-catechin, chlorogenic acid, vanillic acid, syringic acid, sinapic acid, protocatechuic acid, ferulic acid, gallic acid and caffeic acid. The total content of phenolic compounds (TPCC) increased in FIR–HA dried samples compared to those of HA dried tea, except for chlorogenic and syringic acids, which were found in greater amounts in HA dried commercial tea. Results have demonstrated that FIR–HA should be considered as a suitable drying method for mulberry tea with respect to preserving its antioxidant properties and phenolic compounds.

2.8 Infrared radiation

Infrared refers to that part of the electromagnetic spectrum between the visible and microwave regions. Electromagnetic spectrum refers to the seemingly diverse collection of radiant energy, from cosmic rays to X-rays to visible light to microwaves, each of which can be considered as a wave or particle traveling at the speed of light. These waves differ from each other in the length and frequency, as illustrated in
figure 7.

Frequency, ν (nu), is the number of wave cycles that pass through a point in one second. It is measured in Hz, where 1 Hz = 1 cycle/sec. Wavelength, λ (lambda), is the length of one complete wave cycle. It is often measured in cm (centimeters). Wavelength and frequency are inversely related:

$$\nu = \frac{c}{\lambda} \text{ and } \lambda = \frac{c}{\nu}$$

where c is the speed of light, 3×10^{10} cm/ sec

Energy is related to wavelength and frequency by the following formulas:

$$E = h\nu = \frac{hc}{\lambda}$$

where h = Planck's constant, 6.6 x 10^{-34} joules-sec

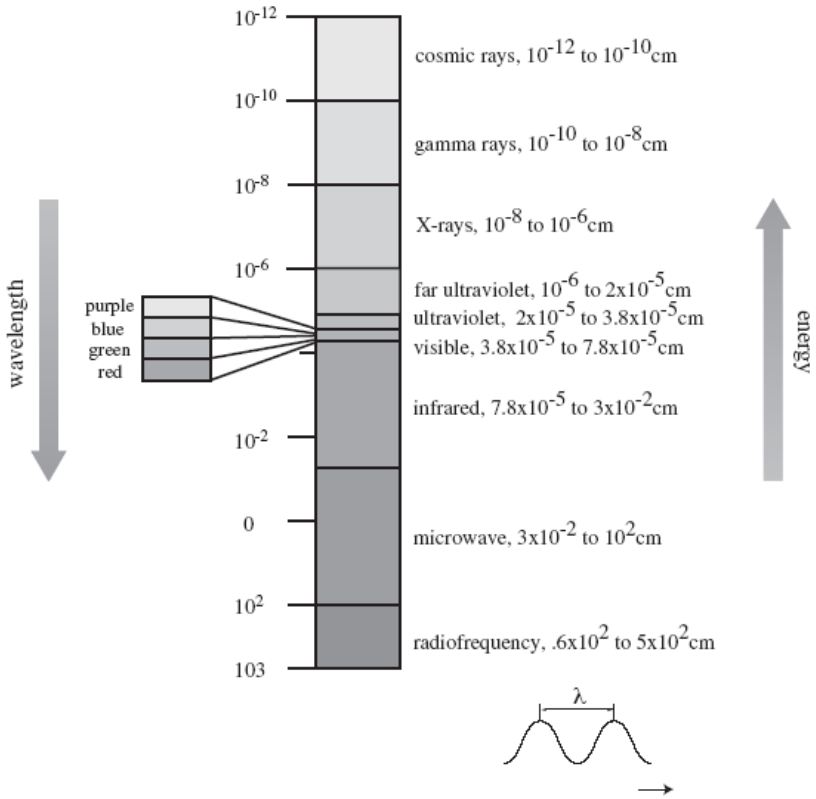


Figure 2.7 The electromagnetic spectrum.

The IR region is divided into three regions: the near, mid, and far IR (Figure 8). The mid IR region is of greatest practical use to the organic chemistry. This is the region of wavelengths between 3 x 10^{-4} and 3 x 10^{-3} cm. Chemists prefer to work with numbers which are easy to write; therefore IR spectra are sometimes reported in μm, although another unit, $\bar{\nu}$ (nu bar or *wavenumber*), is currently preferred.

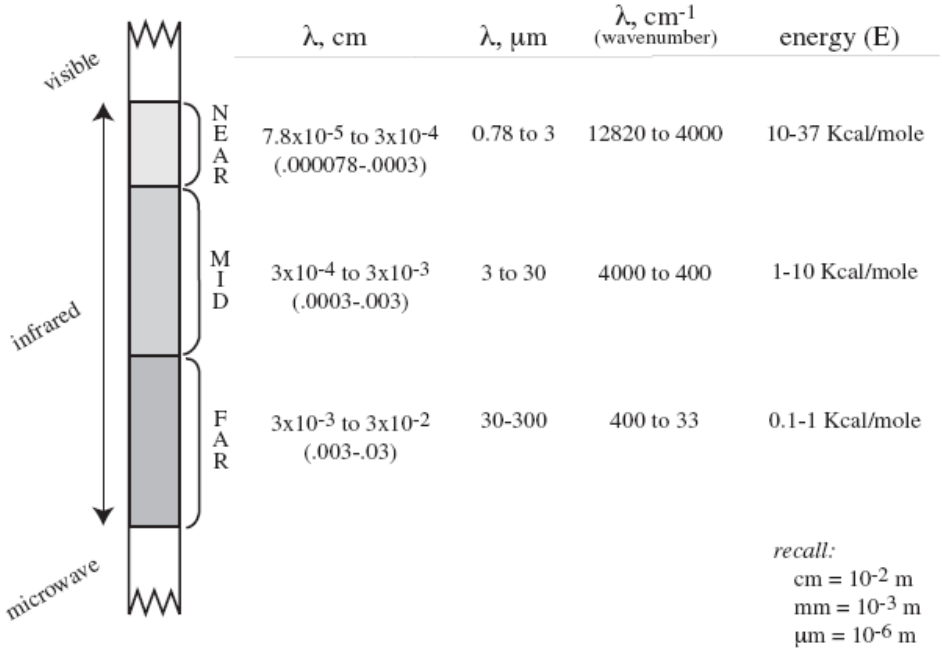


Figure 2.8 The IR regions of the electromagnetic spectrum.

2.9 Drying by using infrared

Often abbreviated NIR, Near-infrared radiation is a type of spectroscopy. The modern application of NIR uses it to measure the composition of unknown samples (i.e., to do chemical analysis), using techniques invented by scientists at the USDA. It has become a very popular technique in a wide variety of industries due to it's speed, accuracy, wide applicability and avoidance of extraneous chemicals. It is widely used in agricultural, chemical, pharmaceutical, textile and many other industries. Far-infrared radiation creates internal heating with molecular vibration of material, i.e., molecules absorb the radiation of certain wavelengths and energy, and cause vibration excitedly. Moreover, the mechanism of far-infrared drying is different from hot air drying (Mongpraneet et al., 2002 : 147-156), and the electromagnetic wave energy is absorbed directly by the dried food with less energy loss. At present, various driers have been developed by using far-infrared radiators. The utilization of far-infrared radiation is a novel process that could increase the drying efficiency, save working space, and result in a clean working environment, etc. (Ratti and Mujumdar, 1995 : 567-588). Yagi and Kunii (1951 : 108-123) attempted to apply far-infrared radiation to the drying of agricultural materials and improved results were reported.

Combination of far-infrared radiation with air convection or vacuum drying had also been tested (Abe and Afzal, 1997 : 289-297; Hasatani, Arai, Itaya and Onoda, 1983 : 193-214; Mongpraneet et al., 2002 : 147-156). Far-infrared radiation drying of potato had attained high drying rates by using infrared heaters of high emissive power (Masamura et al., 1988 : 309-314). Although significant product value increases would occur if vacuum or freeze drying methods were combined with far-infrared radiation treatment, only studies combining far-infrared radiation and vacuum operation has been studied (Itoh and Chung, 1995 : 89-96; Mongpraneet et al., 2002 : 147-156). Lin Tsen and King (2005 : 249-255) studied effects of far-infrared radiation on the freeze drying of sweet potato. The results showed that freeze drying with far-infrared radiation was found to be able to deduce the drying time of sweet potato.

Recent studies have reported the effect of far-infrared radiation and heat treatment on the antioxidant activity of water extracts from peanut hulls. The results showed that antioxidant activities of water extracts peanut hulls (WEPH) increased as the time of heating or FIR-radiation increased. When peanut hulls were FIR-irradiated at 150 °C for 60 min, the values of total phenol contents, radical scavenging activity, and reducing power of water extracts peanut hulls increased from 72.9 to 141.6 μm, 2.34% to 48.83% and 0.473 to 0.910, respectively, compared to the untreated controls (Lee et al., 2006 : 489-493).

FIR rays are biologically active (Inoue and Kabaya, 1989 : 145-150) and transfer heat to the center of materials evenly without degrading the constituent molecules of surface (Niwa, Kanoh, Kasama, and Neigishi, 1988 : 361-372). FIR may have capability to cleave covalent bonds and liberate antioxidants such as flavonoids, carotene, tannin, ascorbate, flavoprotein or polyphenols from repeating polymers (Niwa et al., 1988 : 361-372). In previous study (Lee et al., 2003 : 4400-4403) showed that simple heat treatments could not cleave covalently bound phenolic compounds from rice hulls but FIR treatments could.

Chapter 3

Material and Methods

3.1 Experimental plan

This research will be divided into four experiments including (1) study the variation in bioactive compounds and starch digestibility of different pigmented Thai rice varieties (2) study appropriate application the FIR drying on bioactive compounds, in processed pigmented Thai rice affected FIR and Hot air dryings (3) develop product from pigmented Thai rice as functional food. All experiments will be performed in triplicate.

For experimental plan will be used in this research was completely randomized design (CRD). Analysis of variance will be used to test any difference in resulting from these methods. Duncan method will be used to determine significant differences at $p < 0.05$.

3.2 Instruments and equipments:

3.2.1 High performance liquid chromatography system with diode array detector (LC 20A, Shimadzu)

3.2.2 Gas chromatography system with flame ionization detector (GC-2014, Shimadzu)

3.2.3 Ultraviolet-Visible spectrophotometer (Lambda 12, Perkin Elmer, USA)

3.2.4 Ultra-Turrax® (IKA T25 digital)

3.2.5 Differential scanning calorimetry (DSC)(TA Instruments, Elstree, UK)

3.2.6 FTIR spectroscopy (BUNCHI Rotavapor ® R-3)

3.2.7 Centrifuge (Rotina 48 R)

3.2.8 Rotary evaporator (Buchi)

3.2.9 Column Inetsil ODS-3, C18 (4.6 mm x 250 mm, 5 µm)

3.2.10 Column DB-Wax (0.25 mm x 30 m)

3.2.11 Far infrared radiation dryers

3.2.12 Hot air oven (Memmert)

3.2.13 Incubator shaker

3.2.14 Beaker

3.2.15 Erlenmenyer flask

3.2.16 Volumetric flask

3.2.17 Pipette

3.2.18 Vial

3.3 Materials

Samples

Pigmented Thai rice samples used in this study, including, Hom Mali or KDML 105, Mali Dang (red), Hom Nil (purple), Riceberry (purple), Mun Poo (red rice) and Sung Yod (red) varieties, were collected from northeastern, central and southern Thailand, during the 2014-2017 growing season. Unpolished rice was produced by removing the hull; then this rice was milled to obtain polished rice by a hammer mill. Both unpolished and polished rice grains were dried by HA using a hot-air oven (UFE 600, Memmert, Memmert Company, Germany). Both drying methods have been described by Wanyo, Meeso, Siriamornpun 2014 ..

Chemicals

1) 2,2-Diphenyl-1-picrylhydrazyl , DPPH (Fluka)

2) 2,4,6-Tripiridyl-s-triazine, TBTZ (Fluka)

3) Folin-Ciocalteu's reagent (Fluka)

4) Ferrous sulphate (Carlo)

5) Sodium sulphate (Merck)

6) Acetonitrile (Merck)

7) Standard tocopherols (α-, γ-, and δ-tocopherols) (Fluka)

8) Standard phenolic acids (gallic, ferulic, p-hydroxybenzoic, protocatechuic, p-coumaric, caffeic, syringic, sinapic, chlorogenic and vanillic acids (Sigma)

9) γ-Oryzanol (food grade, 99.9% purity) (Wakayama, Japan).

10) Acetic acid (Fisher Scientific)

11) Methanol (Merck)

12) Porcine-pancreatic α-amylase of a high purity (Grade 1-A)(Sigma)

13) Phosphate buffered saline (PBS)(Sigma)

14) 4-Hydroxybenzoic acid hydrazide (PAHBAH)(Sigma)

15) Anthocyanins standards (malvin, malvidin, keracyanin, cyanidin-3-glucoside, pelargonidin-3-glucoside, delphinidin and dephinidin-3-glucoside (Sigma)

16) The standards of amino acids (lysine, histidine, leucine, phenylalanine, tryptophan, valine, arginine, isoleucine, methionine and threonine)(Sigma)

3.4 Methods

The present study will be divided into four experiments following:

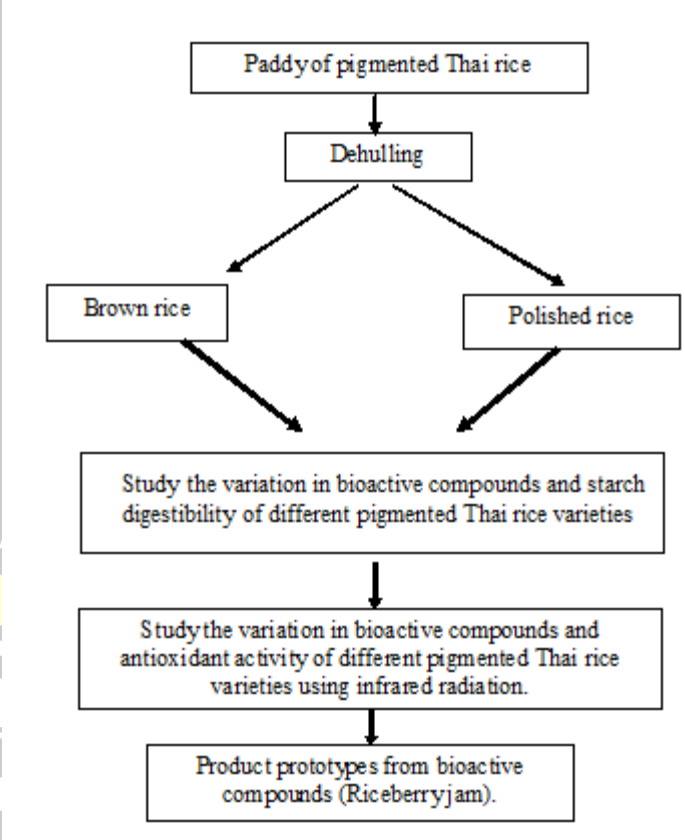


Figure 3.9 Flow chart of experiment procedure

3.4.1 Study the variation in bioactive compounds and starch digestibility of different pigmented Thai rice varieties

1) Food materials

Pigmented Thai rice samples, Mali Dang (red rice) and Riceberry (purple rice) varieties were provided from the field located at Surin province in the northeast of Thailand. Mun Poo (red rice) was harvested from a field located at Pathumthani province in central Thailand while Sung Yod was provided from a field located in Phatthalung province in southern Thailand. A control sample, Thai white rice, Hom Mali or KDML 105 variety was obtained from Roi Et province, northeastern Thailand. Paddy rice samples were de-hulled (NPS450DWA, Satake Corporation, Tokyo, Japan) to obtain pigmented brown rice. Pigmented rice samples were ground by mortar and sieved into flours (−80 mesh).

2) Starch purification

Pigmented riceflour materials (20 g) were soaked with 50 mL of 0·2% (w/v) sodium hydroxide (0·05 M) for 3 h at 25 °C, and homogenized using an Ultra-Turrax® (IKA T25 digital). Starch was isolated according to the NaOH method with minor modifications (Lumdubwong & Seib, 2000). Samples were manually ground by mortar and the slurry was sieved (<75 μm opening) then was centrifuged at 3000 g for 20 min. The supernatant was drained, and the residue was washed 2 times with water (50 mL) and centrifuged. The sediment was neutralized (pH 7) by adding hydrochloric acid (1 M) and centrifuged. The supernatant was drained, the top of the pellet was starch, under which a dark tailing layer. The dark layer was scraped away and the remaining pellet washed with 50 mL of water. This process of centrifuging and scrapping was repeated three times until white starch was obtained with no dark tailings. The starch was dried at 40 °C for 48 h in a convection oven.

3) Determination of total phenolic content

The total phenolic content (TPC) of pigmented rice was determined as sum of total free and bound phenolic content and measured by the Folin–Ciocalteumethod (Singleton, Orthofer & Lamuela-Raventós, 1999). with a slight modification as described by Butsat and Siriamornpun 2010. Briefly, 300 μL of sample extract was

mixed with 2.25 mL of freshly diluted 10 folds Folin-Ciocalteu reagent and incubated at room temperature for 5 min. The mixture was added to 2.25 mL of sodium carbonate (60 g/L) solution and incubated in the dark for 90 min at room temperature. The absorbance was determined at 725 nm using a spectrophotometer against the reagent blank. The content of total phenolic in the mixture was calculated as mg gallic acid equivalents (mg GAE) per 100g of dried weight (DW) by comparison to the linear regression equation of the gallic acid standard curve.

4) Determination of total anthocyanin content

The total anthocyanin content (TAC) of pigmented rice was analyzed using the colorimetric method (Bridle & Timberlake, 1997). with a slight modification as described by Duangkhamchan and Siriamornpun 2015). .Briefly, 10 mg of pigmented rice grains were extracted three times with 10 mL of distilled water. The mixturewas centrifuged at 10,000 g for 10 min and the supernatants were collected. The absorbance was measured immediately at 534 nm using a Beckman Du-640 spectrophotometer (Beckman Coulter, Fullerton, USA). The reactions were performed in triplicate and the results were expressed as 100 g of dried samples (mg/100g) and. All analyses were performed in triplicate.

5) Amylose content

The analysis of amylose content of rice samples was carried out using the iodine dye binding method of Knutson (1986). Five mg of starch samples were dissolved in 10 mL of the solvent that was prepared by dissolving 6 mM iodine in a solution of 90% dimethyl sulfoxide and 10% water. Samples dissolved by placed on a blood rotator (20 rpm and 30° angle) overnight at room temperature. The 100 µL of sample solution was removed to each tube and was then diluted with 800 µL of water. The samples were allowed to stand for 30 min to ensure the stable iodine-amylose complex formation and color. The absorbance was measured at wavelength of 600 nm (libra 550, Biochrom, USA). Amylose from potato was used as the standard to calculate the apparent amylose content and this value was then corrected to amylose and amylopectin contents by the equation:

$$\% \text{ Amylose } = \frac{\% \text{ Apparent amylose } - 6.2}{93.8}$$

6) Identification of phenolic compounds by high performance liquid chromatography (HPLC)

Identification of individual phenolic compounds was perfumed using HPLC (Loomis, 1969) system installed with an Shimadzu LC-20AC pumps, Inetsil ODS-3, C18 (4.6 mm x 250 mm, 5 µm) (Hichrom Limited, Berks, UK) column and SPD-M20A diode array detection (DAD), using an injection volume of 20 µL. The gradient elution was based on the method of Butsat and Siriamornpun 2010 .with 1% (v/v) acetic acid in DI water (solvent A) and acetonitrile (solvent B) at a flow rate of 0.8 mL/min and a column temperature at 38°C. The separated phenolic acids were detected at 280 nm. The authentic phenolic acids were used as external standard.

7) Identification of anthocyanins by high performance liquid chromatography (HPLC)

Anthocyanins determination was operated by RP-HPLC method (Gao & Mazza, 1994) and used the same equipment in determination of phenolic compounds. The samples were extracted followed by previous study (Duangkhamchan & Siriamornpun, 2015). and the conditions of gradient elution and solvent composition were also described. A gradient elution contained 0.1% HCL in methanol at a ratio of 15:85 v/v (mobile phase A) and 8% formic acid in DI water (mobile phase B), at a flow rate of 1 $mLmin^{-1}$. The conditions used in the present study were as follows: column temperature at 30 ◦C, UV-diode array detection at 520 nm, and injection volume of 20µL. The samples and solutions were filtered with 0.45 µm nylon membrane filter before injection. Identifications of the individual anthocyanins were compared with their relative retention time of authentic standard. The compositions and contents of anthocyanins were expressed as µg per 100g dry weight.

8) Differential scanning calorimetry (DSC)

The differential scanning calorimetry (DSC) analysis of Pigmented Thai rice varieties were performed using a Multi-Cell DSC (TA Instruments, Elstree, UK) according to Edwards et al. 2015 with some modifications. Rice purified starch (100

mg) was weighed and added 1.00 g of deionized water into 1.0 mL capacity Hastelloy® ampoules. The reference was only deionized water. Pans were hermitically sealed and loaded into the DSC instrument. The pans were heated from 10 °C to 130 °C at 1 °C min^{-1}, in a furnace continually flushed with Nitrogen at 20 mL min^{-1}. Triplicate measurements were performed on all samples. The enthalpy of gelatinization $\Delta_{gel}H$ (J $_{g-1}$), Onset (T_o), peak (T_p), and conclusion temperatures (T_c) were obtained from each thermogram as described in a previous study (Edwards et al., 2015).

9) FTIR spectroscopy analysis

The starch and flour were dissolved with PBS solvent of starch digestion method and were prepared in the same procedure for digestion analysis. After pre-digestion the samples were collected before enzyme addition. The samples were evaporated at 50 °C, 40 psi (BUNCHI Rotavapor ® R-3) and sited by 100 mesh sieved. The dried powders were collected for FTIR analysis in four powder fractions, namely starch, treated starch (TS), flour and treated flour (TF).

The FTIR spectra of the Thai pigmented rice starches and flours were obtained with Perkin Elmer Frontier FTIR with ATR accessory in the region of 4000-400 cm^{-1}. The average of 16 scans was analyzed at a spectra resolution of 4 cm^{-1}. The spectra were baseline-corrected, and then deconvoluted between 1200 and 900 cm^{-1}. The values of absorbance at 1047 $cm^{-1}$and 1022 cm^{-1} were calculated as an intensity ratio to display the value of ordered crystalline regions to amorphous regions near the surface of starch.

10) Characterization of plant food materials

The content of starch of all rice materials was determined using Megazyme Total Starch Procedure(AOAC 996.11). with minor modifications as follows by Edwards, Warren, Milligan, Butterworth and Ellis 2014. The step of DMSO heat solubilization duration was extended to 16 min and thermostable amylase (6 mL) was diluted at a ratio 1:60 and then this enzyme was used instead diluted amylase (3 mL of 1:30). Total Starch values were used for calculation in the part of starch digestion.

11) Starch digestion

Starch digestion kinetics was determined according to the procedure with some modifications of Warren, Zhang, Waltzer, Gidley and Dhital 2015. Rice samples (100 mg, dry starch basis) were added into 10 mL of phosphate buffered saline (PBS) (Oxoid tablets, pH 7.4 at 37 °C). The suspensions were incubated at 37 °C and placed in a Blood Rotator that was set to 20 rpm, 30° angle for 15 min to equilibrate. Then, the suspensions were incubated with 400 µL of α-amylase (80 units in PBS, pH 7.4) and 100 µL aliquots were collected into tubes containing 100 µL of stop solution (0.3 mol L^{-1} Na_2CO_3, pH 9) at pre-defined time pointsfrom 1 to 60 minutes. Aliquots were centrifuged at 15000 g for 5 min to sediment any unreacted starch. Supernatant (100 µL) was removed to a fresh 1.5 mL Eppendorf® safe-lock™ tube. The starch hydrolysis products were determined using 4-hydroxybenzoic acid hydrazide (PAHBAH) reducing sugar assay, using maltose standards. To the supernatant was added 1mL of a freshly prepared 5% (w/v) solution of PAHBAH in 0.5 M HCl which was diluted to 1:9 with 0.5 M NaOH. Then, the reaction mixture was heated at 100 °C for 5 min in a boiling water bath and was measured at an absorbance at 405 nm using a Shimadzu UV–VIS spectrophotometer (Libra 550, Biochrom, USA). The reducing sugar concentrations (maltose equivalents) were converted to starch equivalents on the basis of the total starch assay results.

The kinetics of the starch digestion data was estimated by a first-order equation (Goñi, García-Alonso & Saura-Calixto, 1997):

$$C_t = C_\infty(1 - e^{-kt})$$

where, C_t is the concentration of starch digested product at time t, C_∞ represents the corresponding concentration of starch digested at the end point of the reaction and k is the digestibility rate constant. The Logarithm of Slope (LOS) plot was constructed by taking the first derivative of the first-order equation in logarithmic form as described by Butterworth, Warren, Grassby, Patel & Ellis 2012.

$$\ln\left(\frac{dC}{dt}\right) = \ln(C_\infty k) - kt.$$

This equation can be extended as described by Edwards et al. 2014 to describe the situation where multiple first order rate constants are observed in a single reaction:

$$C_t = \begin{cases} C_{1\infty}(1 - e^{-k_1 t}) if\ t \leq t_{int} \\ C_{int} + C_{2\infty}\left(1 - e^{-k_2(t - t_{int})}\right) if\ t \geq t_{int} \end{cases}$$

where identifiers define the time-limits of each first order reaction, t_{int} is the time of intersection of the two plots, C_{int} is the concentration of product at t_{int} and is therefore added to the second term to describe total product formation.

3.4.2 Study the variation in bioactive compounds and antioxidant activity of different pigmented Thai rice varieties using drying methods (Far-infrared radiation and hot air dryings)

1)This study application of the FIR drying on bioactive compounds of pigmented Thai rice product.

Drying step

Infrared radiation drying

For FIR treatment, rice grains (10 g) were placed in the sample tray of a stainless-steel drying chamber and irradiated with a far-infrared heater (250W). The sample was irradiated at an FIR intensity of 2k W/m^2 (FIR energy irradiated per FIR heater surface area) in the range 56-59% (±1%) relative humidity (RH) oven. The temperature of drying was set at 40 °C and the air velocity at 1.5 m/s for 2 h (whole grain) or 1 h and 40 min (polished grain) until the moisture content came down to 12–14%.

Hot air drying

The drying conditions involved a set-air velocity of 1.5 m/s at 60 °C (drying temperature) in the range 46-50% (±1%) relative humidity (RH) oven to obtain a moisture content of 12-14% (dry basis) after 4 h and 3.50 h, respectively, for unpolished and polished rice. Moisture contents were measured by the AOAC (1995) method at 103 °C ± 1 °C in a vacuum oven (UFE 600, Memmert, Memmert Company, Germany) for 72 h.

All samples rice grains were crushed to obtain rice powder by a mortar and passed through a 80 mesh sieve. Unheated samples of both unpolished and polished rice powder were stored at 4 °C prior to further analysis.

2) Determination of total soluble and bound phenolic content

2.1) Phenolics extraction

The extraction process was done according to Wanyo et al. (2014) with minor modifications. Briefly, one gram of each sample was extracted three times with 10 mL of 80% acidified with 1.0 N HCl (85:15, v/v) at a ratio of 1:10 (w/v) and shaken on shaker at 180 rpm at room temperature for 2 h. Then, the mixture was centrifuged for 20 min at 1400 g and the supernatant was transferred into a 30 mL vial and stored at -20 °C until analysis for the soluble phenolic, flavonoid contents and antioxidant activity (DPPH and FRAP). All analyses were performed in triplicate.

The extraction of bound phenolic content was extracted according to Butsat and Siriamornpun (2010) with minor modifications. Briefly, rice sample (1 g) was extracted twice with 10 mL of 80% methanol and centrifuged at 2500 rpm for 20 min. The supernatant was discarded and then the residues were hydrolyzed with sodium hydroxide (2M, 20 mL) at room temperature. The mixtures were shacked by incubator for 24 h. Subsequently, 12M hydrochloric acid was adjusted to a pH of 7 and was added hexane to remove lipids. The final solution was extracted five times by ethyl acetate. The ethyl acetate fraction was combined and was evaporated to dryness. Bound phenolic content was dissolved in methanol (10 mL) and stored at -20 °C before analysis. All analyses were performed in triplicate.

The free and bound extracts were used to determine total antioxidant activity, total phenolic, total flavonoid, phenolic acids and flavonoids by using HPLC method.

2.2) Determination of total soluble and bound phenol content

The total phenolic content in sample will be determined by the Folin-Ciocalteu method (George et al., 2005; Zhou & Yu 2006). One ml of extract will be mixed with 0.5 ml of the Folin–Ciocalteu reagent, 3 ml of 20% sodium carbonate and 10 ml of distilled water. The mixture will be incubated for 2 h at ambient temperature and then will be measured the absorbance at 765 nm. The total

phenolic content will be calculated based on the linear regression obtained from standard curve of gallic acid and the result is expressed as mg gallic acid equivalents (GAE) per g dry weight sample (mg GAE/g DW).

3) Determination of total flavonoid content

Total flavonoid content will be investigated using colorimetric method described by Dewanto, Wu, Adom, and Liu 2002. with minor modification. Briefly, 0.5 ml of the extract will be mixed with 2.25 ml of distilled water in a test tube followed by addition of 0.15 ml of 5% $NaNO_2$ solution. After 6 min, 0.3 ml of a 10% $AlCl_3$ $6H_2O$ solution will be added and allowed to stand for another 5 min before 1.0 ml of 1 M NaOH will be added. The mixture was mixed well with vortex. The absorbance was measured immediately at 510 nm using spectrophotometer. Results were expressed as mg rutin equivalents in 1 g of dried sample (mg RE/g).

4) Total anthocyanin content

The total anthocyanin content (TAC) of pigmented rice was analyzed using the colorimetric method (Duangkhamchan and Siriamornpun, 2015). Briefly, 10 mg of pigmented rice grains were extracted three times with 10 ml of distilled water. The mixture was centrifuged at 10,000 g for 10 min and the supernatants were collected. The absorbance was measured immediately at 534 nm using a Beckman Du-640 spectrophotometer (Beckman Coulter, Fullerton, USA). The reactions were performed in triplicate and the results were expressed as 1 g of dried samples (mg/g) and. All analyses were performed in triplicate.

5) Antioxidant activity

5.1) Extraction

The extraction process was done according to Wanyo et al. (2014) with minor modifications. Briefly, one gram of each sample was extracted three times with 10 mL of 80% acidified with 1.0 N HCl (85:15, v/v) at a ratio of 1:10 (w/v) and shaken on shaker at 180 rpm at room temperature for 2 h. Then, the mixture was centrifuged for 20 min at 1400 g and the supernatant was transferred into a 30 mL vial and stored at -20 °C until analysis for the soluble phenolic, flavonoid contents and antioxidant activity (DPPH and FRAP). All analyses were performed in triplicate.

The extraction of bound phenolic content was extracted according to Butsat and Siriamornpun 2010. with minor modifications. Briefly, rice sample (1 g) was extracted twice with 10 mL of 80% methanol and centrifuged at 2500 rpm for 20 min. The supernatant was discarded and then the residues were hydrolyzed with sodium hydroxide (2M, 20 mL) at room temperature. The mixtures were shacked by incubator for 24 h. Subsequently, 12M hydrochloric acid was adjusted to a pH of 7 and was added hexane to remove lipids. The final solution was extracted five times by ethyl acetate. The ethyl acetate fraction was combined and was evaporated to dryness. Bound phenolic content was dissolved in methanol (10 mL) and stored at -20 °C before analysis. All analyses were performed in triplicate.

5.2) DPPH radical-scavenging activity

The hydrogen atom or electron-donation ability of the corresponding extracts and some pure compounds will be measured from the bleaching of a purple-coloured methanol solution of DPPH (Choi, Jeong and Lee, 2007; Kubola and Siriamornpun, 2008). The antioxidant activity of the extracts, on the basis of the scavenging activity of the stable 1,1-diphenyl-2-picrylhydrazyl (DPPH) free radical, will be modified from that of Braca et al. (2001:892-895). Aqueous extract (0.1 ml) will be added to 3 ml of a 0.001 M DPPH in methanol. Absorbance at 517 nm will be determined after 30 min, and the percent inhibition of activity will be calculated as

[(Ao - Ae)/Ao] × 100 (Ao = absorbance without extract; Ae = absorbance with extract).

5.3) Ferric reducing/antioxidant power (FRAP) assay

FRAP assay will be based on the reduction of Fe^{3+} – TPTZ to a blue coloured Fe^{2+} –TPTZ (Benzie and Strain,1996 : 70-76). The FRAP assay will be adapted from Moyer, Hummer, Finn, Frei, and Wrolstad (2002 : 519).

The FRAP reagent will be freshly prepared by mixing 100 ml of acetate buffer (300 mM, pH 3.6), 10 ml TPTZ solution(10 mM TPTZ in 40 mM/HCl), 10 ml $FeCl_3 \cdot 6H_2O$ (20 nM) in a ratio of 10:1:1 and 12 ml distilled water, at 37 °C. To perform the assay, 1.8 ml of FRAP reagent, 180 µl Milli-Q water and 60

µl sample, standard or blank will be added to the same test tubes, and incubated at 37 °C for 4 min; absorbance will be measured at 593 nm, using FRAP working solution as blank. The reading of relative absorbance should be within the range 0–2.0; otherwise, the sample should be diluted. In the FRAP assay, the antioxidant potential of sample will be determined from a standard curve plotted using the $FeSO4 \cdot 7H_2O$ linear regression equation to calculate the FRAP values of the sample.

6) Determination of phenolic compounds and flavonoids by HPLC

6.1) Extraction

The extraction process was done according to Wanyo et al. (2014) with minor modifications. Briefly, one gram of each sample was extracted three times with 10 mL of 80% acidified with 1.0 N HCl (85:15, v/v) at a ratio of 1:10 (w/v) and shaken on shaker at 180 rpm at room temperature for 2 h. Then, the mixture was centrifuged for 20 min at 1400 g and the supernatant was transferred into a 30 mL vial and stored at -20 °C until analysis for the soluble phenolic, flavonoid compounds. All analyses were performed in triplicate.

The extraction of bound phenolic compounds was extracted according to Butsat and Siriamornpun (2010) with minor modifications. Briefly, rice sample (1 g) was extracted twice with 10 mL of 80% methanol and centrifuged at 2500 rpm for 20 min. The supernatant was discarded and then the residues were hydrolyzed with sodium hydroxide (2M, 20 mL) at room temperature. The mixtures were shacked by incubator for 24 h. Subsequently, 12M hydrochloric acid was adjusted to a pH of 7 and was added hexane to remove lipids. The final solution was extracted five times by ethyl acetate. The ethyl acetate fraction was combined and was evaporated to dryness. Bound phenolic compounds were dissolved in methanol (10 mL) and stored at -20 °C before analysis. All analyses were performed in triplicate.

6.2) HPLC–DAD system for analysis of free and bound phenolic compounds HPLC analysis will be performed using Shimadzu LC-20AC pumps, SPD-M20A with diode array detector and chromatographic separations will be performed on a LUNA C-18 column (4.6 × 250 mm i.d., 5 µm). The composition of solvents and used gradient elution conditions will be described previously by Uzelac et al. (2005 : 373-383) with some modifications. The solvent system will be used a

gradient of mobile phase A containing 0.36% phospholic acid in water; solution B will be used acetonitrile. The following gradient will be used: 0–15 min, from 5% A to 9% A, 91% B with a flow rate 0.8 ml/min; 15–22 min, from 9%A, 91% B to 11% A, 89% B with flow rate 0.8 ml/min; 22–38 min, from 11% A, 89% B to 18% A, 82% B with flow rate 0.8 ml/min; 38-43 min, from 18% A, 82% B to 23% A, 77% B with flow rate 0.8 ml/min; 43-44 min, from 23% A, 77% B to 30% A, 70% B with flow rate 0.8 ml/min; 44-55 min, from 30% A, 70% B to 20% A, 80% B with flow rate 0.8 ml/min; 60-65 min 5% A, 95% B with flow rate 0.8 ml/min. Operating conditions will be as follows: column temperature, 38 °C; injection volume, 20 µl; UV-diode array detection at 280 nm.

6.3) HPLC–DAD system for analysis of phenolic compounds HPLC analysis will be performed using Shimadzu LC-20AC pumps, SPD-M20A with diode array detector and chromatographic separations will be performed on a LUNA C-18 column (4.6 × 250 mm i.d., 5 µm). The composition of solvents and used gradient elution conditions will be described previously by Uzelac et al. (2005: 373-383) with some modifications. The solvent system will be used a gradient of mobile phase A containing 0.36% phospholic acid in water; solution B will be used acetonitrile. The following gradient will be used: 0–15 min, from 5% A to 9% A, 91% B with a flow rate 0.8 ml/min; 15–22 min, from 9%A, 91% B to 11% A, 89% B with flow rate 0.8 ml/min; 22–38 min, from 11% A, 89% B to 18% A, 82% B with flow rate 0.8 ml/min; 38-43 min, from 18% A, 82% B to 23% A, 77% B with flow rate 0.8 ml/min; 43-44 min, from 23% A, 77% B to 30% A, 70% B with flow rate 0.8 ml/min; 44-55 min, from 30% A, 70% B to 20% A, 80% B with flow rate 0.8 ml/min; 60-65 min 5% A, 95% B with flow rate 0.8 ml/min. Operating conditions will be as follows: column temperature, 38 °C; injection volume, 20 µl; UV-diode array detection at 280 nm.

7) Identification of anthocyanins by HPLC

The content and composition of anthocyanins were determined by RP-HPLC method using Shimadzu LC-20AC pumps, SPD-M20A diode array detection (DAD) and column Inetsil ODS-3, C18 (4.6mm x 250 mm, 5 µm) (Hichrom Limited, Berks, UK). The conditions of gradient elution and solvent composition were

described by previous study (Duangkhamchan and Siriamornpun, 2015; Kim et al., 2007). A gradient elution contained 0.1% HCL in methanol at a ratio of 15:85 v/v (mobile phase A) and 8% formic acid in purified water (mobile phase B), at a flow rate of 1 mL/min. The conditions used in the present study were as follows: column temperature 30 ◦C, UV-diode array detection at 520 nm, and injection volume 20 µL. The samples and solutions were filtered with 0.45 µm nylon membrane filter before injection. Identifications of the individual anthocyanins were compared with their relative retention time of authentic standard. The compositions and contents of anthocyanins were expressed as mg per g dry weight (µg/g).

8) Extraction and determination of γ-oryzanol and tocopherols contents

Analysis of γ-oryzanol and tocopherols contents was described using the method of Butsat and Siriamornpun (2010). One gram of pigmented rice was extracted by adding acetone at a ratio of 1:10 w/v. The mixture was vortexed for 1 min, centrifuged at 2500 rpm for 20 min at 10 ◦C. The supernatant was collected to test tube, and the solvent was added to residual for the twice extraction using above method. Then, the three supernatants were combined together and evaporated to dryness using under nitrogen gas. The extractions were operated in triplicate. HPLC method was analyzed the γ-oryzanol and tocopherols composition. Before injection, 2 mL of mobile phase was added to crude extracts. The mixture was filtered through 0.45 µm nylon syringe filter. The system of RP-HPLC consists of Shimadzu LC-20AC pumps and column Inertsil ODS (4.6 mm × 250 mm, 5 µm). The mobile phase was prepared using acetonitrile per methanol at a ratio of 25:75 v/v and flow rate at 1.5 mL/min. The UV-array detector was sated at 292 nm for measuring the tocopherols and at 325 nm for the γ-oryzanol. Identifications of the individual tocopherols and γ-oryzanol were compared with their relative retention time of authentic standard.

9) Determination of Amino Acids

The extraction of amino acids in this study was performed according to Liyanaarachchi, Mahanama, Somasiri and Punyasiri (2018). Amino-acid analysis involved an LC–MS-MS (Shimadzu LCMS-8 0 3 0) triple-quadrupole mass

spectrometer, in electrospray ionization (ESI) mode, followed by a Shimadzu HPLC (Shimadzu, Kyoto, Japan) (Chumroenphat, Somboonwatthanakul, Saensouk & Siriamornpun 2019), with some modifications. The conditions were: 0.2 ml/min was the flow rate, the temperatures of autosampler and column oven were set at 4 °C and 38 °C, respectively. Mobile phases used were: (A) demineralized ion (DI) water: formic acid 0.1%, and (B) methanol 50% in DI water: formic acid 0.1% (v/v). Identifications of the amino acids were compared with the ten authentic amino acid standards namely, threonine, isoleucine, tryptophan, phenylalanine, histidine, methionine, arginine, valine, leucine and lysine. The analyses were performed in triplicate.

3.4.3 Product development from pigmented Thai rice as functional food (Riceberry jam).

1) Food product development (Riceberry jam).

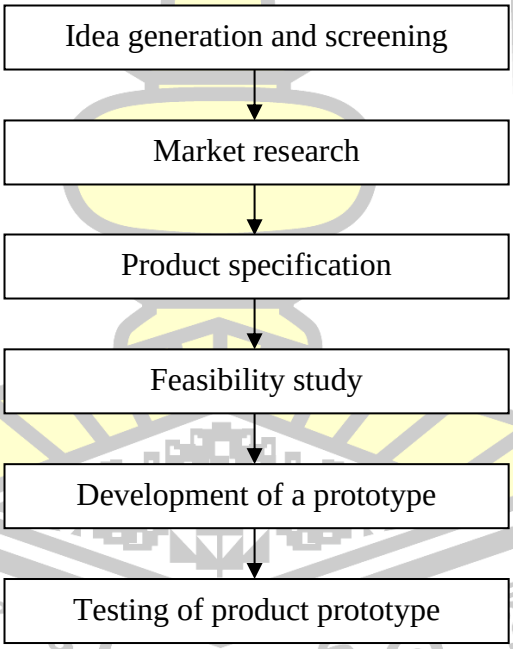


Figure 3.10 Flow chart of food product development steps

1.1) Preparation of Riceberry jam

Riceberry brown rice grains (200 g) were milled to flour and sieved (80 meshes). Riceberry flour was mixed with 200 ml of drinking water and stirred at 150 rpm in an incubator at room temperature for 2 h. The paste was added

ingredient as follow by 2% of pectin, citric acid for adjust pH 2.8 – 3.4 and 65% of sucrose and boiled at 99 ◦C for 20 min. The Riceberry jam was packed directly at high temperature in the bottle.

2) Evaluation of chemical, physical and sensory properties

2.1) Chemical measurements

Measurement of peroxide value (PV)

PV determinations by standard method (Dhaouadi et al. 2006: 270-274) involve dissolution of appropriate amounts of oil (0.3–5 g according to the expected PV) in 25 ml acetic acid-chloroform solution (3:2). Then 1ml of saturated KI solution is added and the flask stoppered. The mixture is stirred for 1 min and then kept in dark for exactly 5 min. After that, 75 ml of deionized water is added and the content is titrated with 0.01N sodium thiosulfate solution in the presence of starch indicator (1%) until the discoloration of the mixture. The same procedure was carried out for a blank solution and was taken into-account in all the titrations. PV is calculated using the following equation:

$$PV\ (\text{mequiv. kg}{-}1) = (1000/m\ ) \times 0.01(V - V\ \text{blank})$$

where V and Vblank in milliliter are the volume of thiosulfate used for titrating sample and blank solution respectively and m in grams is the used mass of oil sample.

2.2) Physical measurements

Colorimetric parameters

Color changes in samples were determined by a Minota CR-300 Chroma Meter (Minota, Japan) using the *L*, *a*, and *b* color scales. Parameters *L*, *a* and *b* determine a three-dimensional color space, in which *L* represents brightness (on a lightness–darkness scale of 1 to 100, respectively) whereas positive and negative *a* values determine the redness and greenness, and positive and negative *b* values determine yellowness and blueness, respectively. The instrument was calibrated against a white standard. Measurements were individually taken for 10 samples per treatment and the average of 10 readings was calculated. The color difference ΔE was calculated from the *L*, *a*, *b* parameters, using the Hunter–Scotfield equation:

$$\Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2}$$

Texture profile analysis

Texture profile analysis of the product prototype will be performed at room temperature by using a TA-XT2 Texture Analyzer (Ltd in Godalming, Surrey UK) with 5-kg load cell. The plunger is then lowered at a constant speed until it compressed the sample to a predetermined degree (percentage of compression). The resulting peak force will be measured in Newton.

2.3) Sensory evaluation

Sensory evaluations of rice product prototype will be conducted by 30 panelists using a nine-point hedonic scale where nine is like extremely and one dislike extremely. Three coded samples will be served and water is provided for rinsing between samples. Control will be used to compare with the product prototype for sensory test.

3) Analysis of bioactive compounds.

Concentration of bioactive compounds

As the sample will be analyzed total phenolic content and evaluated antioxidant activity. The antioxidant activity of extracts will be evaluated by estimating their relative abilities to scavenge the DPPH radical, FRAP assay (Choi, Jeong and Lee, 2007: 130-138), total phenolic content, total flavonoid content and total anthocyanin.

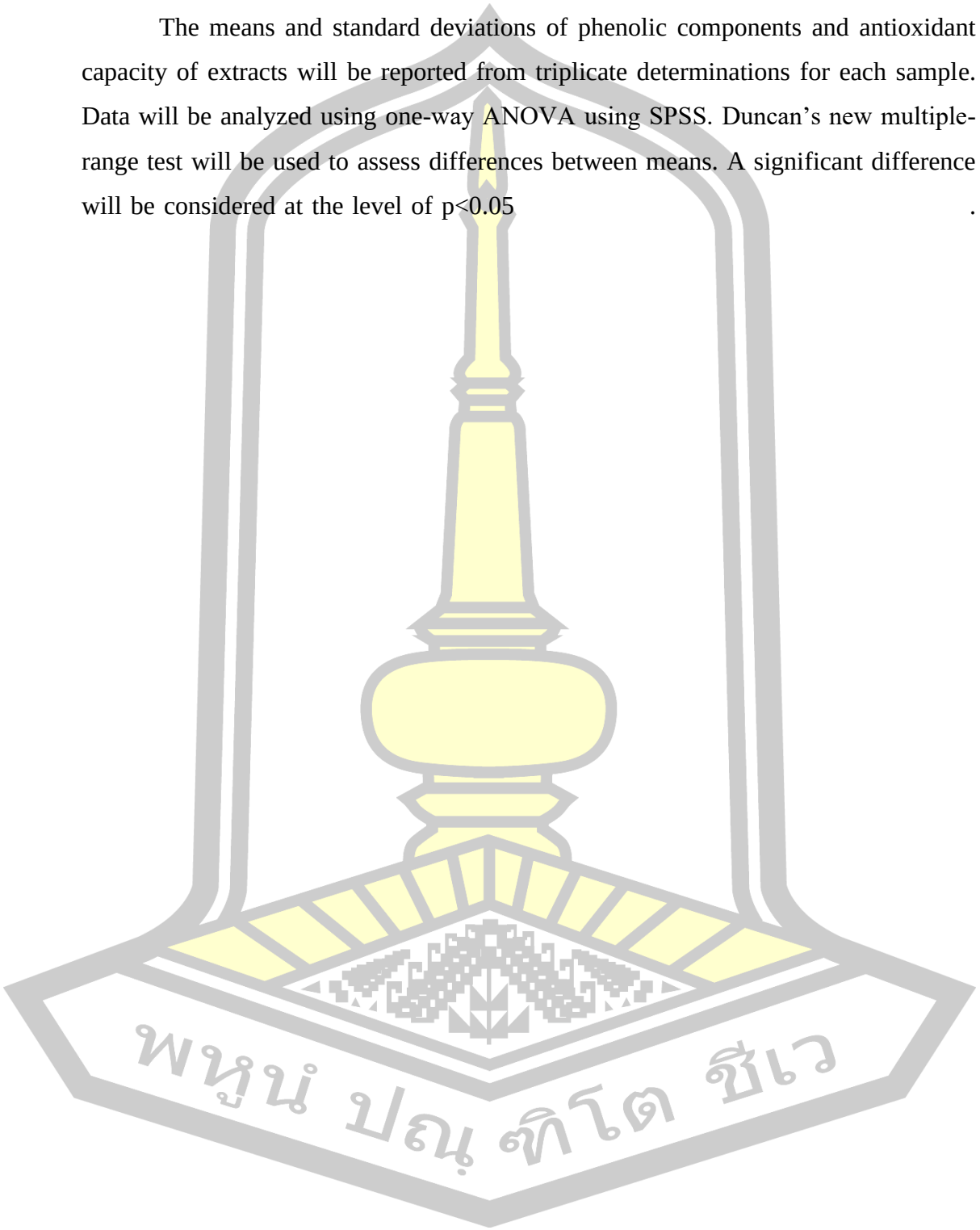
4) Stability of the bioactive compounds during processing and storage.

As the sample will be analyzed:

- Physical, chemical and sensory properties
- Bioactive compounds
- Antioxidant activity.

3.5 Statistical analysis

The means and standard deviations of phenolic components and antioxidant capacity of extracts will be reported from triplicate determinations for each sample. Data will be analyzed using one-way ANOVA using SPSS. Duncan's new multiple-range test will be used to assess differences between means. A significant difference will be considered at the level of $p<0.05$.



CHAPTER 4

Results and Discussion

We studied changes due to drying with two different methods (hot air (HA) and far-infrared radiation (FIR)) on the preservation of bioactive compounds in pigmented rice varieties, as brown or unpolished and polished rice grains of three varieties, with no heat as the “unheated or unprocessed” samples.

4.1 Results and discussions of experiment 2:

Study bioactive compounds and starch digestibility of pigmented Thai rice

4.1.1 Total phenolic content (TPC)

The sum of total free and bound phenolic content of pigmented Thai rice ranged from 182 to 742 mg GAE/100g dw (Table 4.1). In this study, the TPC was significantly different between all the pigmented Thai rice varieties tested. The highest content of the TPC was Mali dang, a red rice variety followed by Riceberry (purple) and the lowest was Hom Mali (white rice). Sompong, Siebenhandl-Ehn, Linsberger-Martin and Berghofer (2011) found a similar distribution of TPC in rice from Thailand, China and Sri Lanka, the highest of TPC was found in red Thai rice (691 mg/100g) followed by black Thai rice (665 mg/100g) cultivars. In contrast, many researchers have reported that black pigmented rice showed higher TPC than red rice, while white rice consistently has the lowest TPC (Ponjanta, Chomsri & Meechoui, 2016).

4.1.2 The total anthocyanin content (TAC)

The levels of the total anthocyanin content (TAC) for the samples examined varied significantly, from 17 to 66 mg /100g dw (Table 4.1). The TAC ranged from 59 to 66 and 17-22 mg/100 g in purple and red rice varieties, respectively. The highest value of the TAC was observed in purple rice varieties (Hom Nil and Riceberry, respectively), followed by red rice varieties. There were significant differences between the purple rice varieties, but no significant difference

was found between the red rice. Black or purple Thai and Chinese rice showed higher TAC (109-256 mg/100 g) than red rice varieties (0.3-1.4mg /100g) in the previous study (Sompong, Siebenhandl-Ehn, Linsberger-Martin & Berghofer, 2011). This was similar to the results of this study, where purple rice's showed the highest TAC, followed by red rice, with non-pigmented rice (Hom Mali) having no detectable anthocyanins TAC, demonstrating that anthocyanins contribute to the pigmentation of rice's.

Tables 4.1 Identifications of anthocyanin and phenolic acids in Thai pigmented rice varieties.

Compounds (µg per 100g)	Hom Mali White	Sung Yod Red	Mun Poo Red	Mali Dang Red	Hom Nil Purple	Riceberry Purple
Phenolic acids						
GA	2.43±0.12^{c}	2.15±0.07^{c}	2.31±0.08^{c}	3.24±0.09^{b}	6.39±0.11^{a}	6.16±0.12^{a}
PCCA	15.18±1.56^{a}	13.66±0.20^{b}	12.75±0.78^{c}	13.13±0.30^{bc}	14.71±0.79^{a}	14.88±0.20^{a}
VA	2.12±0.06^{c}	3.56±0.02^{b}	3.8±0.01^{b}	3.89±0.02^{b}	6.68±0.10^{a}	6.72±0.11^{a}
ChA	2.79±0.06^{b}	1.39±0.03^{d}	2.46±0.01^{b}	1.46±0.02^{c}	2.9±0.04^{a}	2.75±0.05^{b}
CFA	1.46±0.04^{c}	1.28±0.05^{d}	1.43±0.03^{c}	1.59±0.00^{b}	1.73±0.04^{a}	1.75±0.02^{a}
SyA	1.52±0.06^{c}	1.61±0.04^{c}	1.65±0.05^{c}	1.74±0.02^{b}	1.91±0.02^{a}	1.96±0.02^{a}
p-CA	3.38±0.56^{d}	3.76±0.23^{d}	5.8±0.19^{c}	5.24±0.21^{c}	6.78±0.31^{b}	7.14±0.40^{a}
FA	19.50±0.56^{b}	20.05±0.19^{b}	20.03±0.08^{b}	19.71±0.62^{b}	39.11±0.69^{a}	39.32±0.58^{a}
SNA	1.13±0.04^{d}	1.53±0.11^{c}	1.54±0.10^{c}	2.53±0.08^{b}	5.28±0.48^{a}	5.32±0.55^{a}
Anthocyanin						
Cyanidin-3-glucoside	ND	9.63±1.56^{b}	9.54±1.31^{b}	10.22±1.41^{b}	40.27±4.15^{a}	35.94±3.17^{a}
Pelargonidin	ND	0.39±0.01^{c}	0.11±0.01^{e}	0.21±0.02^{d}	2.11±0.06^{a}	1.11±0.02^{b}
Malvidin	ND	1.44±0.09^{d}	1.57 ±0.07^{d}	3.04 ±0.05^{c}	4.02 ±0.11^{a}	3.98 ±0.29^{a}

GA (Gallic), PCCA (Protocatechuic), VA (Vanillic), ChA (chlorogenic), CFA (Caffeic), SyA (Syringic), *p*- CA (*p*-Coumaric), FA (Ferulic) and SNA (Sinapic) acids. Mean values within a line superscripted by the same letter are not significantly different at $p < 0.05$.

4.1.3 Phenolic compounds

The sums of individual free and bound phenolic compound of Thai pigmented rice are presented in Table 4.1 The main phenolic acids in non-pigmented rice were FA and *p*-CA, while PCCA, VA, *p*-CA and FA were the predominant in all pigmented rice. Similar results were reported by previous studies (Zhou, Robards, Helliwell & Blanchard, 2004; Chatthongpisut, Schwartz & Yongsawatdigul, 2015). In addition, in our present study it was found that VA was three-fold greater in all rice and FA was found most in red rice varieties. We have also confirmed the data from previous research that FA is the major phenolic acid in non and pigmented rice. FA may be derived from pectins and arabinoxylans or cross-linked to cell wall polysaccharides in the aleurone and pericarp layers of the rice endosperm cell walls (Clifford, 1999).

4.1.4 Anthocyanin composition

The contents of individual authentic anthocyanin standards of pigmented Thai rice varieties are presented in Table 4.2. It was found that non-pigmented rice (Hom Mali) pigments did not contain any one of those anthocyanins. The five pigmented rice cultivars studied possessed all three anthocyanin pigments. The purple rice cultivars studied had high content of cyanidin 3-glucoside. Abdel-Aal, Young and Rabalski (2006) displayed the similar result that the purple or black rice cultivars are abundant source of anthocyanins especially, cyanidin-3-O-glucoside. The different rice varieties possessed different anthocyanin content which depends on genotypes and possibly also differences in their location in the outermost layer of rice. In addition, malvidin was also showed high content in all red varieties. Similar results have been observed for red rice (Abdel-Aal, Young & Rabalski, 2006; Chen, Nagao, Itani & Irifune, 2012). Moreover, pelargonidin has higher content in purple rice than red rice (Abdel-Aal, Young & Rabalski, 2006). purple Thai and Chinese rice showed higher TAC (109-256 mg/100 g) than red rice varieties (0.3-1.4mg /100g) in the previous study (Sompong, Siebenhandl-Ehn, Linsberger-Martin & Berghofer, 2011). This was similar to the results of this study, where purple rice's showed the highest TAC, followed by red rice, with non-pigmented rice (Hom Mali) having no detectable

anthocyanins TAC, demonstrating that anthocyanins contribute to the pigmentation of rice's.

4.1.5 Amylose content

One of the most important quality parameters of rice is the amylose content which impacts on cooking quality (Adu- Kwarteng, Ellis, Oduro & Manful, 2003). All the rices measured had a low amylose content (below 20%), and there were small but significant differences in amylose content between starches (Table 4.8). Both of the red rice, Mun Poo and Mali Dang had the highest amylose content (15.96% and 15.80%, respectively) and Hom Mali, a white rice variety had the lowest content (12.99%). Moreover, many studies have observed the amylose content of (white, brown, red and purple) Thai rice to range from 2.20 to 28.90% (Ponjanta, Chomsri & Meechoui, 2016; Saikia, Dutta, Saikia & Mahanta, 2012). The classification of amylose content (IRRI, 2018) describes low amylose content rice as having an amylose content in the range of 10 to 20%. In this study, all Thai rice varieties (white, red and purple) are classified as low amylose types (<20%). Generally, low amylose content gives rise to relatively soft and sticky texture after cooking, which is typical of Thai rice's. (Adu- Kwarteng, Ellis, Oduro & Manful, 2003).

Tables 4.2. Total phenolic content, total anthocyanin content and amylose content of Thai pigmented rice varieties

Sample	Color	%TPC (mg GAE /100)	%TAC (mg CyGE /100g)	% Amylose content
Hom Mali	White	112.59± 4.88 ^{f}	N/A	12.99±0.84 ^{c}
Sung Yod	Red	169.11±7.64 ^{d}	21.96±6.95 ^{c}	14.44±0.80 ^{bc}
Mun Poo	Red	452.45±5.49 ^{e}	16.47±5.18 ^{c}	15.96±0.18 ^{a}
Mali Dang	Red	943.53±8.11 ^{a}	18.56±4.78 ^{c}	15.80±0.71 ^{a}
Hom Nil	Purple	588.28±9.10 ^{c}	65.85±7.5 6^{a}	14.15±0.18 ^{b}
Riceberry	Purple	752.55±1.62 ^{b}	58.76±6.49 ^{b}	14.08±0.72 ^{bc}

TPC Total phenolic content, TAC total anthocyanin content, Amylose content are based on DW, dry weigh.Values are mean ± standard deviation of three replicates. Values within a column having the same letter are not significantly different at $p < 0.05$.

4.1.6 Differential scanning calorimetry (DSC)

Gelatinization parameters are shown for purified starch extracted from rice samples in Table 4.3. Sung yod (red) rice starch gelatinized at the highest peak temperature (T_p = 79.11 °C) follow by Hom Nil (purple) (T_p = 69.30 °C), Mun Poo (red) (T_p = 69.07 °C) and Mali Dang (red) rice starches (T_p = 68.85 °C), respectively. There was significant variation observed in gelatinization enthalpy, with Sung yod (12.41 J g^{-1}), Mali Dang (11.50 J g^{-1}) and Riceberry (10.97 J g^{-1}) starch having a higher gelatinization enthalpy than other starches. Gelatinization of Sung Yod, a red pigmented rice starch occurred at a higher T_p, approximately 12 °C higher than that of the white rice purified starch (Hom Mali).

Tables 4.3 Gelatinization parameters of Thai pigmented rice varieties

Samples	Color	To (°C)	Tp (°C)	Tc (°C)	$\Delta_{gel}H$ (J g^{-1}starch)
Hom Mali rice	White	61.08±0.14[d]	67.98±0.03 [e]	74.11±0.30 [d]	9.50±0.97 [d]
Sung Yod	Red	74.12 ± 0.06[a]	79.11±0.06 [a]	82.90±0.10 [a]	12.41±0.22 [a]
Mun Poo	Red	62.51±0.14 [b]	69.07±0.08 [c]	74.94±0.27 [c]	9.46±0.80 [d]
Mali Dang	Red	62.02±0.17[c]	68.85±0.03 [d]	74.94±0.46 [c]	11.50±0.66 [b]
Hom Nil	Purple	60.61±0.12[f]	69.30±0.04[b]	75.64±0.10 [b]	9.84±0.64 [d]
Riceberry	Purple	58.04±0.02[g]	65.75±0.14 [f]	73.75±0.37[e]	10.97±0.22 [c]

Onset (T_o), peak (T_p) a concluding (T_c) temperatures of gelatinization are shown. $\Delta_{gel}H$ is the enthalpy change associated with the gelatinization of 1 g of purified starch. Mean values within a column superscripted by the same letter are not significantly different at $p < 0.05$.

It is known that differences in starch characteristics influence gelatinization behavior, but the starches selected for this study were similar in many respects. Apart from the higher gelatinization temperature of pigmented rice, the starches had similar enthalpies of gelatinization ($\Delta_{gel}H_{g-1}$). DSC thermograms of Thai pigmented rice starches were presented in Figure 4.11. Mostly, pigmented rice samples were observed to have higher gelatinization parameters when compared with non-pigmented rice samples. Riceberry is a crossed-breed between a localnon-glutinous of Jao Hom Nin or Hom Nil (purple) and Khoa Dawk Mali 105 or Hom Mali rice (non-pigmented) by the Rice Science Center, Kasetsart University, Thailand. Although,

Riceberry is a purple color comparable to Hom Nil nevertheless, the gelatinization parameters of this variety were similar to their breed mother.

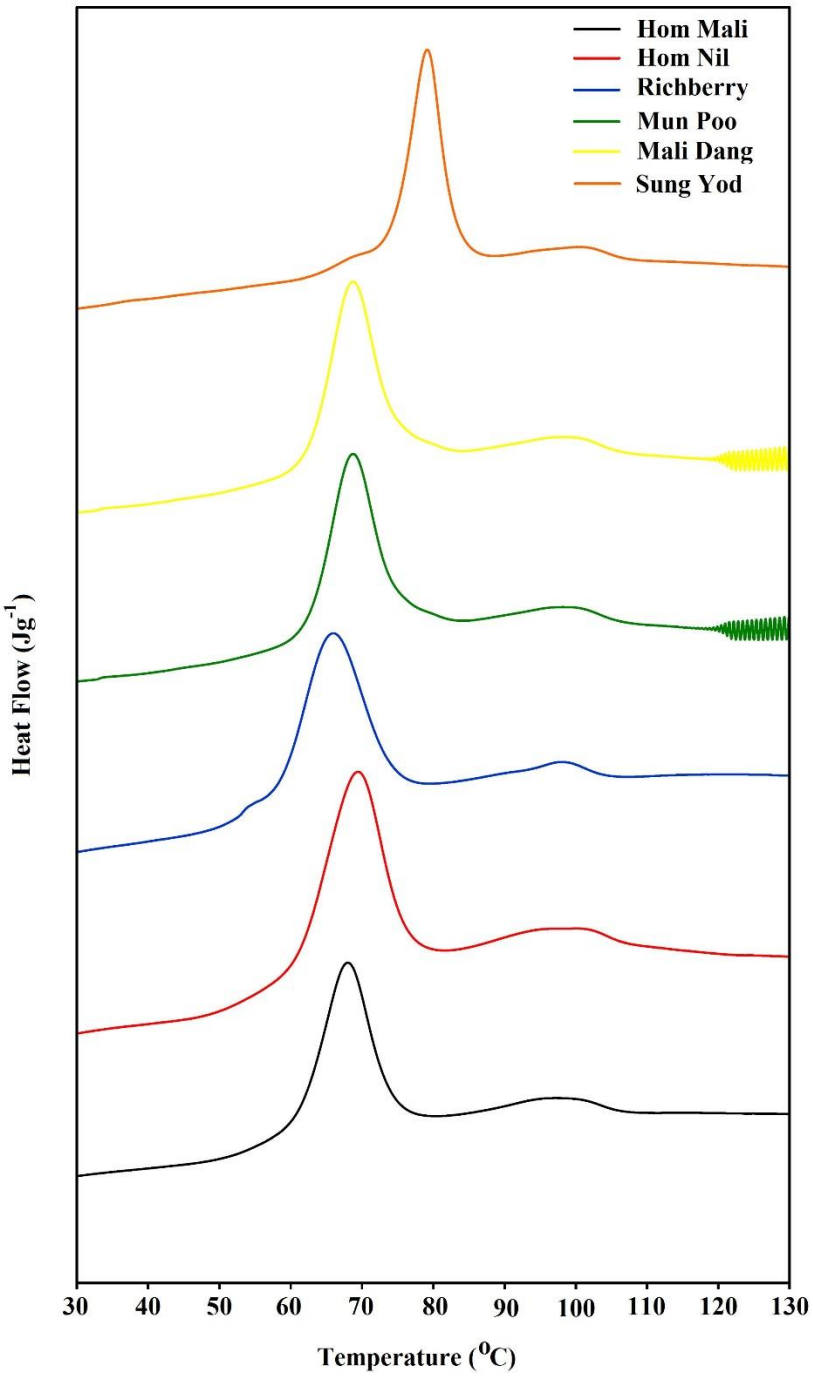


Figure 4.11 DSC thermograms of Thai pigmented rice starches.

4.1.7 FTIR spectroscopy analysis

The FTIR spectra of starches and flours were represented the spectra of starches, flours, treated starch (TS) and treated flour (TF) of pigmented rice (Figure 4.12). All samples presented the similar spectral patterns. The starch crystallinity was determined using FTIR spectroscopy as described in a study (van Soest, Tournois, de Wit & Vliegenthart, 1995). The absorbance band of IR at 1047 cm^{-1} and 1022 cm^{-1} have been associated to ordered or crystalline and amorphous structures of starch, respectively. Therefore, the ratio of absorbance 1047/1022 cm^{-1} was calculated to express the degree instarch and led to represent the amount of crystalline to amorphous phase in rice starch (van Soest, Tournois, de Wit & Vliegenthart, 1995).

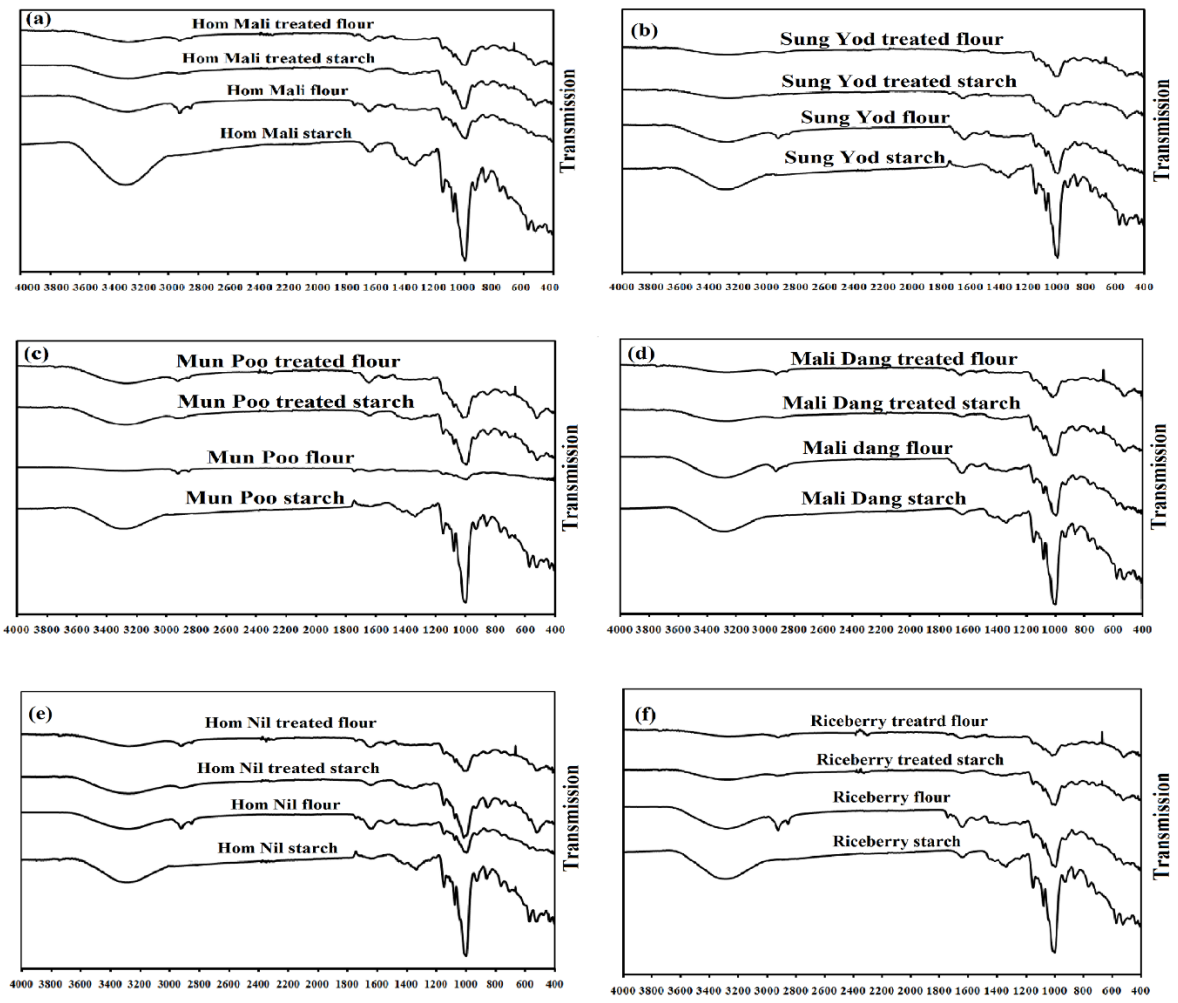


Figure 4.12 The Hom Mali (a), Sung Yod (b), Mun Poo (c), Mali Dang (d), Hom Nil (e) and Riceberry (d), FRIR spectra of Thai pigmented rice varieties.

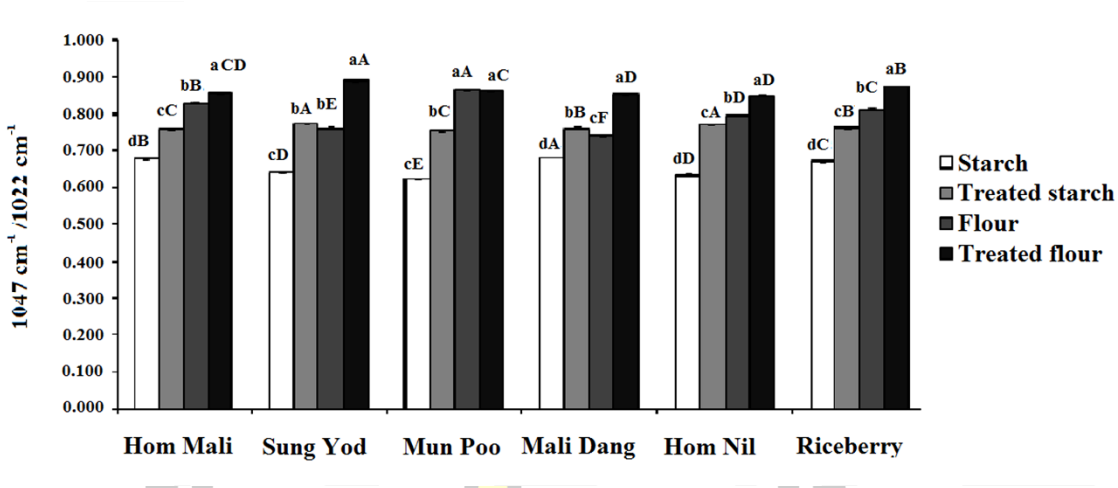


Figure 4.13 The degree of order in the native and treated starches and flours before starch digestion of Thai pigmented rice measured using FTIR spectroscopy. Values in the same column of samples with the same small letters and the capital letters in the same line are compared between varieties are not significantly different ($P<0.05$).

In this present study, the ratio for native and treated starch and flour were investigated (Figure 4.13). The ratio 1047/1022 cm^{-1} for native starches were lower than native flour in all varieties ($p<0.05$). This is likely due to the interference of other, non-starch, components. Small decreases in order were observed in both purified starch and flours following cooking (Figure 4.14). The method was not, however, able to identify differences in order between rice varieties that may impact on digestibility, despite the differences observed by DSC, due to the lower sensitivity of FTIR-ATR to changes in starch crystallinity as demonstrated previously (Warren, Gidley & Flanagan, 2016)

4.1.8 In vitro digestibility

The starch digestibility curves of purified starches and flours of the six pigmented Thai rice varieties were presented in Fig. 4.1. For purified starch, Hom Mali (white) showed the highest levels of starch digested (77%) follow by Sung Yod (red), Riceberry (purple), Mali Dang (red), Mun poo (red) and lowest for Hom Nil (purple) rice. For flour, Hom Mali also showed the highest level of starch digested (%) follow by Riceberry, Mun Poo (red), Sung Yod (red), Hom Nil (purple) and Mali Dang (red), respectively. The starch digested (%) at 60 min were ranged from 58% to 77% and from 9.5%-16.17% of purified starches and flours, respectively. The

digestion curves of the pigmented rice varieties were characterized by as low rate after about 60 min during the small intestinal digestion process (Table 4.4). The pigmented starch varieties were found to contain starch which when purified was digested at a significantly lower rate than the control Hom Mali rice.

LOS analysis was utilized to obtain values for the variables in eqn (1) (see section 2.11). The k values and C∞ were determined by the slope and y-intercept of the LOS plot, respectively. Plots of flour and purified starch digestibility from LOS analysis were each characterized using a single and two phases. Values for kinetic constants calculated from LOS plots are shown in Table 4.10. In this study, all purified starches could have their digestion kinetics described by a single first order rate constant. The k values of purified starches ranged from 0.16 to 0.25 min-1. For the single phase of flour, the values for flours were much lower, reflecting their slower digestion rates, with values ranging from 0.039 to 0.064 min-1. Hom Mali white rice showed the highest of C∞ value in flours (17.11%) and starches (76.85%). Among the pigmented rice flours, Sung Yod, Mali Dang, Hom Nil and Riceberry could have their digestion kinetics best modelled by 2 separate first order rate constants (Figure 4.9). The estimated values of k and C∞ for variables in eqn (3) are presented for those samples in Table 4.4. When the starch digestion occurs two phases, this suggests the presence of a slower phase in digestion. The k2 values of four varieties were in the following order; Mali Dang >Hom Nil and Riceberry> Sung Yod, which can be compared to the single rate constant where amylolysis appears as a single-phase process in flour and starch.

The extent of amylolysis (C_∞) was similarly increased in purified starch when compared to flour. The first-order kinetic data described the amylolysis of starch in purified rice and rice flour from several pigmented and non-pigmented varieties of Thai rice are described in the present paper. LOS analysis is different the widely used Englyst method, and employs only two variables, C_∞ and *k*, to predict the release of hydrolyzed products from amylolysis (Englyst, Kingman & Cummings, 1992). This method provides a sensitive and less arbitrary means of identifying fractions of digested starches at different intrinsic rates and to different extents.

The percentages of starch digested after 60 min, and also the C_∞ values, during *in vitro* digestion were significantly higher for all purified starches when compared to

rice flours.This is likely due to the other components of rice flour, including phenolics and anthocyanins, but also non-starch components such as cell wall reducing the rate of starch digestion (Table 4.10). The non-pigmented rice (Hom Mali) displayed the highest amount of starch digestibility over all in both the flour and purified starch forms. Unlike the other rice varieties tested in this study, the Hom Mali, as a white rice, contains no anthocyanins, although it does contain other phenolic compounds (Butsat & Siriamornpun, 2010). This may contribute to the higher digestibility of the Hom Mali rice in the flour form, relative to the pigmented varieties, although the Hom Mali did also show slightly higher intrinsic starch digestibility in the purified starch form, in the absence of anthocyanins. This may also indicate that the starch in pigmented rice has a lower intrinsic digestibility, even in the absence of phenolic compounds. These results indicated a possible effect of phenolic compounds and anthocyanins on starch digestibility in pigmented rice. Anthocyanins are widely found in fruits and vegetables and have been shown to possess *in vitro* inhibition of the activity of α-glucosidase enzyme. (McDougall et al., 2005). Ramdath, Padhi, Hawke, Sivaramalingam and Tsao (2014) found significant α-glucosidase inhibitory activity of anthocyanins and polyphenols from extracted pigmented potatoes and showed that these compounds reduced starch digestibility *in vitro*. Several studies have been reported that showthat cyanidin 3-glucoside and peonidin 3-glucoside were the major anthocyanins in pigmented rice varieties and contain more TPC and TAC than non-pigmented or white rice (Chatthongpisut, Schwartz & Yongsawatdigul, 2015; Sompong, Siebenhandl-Ehn, Linsberger-Martin & Berghofer, 2011; Ponjanta, Chomsri & Meechoui, 2016). Cyanidin 3-glucoside was reported as a potent inhibitor of α-glucosidase activity (Adisakwattana, Charoenlertkul & Yibchok-anun, 2009). Furthermore, α-amylase and α-glucosidase were shown to beinhibited by phenolic compound in millet extracts suggesting that phenolic compounds may play an important role in reducing glucose liberation and absorption in the small intestine hence may play a role in controlling post-prandial glycaemia in diabetics (Pradeep & Sreerama, 2015). The findings from our present study may support those studies that cyanidin 3-glucoside might play a role in inhibiting α-amylase activity in pigment rice flours. Our research has demonstrated that not only starch structure but also

anthocyanins of pigmented rice influence lower digestibility, compared to white rice. Consumption of starches which are digested slowly is associated with a reduced risk of developing diabetes and cardiovascular disease, and obesity.

Therefore our findings have provided useful information for development of slow release functional food materials for use in the dietary management of metabolic disorders such as type 2 diabetes.

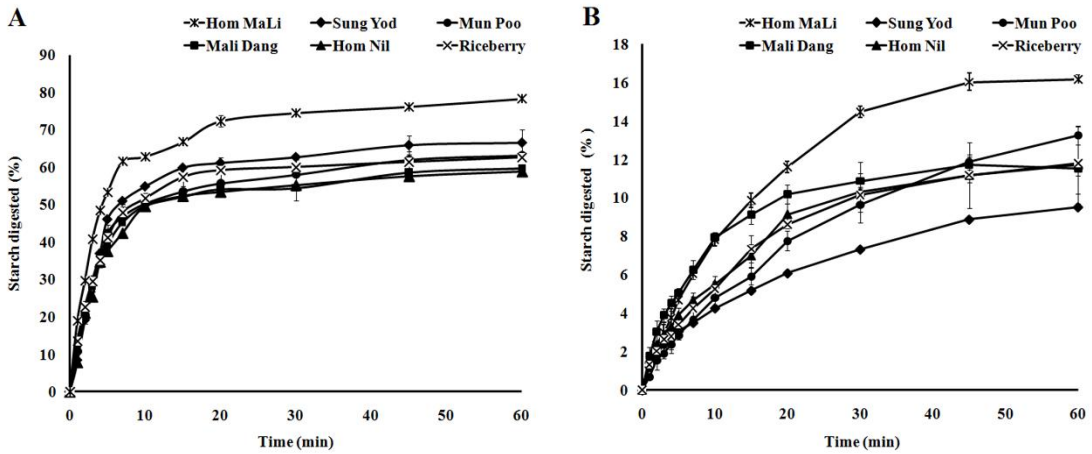


Figure 4.14 Starch digestibility curves of purified starches and (A) and flours (B). Values are mean ± standard deviation of three replicates. Different letters indicate significant differences (P <0.05) between curves for both purified starches and flours of Thai pigmented rice varieties .

Tables 4.4 *The estimate values from LOS plots for all purified starches and flours of pigmented Thai rice varieties*

Sample	Color	Type	%Starch digested at 60 min.	Single or slower phase $C_{1\infty}$ (%)	K_1 (min^{-1})	$C_{2\infty}$ (%)	K_2 (min^{-1})	Total C_∞ (%)
Hom Mali	White	Starch	78.28±0.87[a]	72.85±0.85[a]	0.257±0.009 [c]	N/A	N/A	72.85±0.85 [a]
Sung Yod	Red	Starch	66.55±3.49[b]	63.52±0.73[b]	0.182±0.004[f]	N/A	N/A	63.52±0.73 [b]
Mun Poo	Red	Starch	63.13±0.08[b]	59.55±1.37[c]	0.175±0.002[g]	N/A	N/A	59.55±1.37 [c]
Mali Dang	Red	Starch	65.15±2.04[b]	58.72±0.97[c]	0.199±0.018[e]	N/A	N/A	58.72±0.97 [c]
Hom Nil	Purple	Starch	58.79±0.33[c]	54.50±3.87[c]	0.158±0.003[g]	N/A	N/A	54.50±3.87 [c]
Riceberry	Purple	Starch	62.63±1.06 [b]	56.60±1.90[c]	0.219±0.018[d]	N/A	N/A	56.60±1.90 [c]
Hom Mali	White	flour	16.17±0.19 [d]	17.81±0.59[d]	0.064±0.001[h]	N/A	N/A	17.81±0.59[d]
Sung Yod	Red	flour	9.52±0.02 [f]	3.46±0.11[h]	0.193 ±0.001[e]	8.96±0.14[d]	0.036±0.001[d]	12.43±0.75[g]
Mun Poo	Red	flour	13.25±0.49 [ef]	13.54±2.23[e]	0.039±0.003[j]	N/A	N/A	N/A
Mali Dang	Red	flour	12. 19±1.49[ef]	6.00±0.71[f]	0.353±0.004[b]	9.79±0.21[ac]	0.076±0.001[a]	15.79±0.12[e]
Hom Nil	Purple	flour	11.71±2.00 [ef]	3.89±0.49[g]	0.458±0.001[a]	9.13±0.31[d]	0.059±0.001[b]	13.02±0.15[g]
Riceberry	Purple	flour	12.46±1.85[ef]	4.96±0.07[e]	0.308±0.004[i]	10.11±0.52[b]	0.057±0.004[c]	15.09±0.07[f]

Values are estimated from LOS plots with one–phases. *k* is the rate constant. C_∞ is the extent of starch amylosysis for each digestive phase. Values for the rapid phase and the v are therefore not applicable (N/A). Mean values within a column superscripted by the same letter are not significantly different at $p < 0.05$.

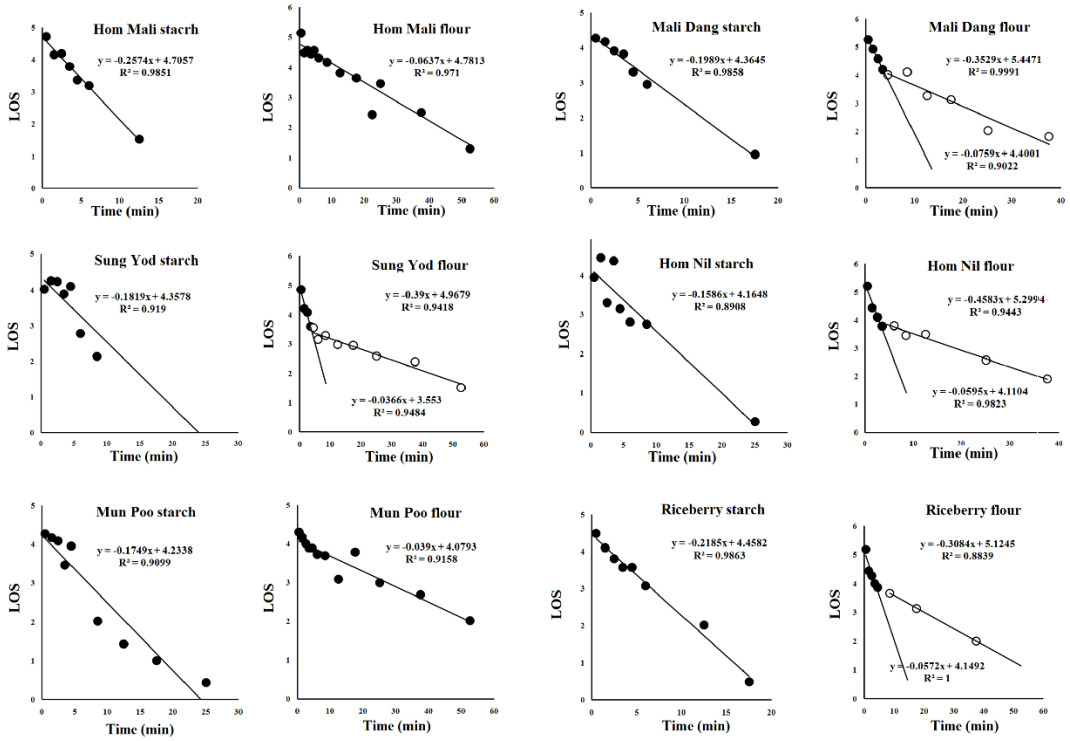


Figure 4.15 LOS plots of purified starches and flours from Thai pigmented rice varieties. The linear phase is shown single and two phases of starch digestion which can be estimated k, C∞ values. (A) Hom Mali; (B) Sung Yod; (C) Mun poo; (D) Mali Dang; (E) Hom Nil and (F) Riceberry.

4.2 Results and discussions of experiment 1:

Study the variation in bioactive compounds and antioxidant activity of different pigmented Thai rice varieties using drying methods (Far-infrared radiation and
hot air dryings).

4.2.1 Total phenolic content

Recently, several phenolic compounds have been widely identified in various plants, especially cereals, vegetables and fruits, because they have potent biological activities (Li et al. 2006). Changes in the total soluble and bound phenolic contents of pigmented rice varieties, as affected by HA and FIR treatments are shown

in Figure 4.16 The soluble TPC of unprocessed pigmented brown rice (13.05- 76.38 mg GAE/g dw) was higher than that polished rice (7.32 - 29.37 mg GAE/g dw). The highest content of the soluble TPC in FIR dried unpolished were observed at the ranging 51-63 mg GAE/g dw. Compared with the unpolished samples, regardless the thermal treatment, the concentration of soluble TPC decreased considerably in unheated-polished samples in all varieties ($p<0.05$). The highest level of soluble TPC reduction was approximately 60% in Mali Dang (red), polished rice (Fig 4.1). KDML 105 has lowest concentration of soluble and bound phenolic contents when compared to all pigmented rice varieties. Similar results have been reported as reductions in the levels of total soluble TPC: 92% in red and 97% in black rice grains and 62 % in the light brown pericarp colour, respectively (Walter et al., 2013). This report indicates that when polishing removes the external layers of the grains, it also removes the TPC; thus, TPC in rice are mainly linked with the pericarp of the rice grains (Walter et al., 2013). Similar results were reported by many researchers, the soluble phenolic content of white rice grains ranged from 38% (Adom and Liu, 2002) to 70 % (Zhou et al., 2004), and about 81% in red and black external layer coloured (Mira et al., 2009). Moreover, the occurrence of polyphenols in rice is influenced by a combination of genetic factors, genotype and environmental conditions (Butsat & Siriamornpun, 2010). According to a previous study of Brazilian rice, the soluble TPC was about four times higher than bound TPC (de Mira, Massaretto, Pascual & Marquez, 2009). Our results suggest that the TPC in pigmented rice cultivars arises mostly in the bound form rather than the soluble form.

When compared between heat treatment, the highest content of soluble TPC was observed in FIR-dried unpolished samples. After FIR radiation, the concentration of soluble TPC from unheated pigmented rice (Hom Nil, Mali Dang and Riceberry) increased significantly to 18%, 10% and 7.5%, respectively, while HA significantly decreased soluble TPC to 10%, 21% and 30% of the TPC in the varieties($p<0.05$). KDML 105 has lowest concentration of soluble and bound phenolic contents after FIR and HA dryings treated when compared to all pigmented rice varieties. FIR radiation caused an increase of soluble and bound TPC in all varieties, greater than for unheated and hot-air-treated samples. The total soluble and bound phenolic contents of unpolished and polished grains as affected by FIR and HA were

similar trends. These results indicate that the increases of both soluble and bound TPC were induced by FIR radiation.

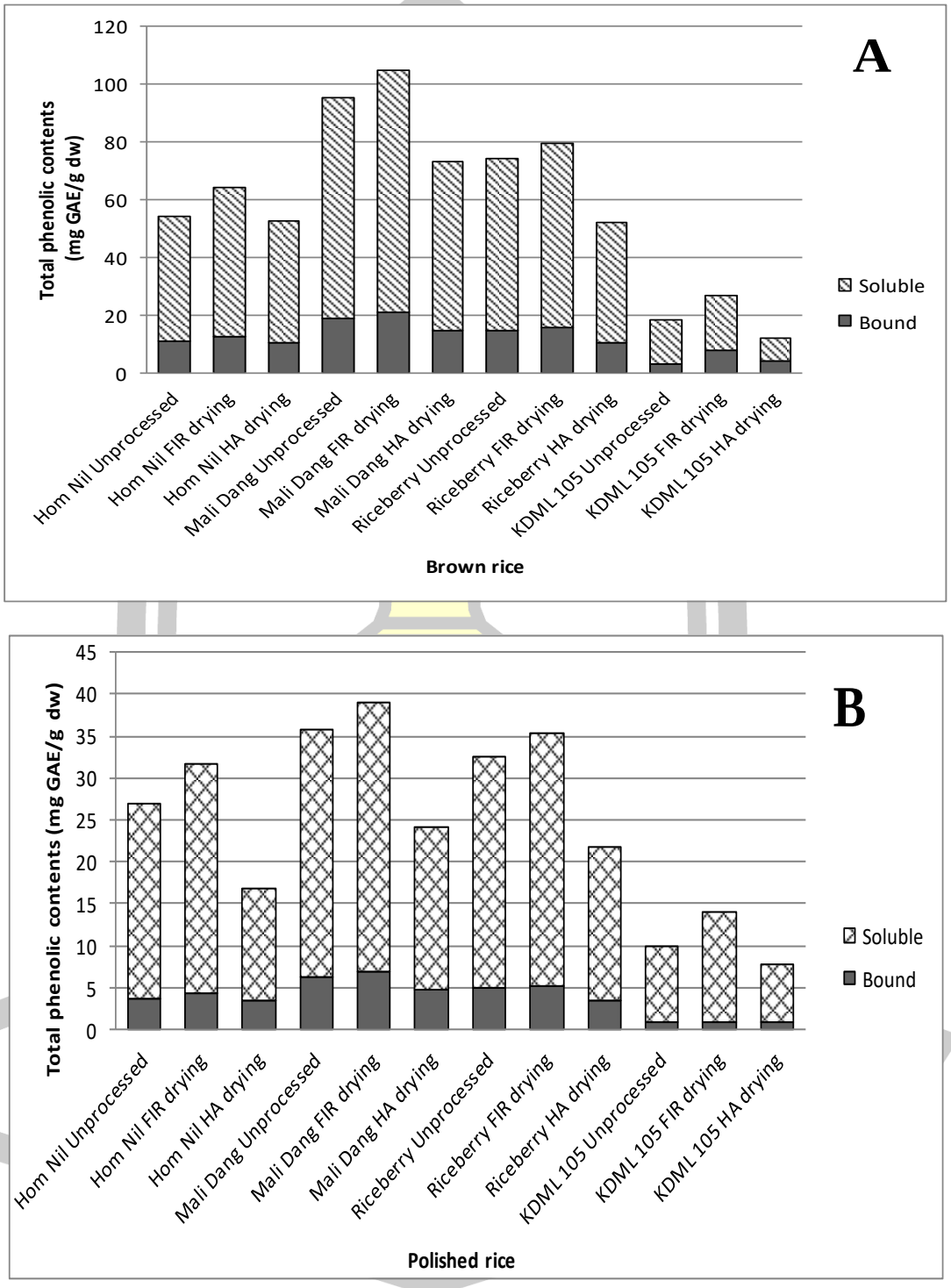


Figure 4.16 Effect of FIR and HA treatments on total soluble and bound phenolic contents of brown or unpolished (A) and polished (B) pigmented Thai rice. Each value is the mean ± the standard deviation (n = 3). Means

Similar results were reported in other studies, the concentration of TPC being increased by the combined FIR-HA drying in mulberry leaves (increased by 75%)(Wanyo et al., 2011), marigold flower (8%)(Siriamornpun, Kaisoon & Meeso, 2012) and kaprow leaves (5%)(Raksakantong, Siriamornpun, Ratseewo & Meeso, 2011). In addition, Adak, Heybeli and Ertekin (2017) reported that an increase total phenolic content (10 times) in infrared-dried strawberry; conditions of infrared drying (air velocity and infrared power) were similar. The may be explained that the FIR is converted into heat via molecular vibrations and absorbed rapidly and steadily to the center of the materials evenly during drying. This treatment may break down the covalent bonds which is not strong therefore heating could release and activate the small molecule phenolic compounds in plants (Soong & Barlow, 2004; Yao, Fan & Duan, 2019) which would increase the TPC in dried pigmented rice.

Thermal processing can cause some reactions inside the rice grain. For example, the use of a microwave roasting process caused intense molecular movement, thereby providing more soluble (increase by 10 times) and insoluble (decrease by 2 times) phenolic compounds in peanuts (Ferreira et al., 2016). These compounds could be released when wall structures, proteins, pectins and fibers are hydrolyzed, caused by the breaking covalent bonds (Zhang, Lv, Pan & Fan, 2012). However, in some cases, such as for total phenolics, there may be an increase or decrease due to thermal instability (Ferreira et al., 2016). We speculate that the HA and FIR dryings may have a significant effect on the internal structure of the grain, which may increase the yield of extraction of all the components, including the phenolic compounds.

4.2.2 Total flavonoid contents

Flavonoids are the most important group of polyphenols due to their potential biological and pharmacological activities, including antioxidant, anti-viral, anti-inflammatory and anti-cancer effects (Ferreira et al., 2016). The total free flavonoid content (TFC) of these pigmented rice grains ranged from 1.16 to 4.99 mg rutin equivalent/g DW . The results shown that the free TFC of Mali dang (4.57 mg RE/g dw), Riceberry (3.65 mg RE/g dw), Hom Nil (2.80 mg RE/g dw) and Khao Dawk Mali (1.50 mg RE/g dw) brown rice were significantly higher than those of

polished rice. When compared between the unpolished and polished samples, regardless the thermal treatment, all polished samples had significantly ($p<0.05$) lower contents of soluble and bound TFC compared to unpolished rice (Table 4.1), with the highest decrease being 57% in Mali Dang (red) rice.

When compared between heat treatment, all pigmented rice varieties show a significant increase the content of total flavonoids after FIR treatment in both unpolished and polished samples. The bound TFC of FIR dried samples had the highest (2.12 - 2.19 mg RE/g dry weight) TFC while, HA dried samples showed the lowest (1.12 – 1.61 mg RE/g dry weight) . Similarly, the soluble TFC of pigmented unpolished rice grains, as treated by FIR and HA drying, was significantly higher than those of polished rice ($p<0.05$). The bound TFC of FIR-dried samples had the highest content, while the lowest content was found in HA-dried samples (Fig. 1). According to Kaisoon et al. (2010) found that the soluble extracts of edible flowers had higher the content of total flavonoid than bound extracts. Whereas, Adom and Liu (2002) presented that free fraction of normal rice, wheat, oat and corn contained a lesser TFC than their bound counterparts. Our results found that the flavonoid content in pigmented rice occurred mostly in the free form rather than bound form. The pigmented brown and polished rice grains as radiated by FIR had the highest free TFC while, hot air dried pigmented rice grains had the lowest free TFC. The free TFC of Hom Nil, Mali Dang and Riceberry pigmented rice cultivars were increased up to 15%, 9.19 and 6% in FIR irradiated samples, respectively, compared to unprocessed. However, the amount of free TFC was significantly different among the various pigmented rice grains ($p < 0.05$) (Table 1). FIR may be able to break the covalent bond and released low-molecular-weight of phenolic compounds such as phenolic acids and flavonoids from polymers (Niwa et al., 1988; Lee et al., 2006). FIR dried rice may increase TFC that are similar to TPC. The antioxidant compounds, namely phenolics, flavonoids, tannin, ascorbate including anthocyanins, were released and liberated as low-molecular-weight antioxidants in plants by the application of FIR (Zhang, Lv, Pan & Fan, 2012; Lee et al., 2006).

4.2.3 Total anthocyanin contents

The level of the total anthocyanin content (TAC) of the studied samples varied significantly, from 0.07 to 0.88 mg /g dw (Fig 4.2). Black or purple Thai and Chinese rice showed higher TAC (109-256 mg/100 g) than red rice varieties (0.3-1.4mg /100g) in the previous study (Sompong, Siebenhandl-Ehn, Linsberger-Martin & Berghofer, 2011). This was similar to the results of this study, where purple rice's showed the highest TAC, followed by red rice, with non-pigmented rice (Hom Mali) having no detectable anthocyanins TAC, demonstrating that anthocyanins contribute to the pigmentation of rice's.

The highest value of TAC was observed in FIR dried samples, followed by unprocessed and HA dried samples of all rice varieties. Rice dried by FIR heating presented the highest increasing in TAC approximately 35% (Hom Nil), 25% (Mali Dang) and 23% (Riceberry), respectively. While, the pigmented polished rice of all varieties were not detected. Similar result was also observed by Zhou et al., (2004), with the anthocyanin content of the rice bran amount for 85%. The results demonstrated that the content of anthocyanin in pigmented rice grains are mainly linked with the external layers of the rice grains. The pigmented rice is a rich source of anthocynins as the major antioxidant activities. FIR may increase the TAC that similar to phenomenal in TFC and TPC. The antioxidants compounds namely phenolics, flavonoids, tannin, ascorbate including anthocyanin were released and liberated low molecule weighted antioxidants in plants by FIR application (Niwa and Miyachi, 1986; Lee et al., 2006).

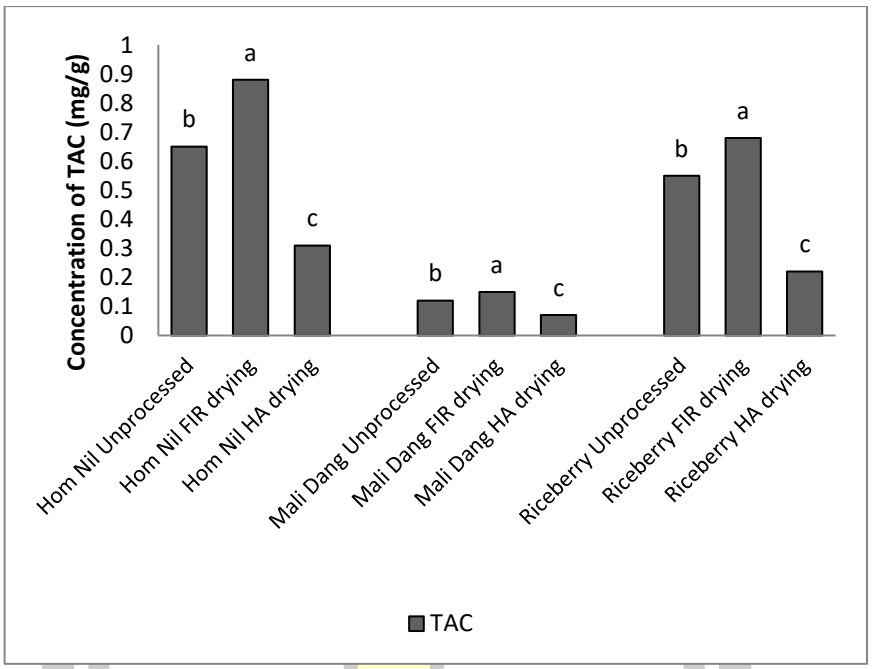


Figure 4.17 Effect of FIR and HA treatments on total anthocyanin contents of brown rice pigmented Thai rice while polished rice was not detected TAC. Each value is the mean ± the standard deviation (n = 3). Means with different letters in the same rice variety as affected by different drying methods were significantly different at the level $p < 0.05$.

4.2.4 Change in antioxidant activity

In this study, the antioxidant activities of soluble and bound phenolic fractions from the unpolished and polished pigmented rice grains, as affected by different treatments, were determined by DPPH radical scavenging activity and FRAP assays . In a manner similar to changes in the concentrations of TPC, a significant decrease ($p < 0.05$) in antioxidant activities of the soluble phenolic fraction were observed for the polished samples when compared with unpolished samples regardless the thermal treatment. This indicated that the difference in antioxidant activities of rice grains depending on pericarp color. In all treatments of pigmented rice, the percent inhibition of DPPH ranged from 23 to 87%.

After dried rice, the highest antioxidant activity, as determined by DPPH radical scavenging activity, was observed for unheated unpolished and polished samples with FIR, whereas the lowest was found in HA dried grains of all rice varieties when compared to unheated samples. Similarly, we found that the

concentration of antioxidant activity as determined by FRAP was increased by the FIR treatment in all varieties of rice grains. In the case of HA drying, the antioxidant activities were significantly decreased when compared with unprocessed samples of all rice varieties. The results indicated FIR radiation increased antioxidant activities (DPPH and FRAP). Similarly, DPPH radical scavenging capability of bound phenolic extracts of brown pigmented rice samples ranged from 11.5% in HA dried Hom Nil to 32.97% in FIR dried Mali Dang while, %inhibition of polished pigmented rice samples ranged from 11.29 % in HA dried Hom Nil to 16.97% in FIR dried Riceberry. The results indicated FIR radiation increased antioxidant activities (DPPH and FRAP). Evaluation of antioxidant capacity should be performed by more than one method because each method has advantages and disadvantages. The mechanism of action for each assay is different depending on the chemical properties and functionality of targeted compounds. For instance, the DPPH radical scavenging, and FRAP assays were used to evaluate the antioxidant capacities of pigmented rice samples. DPPH is a stable free-radical compound widely used to test the free-radical scavenging ability of various samples (Kubola & Siriamornpun, 2008). The FRAP assay measures the reducing potential of an antioxidant reacting with a ferric tripyridyltriazine (Fe^{3+}–TPTZ) complex to produce a coloured ferrous tripyridyltriazine (Benzie & Strain, 1996). Generally, the reducing properties are associated with the presence of compounds which exert their action by breaking the free-radical chain by donating a hydrogen atom. The reduction of the Fe^{3+}–TPTZ complex to a blue-coloured Fe^{2+}–TPTZ occurs at low pH (Benzie & Strain, 1996). Similar results were found for the antioxidant capacities which increased after FIR treatment of rice husk (35%) and rice bran (20%) (Wanyo, Meeso & Siriamornpun, 2014), tomato (21%) and papaya (21%) (Siriamornpun, Ratseewo, Kaewseejan & Meeso, 2015). In addition, Adak, Heybeli and Ertekin (2017) reported the increase by 8-18 times of antioxidant activity was found in infrared-dried strawberry, using similar conditions of air velocity and infrared power. Many antioxidants are naturally bound in covalent form to insoluble polymers. FIR drying could release and activate low-molecular-weight natural antioxidants such as phenolic acids, flavonoids, carotene and flavoproteins in samples if this bonding is weak (Lee et al., 2006).

Tables 4.5 Effect of FIR and HA treatments on total flavonoid and total anthocyanin contents, and antioxidant capacity of pigmented Thai rice.

Samples	Total flavonoid content (mg RE/g dw)				DPPH (% inhibition)				FRAP (µmol FeSO4/g DW)			
	Soluble		Bound		Soluble		Bound		Soluble		Bound	
	Brown	Polished	Brown	Polished	Brown	Polished	Brown	Polished	Brown	Polished	Brown	Polished
Hom Nil												
Unprocessed	2.80±0.03^{b}	1.71±0.01^{b}	1.70±0.04^{b}	0.21±0.01^{b}	62.70±0.41^{b}	34.70±0.38^{b}	27.33±0.42^{b}	14.50±0.38^{b}	37.59±0.27^{b}	31.07±0.35^{b}	51.59±0.99^{b}	35.07±0.35^{b}
FIR drying	3.22±0.03^{a}	1.93±0.04^{a}	2.12±0.04^{a}	0.35±0.04^{a}	72.93±0.52^{a}	38.34±0.57^{a}	32.22±0.32^{a}	16.22±0.57^{a}	53.19±1.94^{a}	33.41±0.84^{a}	62.22±0.87^{a}	38.41±0.84^{a}
HA drying	2.72±0.01^{c}	1.16±0.00^{c}	1.15±0.04^{c}	0.12±0.02^{c}	42.75±0.78^{c}	23.23±1.07^{c}	12.15±0.31^{c}	11.29±1.07^{c}	29.78±0.29^{c}	28.64±1.40^{c}	39.64±0.71^{c}	31.64±0.56^{c}
Mali Dang												
Unprocessed	4.57±0.04^{b}	2.03±0.01^{b}	1.56±0.05^{b}	0.13±0.03^{b}	79.17±0.34^{b}	45.15±0.14^{b}	25.17±1.11^{b}	13.18±0.21^{b}	48.25±0.27^{b}	43.09±1.32^{b}	55.25±0.97^{b}	50.09±0.74^{b}
FIR drying	4.99±0.05^{a}	2.17±0.04^{a}	2.17±0.03^{a}	0.35±0.04^{a}	86.97±0.32^{a}	49.80±0.78^{a}	32.97±1.12^{a}	15.32±0.32^{a}	56.16±0.98^{a}	50.31±0.53^{a}	60.43±0.99^{a}	55.31±0.65^{a}
HA drying	3.61±0.00^{c}	1.49±0.01^{c}	1.61±0.03^{c}	0.15±0.03^{c}	57.49±1.41^{c}	29.17±0.77^{c}	12.49±1.14^{c}	11.51±0.35^{c}	40.71±0.66^{c}	38.39±0.58^{c}	43.71±0.87^{c}	38.39±0.58^{c}
Riceberry												
Unprocessed	3.65±0.06^{b}	1.94±0.02^{b}	1.55±0.04^{b}	0.24±0.03^{b}	69.67±0.48^{b}	41.79±0.08^{b}	29.67±0.55^{b}	14.79±0.33^{b}	42.66±0.37^{b}	34.32±1.16^{b}	52.66±0.37^{b}	38.32±1.16^{b}
FIR drying	3.89±0.07^{a}	2.07±0.01^{a}	2.19±0.04^{a}	0.37±0.02^{a}	80.46±0.29^{a}	47.97±0.90^{a}	30.46±0.53^{a}	16.97±0.53^{a}	53.86±0.17^{a}	41.54±0.73^{a}	62.16±0.60^{a}	44.54±0.99^{a}
HA drying	2.71±0.01^{c}	1.44±0.04^{c}	1.21±0.06^{c}	0.14±0.03^{c}	42.20±0.87^{c}	27.34±0.99^{c}	12.20±0.62^{c}	11.34±0.61^{c}	35.04±0.60^{c}	33.25±0.08^{b}	44.04±0.54^{c}	35.88±0.52^{b}
KDML 105												
Unprocessed	1.50±0.02^{a}	1.28±0.02^{a}	0.40±0.02^{a}	0.05±0.01^{a}	19.40±0.33^{b}	12.45±0.39^{b}	8.20±0.33^{b}	6.20±0.33^{b}	21.38±0.52^{b}	11.59±0.37^{b}	29.38±0.52^{b}	14.57±0.08^{b}
FIR drying	1.15±0.03^{c}	0.94±0.01^{c}	0.65±0.02^{c}	0.8±0.01^{c}	25.29±0.08^{a}	15.52±0.59^{a}	12.39±0.08^{a}	7.39±0.08^{a}	25.52±0.37^{a}	12.09±0.18^{a}	35.52±0.37^{a}	17.05±0.09^{a}
HA drying	1.28±0.02^{b}	0.89±0.01^{b}	0.38±0.02^{b}	0.03±0.01^{b}	11.96±1.88^{c}	10.26±1.00^{c}	5.74±0.08^{c}	5.41±0.08^{c}	15.50±0.34^{c}	10.17±0.61^{c}	19.50±0.34^{c}	13.44±0.09^{c}

Values are expressed as mean ± standard deviation (n = 3). Means with different letters in the same column were significantly different at the level $p < 0.05$. ND, not detected

4.2.5 Changes in the content and composition of soluble and bound phenolic acids

Mostly, phenolic acids are active antioxidant derivatives in plants and exist in pericarp rice grains (Walter et al., 2013). These compounds are mostly found in the outer layer of plants such as the hull, shell and peel and they can be protected the inner components (Bors et al., 2001).The contents of phenolic acids are associated to different cell-wall components, such as proteins and arabinoxylans (Hartley et al., 1990). Identifications of phenolic compounds in rice bran and rice hull were reported by Germano et al., (2006) who found that the phenolic acids, glycosides, esters and bound complexes were often occurred in plants from hydroxylated derivatives of hydrocinnamic (HCA) and hydrobenzoic (HBA). In the present study, change in the soluble and bound phenolic acids content and composition of all samples is presented in Table 4.2 and 4.3. For the soluble phenolic acids, all the nine phenolic acids found in all samples were caffeic, protocatechuic, gallic, vanillic, *p*-coumaric, syringic, chlorogenic, ferulic and sinapic acids. When compared between the unpolished and polished samples, regardless the thermal treatment, polished samples had significantly ($p<0.05$) lower contents of soluble and bound phenolic acids compared to unpolished samples in all varieties. The most abundant bound phenolic acids, ferulic, protocatechuic, vanillic and *p*-coumaric acids, were found in all varieties, especially in unpolished samples (Table 4.2 and 4.3). In this study, ferulic acid is a major soluble and bound phenolic acid. Our result was in agreement with the previous studies reported that protocatechuic acid is an abundant phenolic acid found in purple rice (Hiemori, Koh & Mitchell, 2009), while ferulic and *p*-coumaric acids are major phenolic acids in brown (unpolished) and white (polished) rice (Zhou, Robards, Helliwell & Blanchard, 2004). When compared to soluble phenolic acids, bound phenolic values were three-fold greater for ferulic acid in all unpolished samples and two-fold greater in all polished samples (Table 4.2 and 4.3). Polishing may cause the loss of soluble and bound phenolics in all polished samples. Mostly, phenolic acids are active antioxidant derivatives in plants and exist in the pericarp of rice grains (Walter et al., 2013). These compounds are mostly found in the outer layer of plants such as the hull, shell and peel where they may protect the inner components (Bors, Michel & Stettmaier, 2001). The contents of phenolic acids are associated with

various cell-wall components, such as proteins and arabinoxylans (Germano et al., 2006). Bound phenolic acids in plants cell walls, specifically ferulic and *p*-coumaric acids, are known to be ester-linked to various cell-wall polymers, namely, polysaccharides and the lignin component. The increase of bound phenolic acid content may result from esterification of pectins and arabinoxylans or cross-linked to cell wall polysaccharides in the form of dimers, such as dehydroferulates and truxillic acid in the aleurone and pericarp layers (Shibuya, 1984)

For comparison in two drying treatments, the increase and decrease in phenolic acids in unpolished and polished samples depended on the drying methods (Table 4.2 and 4.3). However, the alteration trends of individual soluble and bound phenolic acids of both samples (polished and unpolished) were similar after drying treatments. FIR was the only treatment that caused an increase of most phenolic acids, while caffeic acid was unchanged when compared to all the unheated samples. Protocatechuic, chlorogenic, syringic, vanillic and *p*-coumaric acids also increased after HA treated of unpolished and polished in all varieties. Gallic, ferulic and synapic acids were significantly ($p<0.05$) increased by FIR in all samples. Similar results were observed in that chlorogenic and *p*-coumaric acids of tomato (9.8 and 1.2 times) and papaya (0.5 and 1.8 times) were increased by FIR treatment (Siriamornpun, Ratseewo, Kaewseejan & Meeso, 2015).

The mechanism of changes for phenolic acid can be proposed as being similar to the phenomena for TPC, in that FIR may be able to break covalent bonds and release more bound or small polyphenol molecules such as phenolic acids from polymers (Wanyo, Meeso & Siriamornpun, 2011; Lee et al., 2006; Zhang, Lv, Pan & Fan, 2012), resulting in an enhancement of molecules that are more active, consequently providing greater antioxidant activity. The degradation of antioxidant compounds could be due to the actions of oxidative and hydrolytic enzymes, such as polyphenol oxidase (PPO), released from the cell wall of plants by thermal processes (Lv et al., 2017). On the other hand, thermal processing can increase the extraction of phenolic antioxidants by breaking cell walls, thus releasing more previously bound and small molecules (Haard & Chism, 1996) .

Tables 4.6 Effect of FIR and HA treatments on soluble phenolic acid contents (mg/g) of pigmented Thai rice.

Samples	Gallic acid		Protocatechuic acid		Vanillic acid		Chlorogenic acid		Syringic acid	
	Brown	Polished	Brown	Polished	Brown	Polished	Brown	Polished	Brown	Polished
Hom Nil										
Unprocessed	3.04±0.58^{b}	1.44±0.20^{b}	9.56±0.04^{b}	7.31±0.17^{b}	2.03±0.05^{b}	0.74±0.02^{b}	1.15±0.05^{c}	0.42±0.01^{c}	1.57±0.18^{c}	1.11±0.11^{b}
FIR drying	5.32±0.03^{a}	2.12±0.11^{a}	13.34±0.28^{a}	8.56±0.18^{a}	3.44±0.18^{a}	1.07±0.11^{a}	1.52±0.11^{b}	0.95±0.06^{b}	2.60±0.23^{b}	1.41±0.09^{a}
HA drying	3.04±0.05^{b}	1.40±0.07^{b}	9.59±0.31^{b}	8.60±0.22^{a}	2.06±0.06^{b}	0.71±0.04^{b}	1.92±0.01^{a}	1.12±0.10^{a}	3.12±0.17^{a}	1.40±0.09^{a}
Mali Dang										
Unprocessed	3.35±0.85^{b}	1.49±0.01^{b}	9.25±0.05^{b}	6.38±0.54^{b}	2.17±0.01^{b}	0.86±0.06^{c}	1.25±0.19^{c}	0.52±0.04^{b}	1.53±0.09^{c}	1.17±0.16^{b}
FIR drying	5.65±0.17^{a}	2.56±0.02^{a}	13.65±0.21^{a}	7.97±0.15^{a}	3.64±0.29^{a}	1.17±0.16^{b}	1.45±0.08^{b}	1.05±0.10^{ab}	2.49±0.04^{b}	1.54±0.19^{a}
HA drying	3.32±0.08^{b}	1.54±0.04^{b}	9.26±0.11^{b}	8.03±0.21^{a}	2.18±0.03^{b}	2.18±0.03^{a}	1.94±0.03^{a}	1.25±0.37^{a}	3.19±0.10^{a}	1.44±0.10^{a}
Riceberry										
Unprocessed	3.23±0.80^{b}	1.62±0.10^{b}	9.41±0.03^{b}	6.4±0.32^{b}	2.18±0.06^{b}	0.88±0.11^{b}	1.31±0.02^{b}	0.54±0.03^{b}	1.57±0.21^{c}	1.19±0.15^{b}
FIR drying	5.59±0.20^{a}	2.49±0.19^{a}	13.95±0.05^{a}	8.03±0.23^{a}	3.64±0.32^{a}	1.17±0.22^{a}	1.48±0.29^{b}	0.84±0.27^{a}	2.57±0.12^{b}	1.49±0.08^{a}
HA drying	3.27±0.14^{b}	1.49±0.18^{b}	9.42±0.18^{b}	8.03±0.22^{a}	2.19±0.08^{b}	0.88±0.10^{b}	1.88±0.07^{a}	1.08±0.07^{a}	3.04±0.06^{a}	1.49±0.21^{a}
KDML 105										
Unprocessed	3.11±0.10^{b}	1.53±0.10^{b}	9.38±0.03^{b}	6.68±0.21^{b}	2.47±0.01^{b}	1.34±0.21^{b}	1.08±0.01^{c}	0.55±0.04^{b}	1.46±0.02^{c}	1.03±0.06^{b}
FIR drying	5.38±0.05^{a}	5.38±0.05^{a}	12.55±0.23^{a}	7.71±0.23^{a}	4.41±0.16^{a}	2.56±0.11^{a}	1.49±0.08^{b}	0.82±0.22^{a}	2.43±0.07^{b}	1.30±0.01^{a}
HA drying	3.17±0.11^{b}	1.36±0.10^{c}	9.45±0.81^{b}	7.74±0.07^{a}	2.47±0.09^{b}	1.37±0.22^{b}	1.85±0.41^{a}	0.99±0.08^{a}	2.99±0.02^{a}	1.27±0.25^{a}

Values are expressed as mean ± standard deviation (n = 3). Means with different letters in the same column were significantly different at the level $p < 0.05$.

Tables 4.7 Effect of FIR and HA treatments on soluble phenolic acid contents (mg/g) of pigmented Thai rice (continue).

Samples	Caffeic acid		*p*-Coumaric acid		Ferulic acid		Sinapic acid	
	Brown	Polished	Brown	Polished	Brown	Polished	Brown	Polished
Hom Nil								
Unprocessed	1.52±0.25^{a}	1.10±0.07^{a}	1.23±0.02^{b}	0.81±0.03^{b}	10.26±0.26^{b}	6.59±0.34^{b}	2.33±0.01^{b}	1.22±0.10^{b}
FIR drying	1.49±0.21^{a}	1.07±0.03^{a}	1.28±0.04^{a}	0.91±0.03^{a}	13.06±0.15^{a}	7.59±0.34^{a}	2.66±0.10^{a}	1.39±0.10^{a}
HA drying	1.49±0.21^{a}	1.11±0.07^{a}	1.31±0.04^{a}	0.94±0.07^{a}	10.42±0.17^{b}	6.85±0.12^{b}	2.21±0.17^{b}	1.22±0.01^{b}
Mali Dang								
Unprocessed	1.58±0.04^{a}	1.17±0.14^{a}	1.13±0.07^{b}	0.81±0.02^{b}	9.75±0.22^{b}	6.57±0.28^{c}	2.40±0.04^{b}	1.22±0.18^{b}
FIR drying	1.60±0.06^{a}	1.14±0.17^{a}	1.33±0.10^{a}	0.91±0.07^{a}	12.75±0.22^{a}	7.57±0.28^{a}	2.65±0.21^{a}	1.35±0.04^{a}
HA drying	1.64±0.09^{a}	1.17±0.14^{a}	1.36±0.10^{a}	0.95±0.03^{a}	10.32±0.72^{b}	6.91±0.04^{b}	2.37±0.03^{b}	1.23±0.16^{b}
Riceberry								
Unprocessed	1.50±0.16^{a}	1.08±0.04^{a}	1.19±0.05^{b}	0.77±0.08^{b}	9.83±0.28^{b}	6.45±0.11^{c}	2.42±0.04^{b}	1.22±0.07^{b}
FIR drying	1.50±0.16^{a}	1.11±0.02^{a}	1.30±0.03^{a}	0.91±0.05^{a}	12.66±0.28^{a}	7.45±0.11^{a}	2.59±0.11^{a}	1.37±0.06^{a}
HA drying	1.53±0.18^{a}	1.07±0.02^{a}	1.33±0.02^{a}	0.97±0.04^{a}	10.38±0.18^{b}	6.82±0.13^{b}	2.45±0.04^{ab}	1.22±0.06^{b}
KDML 105								
Unprocessed	1.55±0.03^{a}	1.08±0.06^{b}	1.10±0.02^{b}	0.75±0.16^{a}	8.03±0.01^{b}	6.03±0.06^{c}	2.03±0.02^{b}	1.15±0.06^{b}
FIR drying	1.58±0.03^{a}	1.08±0.05^{b}	1.23±0.10^{a}	1.06±0.21^{a}	11.03±0.01^{a}	7.36±0.13^{a}	2.58±0.05^{a}	1.56±0.09^{a}
HA drying	1.61±0.06^{a}	1.09±0.05^{b}	1.25±0.10^{a}	1.06±0.21^{a}	8.36±0.56^{b}	6.63±0.23^{b}	1.80±0.44^{b}	1.11±0.01^{b}

Values are expressed as mean ± standard deviation (n = 3). Means with different letters in the same column were significantly different at the level $p < 0.05$.

Tables 4.8 Effect of FIR and HA treatments on bound phenolic acid contents (mg/g) of pigmented Thai rice.

Samples	Gallic acid		Protocatechuic acid		Vanillic acid		Chlorogenic acid		Syringic acid	
	Brown	Polished	Brown	Polished	Brown	Polished	Brown	Polished	Brown	Polished
Hom Nil										
Unprocessed	2.76±0.11^{b}	0.72±0.03^{b}	5.62±0.05^{b}	4.30±0.04^{b}	6.09±0.03^{b}	0.89±0.03^{b}	0.51±0.06^{c}	0.06±0.02^{c}	0.39±0.02^{c}	0.16±0.01^{b}
FIR drying	4.83±0.04^{a}	1.06±0.04^{a}	7.85±0.11^{a}	5.04±0.07^{a}	10.32±0.05^{a}	1.28±0.05^{a}	0.64±0.06^{b}	0.14±0.02^{b}	0.65±0.02^{b}	0.20±0.01^{a}
HA drying	2.76±0.06^{b}	0.70±0.03^{b}	5.63±0.01^{b}	5.06±0.02^{a}	6.18±0.03^{b}	0.85±0.03^{b}	0.42±0.03^{a}	0.16±0.04^{a}	0.78±0.02^{a}	0.20±0.03^{a}
Mali Dang										
Unprocessed	3.04±0.12^{b}	0.75±0.02^{b}	5.46±0.04^{b}	3.75±0.02^{b}	6.51±0.01^{b}	1.03±0.02^{c}	0.48±0.02^{c}	0.07±0.03^{c}	0.38±0.03^{c}	0.17±0.02^{b}
FIR drying	5.13±0.06^{a}	1.28±0.03^{a}	8.03±0.08^{a}	4.69±0.09^{a}	10.92±0.07^{a}	1.40±0.02^{b}	0.65±0.05^{b}	0.15±0.03^{b}	0.62±0.03^{b}	0.22±0.03^{a}
HA drying	3.03±0.13^{b}	0.77±0.03^{b}	5.44±0.03^{b}	4.72±0.04^{a}	6.54±0.02^{b}	2.62±0.01^{a}	1.94±0.04^{a}	0.18±0.02^{a}	0.80±0.02^{a}	0.21±0.03^{a}
Riceberry										
Unprocessed	2.93±0.21^{b}	0.81±0.05^{b}	5.47±0.04^{b}	3.76±0.02^{b}	6.54±0.04^{b}	1.06±0.01^{b}	0.44±0.03^{b}	0.08±0.01^{b}	0.39±0.02^{c}	0.17±0.02^{b}
FIR drying	5.08±0.13^{a}	1.25±0.01^{a}	8.21±0.04^{a}	4.72±0.04^{a}	10.92±0.09^{a}	1.40±0.01^{a}	0.49±0.03^{b}	0.12±0.01^{a}	0.64±0.02^{b}	0.21±0.04^{a}
HA drying	2.97±0.11^{b}	0.75±0.03^{b}	5.54±0.05^{b}	4.71±0.02^{a}	6.57±0.03^{b}	1.04±02^{b}	0.63±0.02^{a}	0.15±0.03^{a}	0.76±0.03^{a}	0.21±03^{a}
KDML 105										
Unprocessed	2.01±0.10b	0.53±0.10b	5.38±0.03b	3.68±0.21b	5.47±0.01b	0.54±0.21b	0.20±0.01c	0.55±0.04b	0.36±0.02c	1.03±0.06b
FIR drying	2.38±0.05a	1.08±0.05a	7.55±0.23a	4.71±0.23a	8.41±0.16a	0.86±0.11a	0.22±0.03b	0.82±0.22a	0.33±0.07b	1.30±0.01a
HA drying	2.07±0.11b	0.36±0.10c	5.45±0.81b	4.74±0.07a	5.47±0.09b	0.57±0.22b	0.30±0.01a	0.99±0.08a	0.49±0.02a	1.27±0.25a

Values are expressed as mean ± standard deviation (n = 3). Means with different letters in the same column were significantly different at the level $p < 0.05$

Tables 4.9 Effect of FIR and HA treatments on bound phenolic acid contents (mg/g) of pigmented Thai rice (continue).

Samples	Caffeic acid		*p*-Coumaric acid		Ferulic acid		Sinapic acid	
	Brown	Polished	Brown	Polished	Brown	Polished	Brown	Polished
Hom Nil								
Unprocessed	1.27±0.03^{a}	0.28±0.01^{a}	6.15±0.02^{b}	2.43±0.03^{b}	30.78±0.11^{b}	13.18±0.05^{b}	2.80±0.03^{b}	0.31±0.01^{b}
FIR drying	1.24±0.02^{a}	0.27±0.01^{a}	6.50±0.03^{a}	2.73±0.03^{a}	39.18±0.15^{a}	15.18±0.07^{a}	3.19±0.00^{a}	0.35±0.01^{a}
HA drying	1.24±0.02^{a}	0.28±0.01^{a}	6.55±0.03^{a}	2.82±0.07^{a}	31.06±0.11^{b}	13.20±0.06^{b}	2.65±0.05^{b}	0.31±0.01^{b}
Mali Dang								
Unprocessed	1.32±0.02^{a}	0.29±001^{a}	5.65±0.03^{b}	2.41±0.02^{b}	29.25±0.09^{b}	13.14±0.06^{c}	2.88±0.04^{b}	0.31±0.02^{b}
FIR drying	1.33±0.03^{a}	0.29±0.01^{a}	6.75±0.04^{a}	2.73±0.07^{a}	38.25±0.22^{a}	15.14±0.09^{a}	3.18±0.21^{a}	0.34±0.01^{a}
HA drying	1.37±0.03^{a}	0.29±0.01^{a}	6.80±0.03^{a}	2.85±0.03^{a}	30.16±0.12^{b}	13.12±0.05^{b}	2.84±0.03^{b}	0.31±0.02^{b}
Riceberry								
Unprocessed	1.25±0.03^{a}	0.27±0.03^{a}	5.95±0.03^{b}	2.31±0.02^{b}	29.49±0.28^{b}	12.90±0.09^{c}	2.90±0.04^{b}	0.31±0.02^{b}
FIR drying	1.25±003^{a}	0.28±0.03^{a}	6.50±0.03^{a}	2.77±0.05^{a}	37.98±08^{a}	14.90±0.08^{a}	3.11±0.01^{a}	0.34±0.03^{a}
HA drying	1.28±0.02^{a}	0.27±0.03^{a}	6.65±0.03^{a}	2.87±0.06^{a}	31.14±0.11^{b}	13.64±0.04^{b}	2.94±0.02^{b}	0.31±0.02^{b}
KDML 105								
Unprocessed	1.05±0.03^{a}	0.13±0.03^{a}	3.15±0.03^{b}	1.31±0.02^{b}	11.29±0.28^{b}	8.70±0.09^{c}	2.33±0.12^{b}	0.08±0.03^{b}
FIR drying	1.05±003^{a}	0.15±0.03^{a}	3.50±0.03^{a}	1.55±0.05^{a}	14.98±0.18^{a}	9.90±0.08^{a}	2.88±0.12^{a}	0.12±0.02^{a}
HA drying	1.08±0.02^{a}	0.14±0.03^{a}	3.55±0.03^{a}	1.46±0.06^{a}	11.14±0.11^{b}	8.64±0.04^{b}	2.30±0.22^{b}	0.09±0.01^{b}

Values are expressed as mean ± standard deviation (n = 3). Means with different letters in the same column were significantly different at the level $p < 0.05$

4.2.6 Changes in the content and composition of soluble and bound flavonoids

Flavonoids are one of the most important polyphenolic compounds, providing human health benefits due to their potent antioxidant effects (Siriamornpun, Ratseewo, Kaewseejan & Meeso, 2015). In our study, five flavonoids, rutin, myricetin, luteolin, quercetine, apigenin and kaempferol were identified and quantified in pigmented rice varieties as affected by FIR and HA using RP-HPLC. The distribution of free and bound flavonoids is presented in Table 4.4 and 4.5. In the case of soluble flavonoids component, the results showed that brown pigmented rice of all varieties studied contained all five soluble flavonoids identified with myricetin and quercetin being predominant, whereas polished rice contained only a trace amount of kaempferol (0.40-0.77 µg/100g). Unprocessed pigmented brown rice grains were rich in Myricetin, with amounts ranging from 19.75-22.29 µg/100g. The greatest value of quercetin was found in FIR dried samples; for examples, the content of quercetin of Mali Dang was 28.16 µg/100g, Riceberry was 23.83 µg/100g and Hom Nil was 22.12 µg/100g. The individual of soluble flavonoids were not detected in KDML 105 except keamferol. The result indicated that the keamferol is the main flavonoids in KDML 105. The result showed that polished samples had significantly ($p<0.05$) lower contents of soluble and bound of flavonoids when compared with unpolished samples regardless the thermal treatment. For the bound flavonoids, rutin, myricetin, quercetin and apigenin were found in all unpolished rice samples while, only rutin of bound flavonoid extracts was detected in polished rice varieties. The content of myricetin had the highest value of bound flavonoids in all pigmented rice varieties although it decreased when compared with soluble flavonoid extracts. Unexpectedly, kaempferol was not detected in all bound extracted samples. The contents of myricetin, quercetin and apigenin from bound flavonoids extracts were less than these in soluble flavonoids. On the other hand, the value of rutin in bound extracted rice was two-fold higher than rutin in soluble extracted pigmented rice. The results suggested that flavonoids should be classified as soluble and bound flavonoids, as well as for phenolic acids. In the case of soluble flavonoid compositions, the results showed that unpolished pigmented rice of all varieties studied contained all five soluble flavonoids identified, with myricetin and quercetin being predominant, whereas polished rice in

all varieties contained only trace amounts of kaempferol (0.40-0.77 µg/100g). Unheated unpolished pigmented rice grains were rich in myricetin. Therefore, the flavonoids forms were removed from the bran layer including pericarp, aleurone and embryo of unpolished rice during polishing process.

For comparison in two drying treatments, the greatest values of quercetin were found in FIR-dried samples of three rice varieties, ranging from 22 to 28 µg/100g. The application of FIR to all pigmented rice varieties caused increases in quercetin and apigenin contents, while other flavonoids identified (rutin, myricetin and kaempferol) decreased significantly ($p<0.05$) when compared to unheated samples. Quercetin and apigenin contents increased significantly up to two- and three-fold, as affected by FIR, respectively. HA drying could increase quercetin content slightly in all varieties and provide the highest content of apigenin in all rice varieties. The effect of FIR drying on bound flavonoids had results similar to those for soluble flavonoids. The flavonoids from bound fractions namely, quercetin and apigenin, increased in FIR-dried pigmented rice, while myricetin decreased with FIR drying. This result is in agreement with the finding that FIR treatment increased the quercetin (4.7 times) production in buckwheat sprouts (Ghimeray et al., 2014). FIR increases quercetin and apigenin in tomato (20.2 and 3.18 times) and myricetin in papaya (1.2 times) (Siriamornpun, Ratseewo, Kaewseejan & Meeso, 2015). Rutin has a chemical structure similar to that of quercetin, which has an extra glycone flavonoid (Vetrova, et al., 2019)(Table 4.4 and 4.5). According to these results, the increase in quercetin and apigenin accumulation may result from the breakage of the glycoside bonds of rutin by FIR. In addition, another possible reason may be the transformation of high-molecular-weight compounds to low-molecular-weight compounds resulting from the breakage of covalent bonds of polymerized polyphenols (Lee et al., 2006; Zhang, Lv, Pan & Fan, 2012).

Tables 4.10 Effect of FIR and HA treatments on the levels of free flavonoids (µg/100g) of pigmented Thai rice.

Samples	Rutin		Myricetin		Quercetin		Apigenin		Kaempferol	
	Brown	Polished	Brown	Polished	Brown	Polished	Brown	Polished	Brown	Polished
Hom Nil										
Unprocessed	5.12±0.03^{a}	ND	22.29±0.07^{a}	ND	14.14±0.06^{c}	ND	3.41±0.06^{c}	ND	5.45±0.04^{a}	0.71±0.02^{a}
FIR drying	4.42±0.02^{b}	ND	18.65±0.08^{b}	ND	22.12±0.08^{a}	ND	7.52±0.07^{b}	ND	3.70±0.03^{b}	0.58±0.03^{b}
HA drying	3.11±0.04^{c}	ND	16.69±0.10^{c}	ND	15.79±0.06^{b}	ND	11.54±0.04^{a}	ND	3.12±0.04^{c}	0.40±0.02^{c}
Mali Dang										
Unprocessed	5.43±0.05^{a}	ND	19.75±0.09^{b}	ND	14.11±0.04^{c}	ND	3.25±0.19^{c}	ND	5.50±0.03^{a}	0.77±0.06^{a}
FIR drying	4.68±0.04^{b}	ND	16.78±0.08^{a}	ND	28.16±0.09^{a}	ND	9.45±0.08^{b}	ND	3.76±0.04^{b}	0.63±0.04^{b}
HA drying	3.36±0.03^{c}	ND	15.63±0.08^{b}	ND	17.04±0.03^{b}	ND	13.27±0.03^{a}	ND	3.19±0.03^{c}	0.54±0.03^{c}
Riceberry										
Unprocessed	5.23±0.09^{a}	ND	19.77±0.04^{a}	ND	13.18±0.05^{c}	ND	3.31±0.02^{c}	ND	5.47±0.05^{a}	0.73±0.04^{a}
FIR drying	4.55±0.04^{b}	ND	17.02±0.07^{b}	ND	23.83±0.07^{a}	ND	9.48±0.29^{b}	ND	3.71±0.04^{b}	0.59±0.04^{b}
HA drying	3.31±0.06^{c}	ND	16.54±0.08^{c}	ND	16.19±0.08^{b}	ND	12.88±0.07^{a}	ND	3.15±0.06^{c}	0.51±0.03^{c}
KDML 105										
Unprocessed	ND	ND	ND	ND	ND	ND	ND	ND	1.32±0.05^{a}	0.20±0.01^{a}
FIR drying	ND	ND	ND	ND	ND	ND	ND	ND	0.97±0.04^{b}	0.12±0.01^{b}
HA drying	ND	ND	ND	ND	ND	ND	ND	ND	0.70±0.06^{c}	0.07±0.01^{c}

Values are expressed as mean ± standard deviation (n = 3). Means with different letters in the same column were significantly different at the level $p < 0.05$. ND, not detected

Tables 4.11 Effect of FIR and HA treatments on the levels of bound flavonoids (µg/100g) of pigmented Thai rice.

Samples	Rutin		Myricetin		Quercetin		Apigenin		Kaempferol	
	Brown	Polished	Brown	Polished	Brown	Polished	Brown	Polished	Brown	Polished
Hom Nil										
Unprocessed	10.01±0.05^{a}	0.54±0.01^{a}	11.29±0.05^{a}	ND	4.01±0.04^{c}	ND	6.41±0.04^{c}	ND	ND	ND
FIR drying	8.32±0.04^{b}	0.34±0.01^{b}	9.65±0.05^{b}	ND	7.52±0.04^{a}	ND	12.52±0.05^{b}	ND	ND	ND
HA drying	6.23±0.04^{c}	0.23±0.01^{c}	8.69±0.03^{c}	ND	5.28±0.03^{b}	ND	16.54±0.05^{a}	ND	ND	ND
Mali Dang										
Unprocessed	10.33±0.05^{a}	0.50±0.01^{a}	10.65±0.07^{b}	ND	4.71±0.02^{c}	ND	6.25±0.19^{c}	ND	ND	ND
FIR drying	8.43±0.04^{b}	0.33±0.01^{b}	8.56±0.07^{a}	ND	7.16±0.05^{a}	ND	15.45±0.08^{b}	ND	ND	ND
HA drying	6.21±0.03^{c}	0.22±0.01^{c}	8.20±0.05^{b}	ND	5.74±0.03^{b}	ND	17.27±0.03^{a}	ND	ND	ND
Riceberry										
Unprocessed	10.24±0.07^{a}	0.54±0.01^{a}	10.84±0.05^{a}	ND	4.68±0.04^{c}	ND	6.31±0.03^{c}	ND	ND	ND
FIR drying	8.65±0.04^{b}	0.35±0.01^{b}	8.72±0.06^{b}	ND	7.73±0.04^{a}	ND	15.48±0.05^{b}	ND	ND	ND
HA drying	6.24±0.04^{c}	0.24±0.01^{c}	8.32±0.06^{c}	ND	5.46±0.04^{b}	ND	17.88±0.07^{a}	ND	ND	ND
KDML 105										
Unprocessed	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
FIR drying	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
HA drying	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

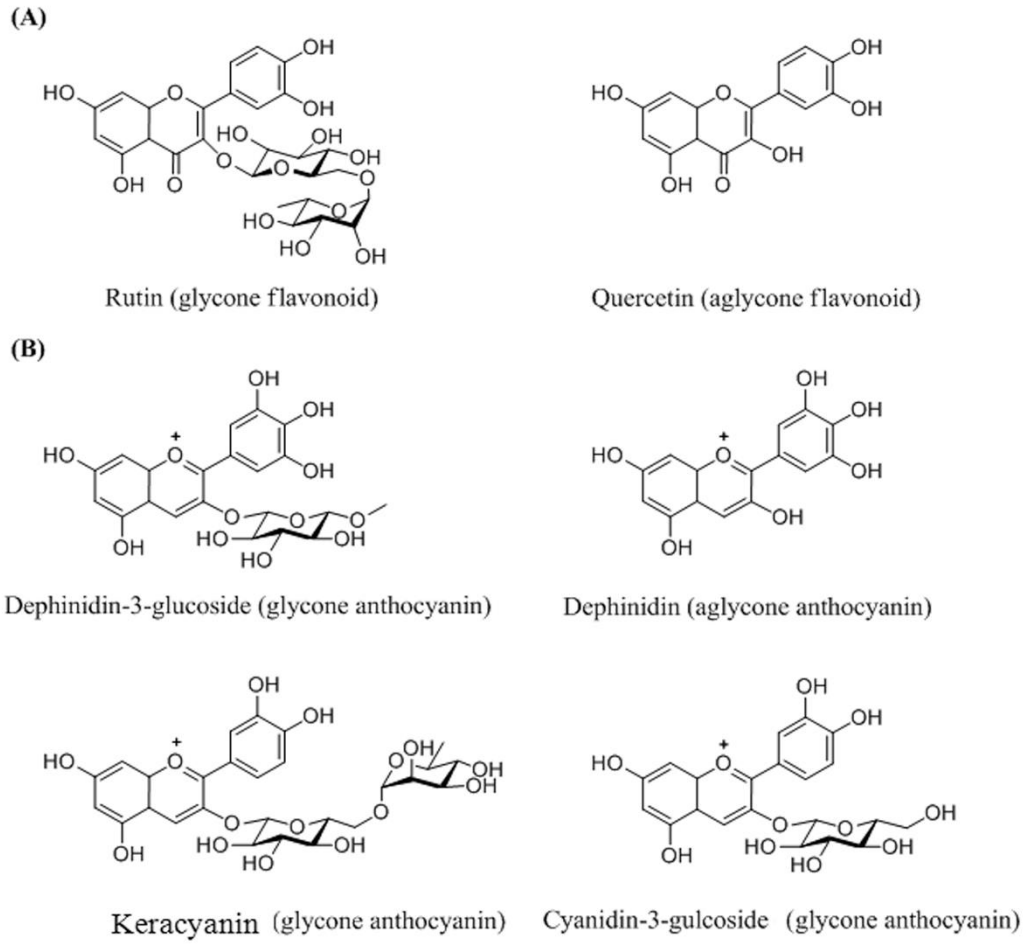


Figure 4.18 Chemical structure of some aglycone and glycone of flavonoids (A) and anthocyanins (B)

4.2.7 Changes in the content and composition of anthocyanins

Anthocyanin composition and content, as determined using HPLC, are shown in Table 4.6. According to our available authentic standards, it was possible to identify seven anthocyanins, namely delphinidin, dephinidin-3-glucoside, cyanidin-3-glucoside, keracyanin, malvin, malvidin and pelargonidin-3-glucoside in pigmented unpolished and polished rice samples.

When compared between the unpolished and polished samples, regardless the thermal treatment, anthocyanins had shown in unpolished samples and disappeared from all polished rice varieties. The unpolished pigmented rice varieties were a rich source of anthocyanins especially, cyanidin-3-glucoside. Similar results were reported indicating that the most abundant anthocyanins, especially cyanidin-3-glucosides and their derivatives, were found in black and red rice (Abdel-Aal, Young & Rabalski, 2006). Our results show that cyanidin-3-glucoside content had the highest of the anthocyanin values in the three cultivars of unheated-unpolished pigmented rice, in the order: Hom Nil, Riceberry and Mali Dang. The results indicated that the contents of individual anthocyanins varied among pigmented rice varieties; this may be due to differences between genotypes and possibly also to differences in their location in the outermost pericarp layer (Butsat & Siriamornpun, 2010; Walter et al., 2013).

For comparison in two drying treatments, the results show that FIR-dried samples showed the highest levels of total anthocyanin content when compared to unpolished rice in all varieties. Similarly, a previous study reported that infrared-dried strawberry had the highest values of total anthocyanin content (1.4-7.5 times) when compared to fresh samples (Adak, Heybeli & Ertekin, 2017) Dephinidin-3-glucoside, keracyanin and malvin contents decreased after FIR and HA drying, compared with the unheated samples of each of the pigmented rice grains. This result was also supported by the reported from Zhou, Chen, Bi, Wang & Wu, (2017) who revealed the anthocyanins degradation in HA drying approximately 55%-60%. A significant reduction of anthocyanin content after HA drying was observed in all rice varieties. For example, keracyanin drastically decreased after hot-air dried in Mali Dang (72%), Hom Nil (63%) and Riceberry (54%).

The thermal processes exert important influences on the stability of anthocyanins. According to a previous study, the greatest loss of their compounds was by the pressure cooking of Californian black rice with a 80% reduction (Hiemori, Koh & Mitchell, 2009). Degradation rates for anthocyanins in Korean black rice were high; due to roasting (94%) or boiling (77%)(Surh & Koh, 2014). In addition, the top-spray fluidized bed coating method degraded anthocyanins at the high temperature of coating rice with the water extract of purple-corn cob which may be caused by non-enzymatic browning (Maillard reaction) during thermal processing (Duangkhamchan & Siriamornpun, 2015). The improvement of a decreased content of anthocyanins by HA may be explained by these results being consistent with other reports, indicating that the stability of anthocyanins in thermal foods is predominantly dependent on the processed temperature. The degradation of anthocyanins by thermal is related to their hydrolysis at glycoside linkages to form α-diketones or chalcone. Overall, the reduction of anthocyanins in pigmented rice may be attributed to their leaching loss in their interaction with other compounds and, predominantly, their thermal degradation or decomposition (Surh & Koh, 2014; Zhou, Chen, Bi, Wang & Wu, 2017). Unexpectedly, in this present study only delphinidin was detected in FIR irradiated Riceberry rice. Moreover, the results showed that delphinidin and cyanidin-3-glucoside all increased as a result of FIR for the rice grains, with increases of approximately 3.0- and 3.2-fold, respectively. Malvidin and pelargonidin-3-glucoside increased slightly after FIR treatment. The anthocyanins are a group of reddish to purple water-soluble flavonoids, and are thought as the primary functional components of coloured rice (Hiemori, Koh & Mitchell, 2009). Previously, the flavonoid compounds, for instance rutin was thought to be the hydrolysis pathway to quercitin (Vetrova et al., 2019). It is observed that keracyanin and dephinidin-3-glucoside have similar structures to cyanidin-3-glucoside and dephinidin, respectively, which have more an extra glycoside group on ring as indicated in Fig 4.18. The results suggest that the decrease in keracyanin and dephinidin-3-glucoside may result from the rupture of glycoside bonds by FIR treatment, which due to the deglycosylation of glycone flavonoids (like rutin) (Vetrova et al., 2019) and glycone anthocyanins. In other words, the plausible explanation of how cyanidin-3-glucoside and dephinidin anthocyanins were increased in the pigmented rice kernels may

involve the linkages or bindings if the glycoside group was removed and FIR. The results may also demonstrate that the structures of keracyanin and dephinidin-3-glucoside are transformed from high-molecular-weight anthocyanin compounds to low-molecular-weight products could cleave and release low-molecular-weight natural antioxidants in plants (Lee et al., 2006; Zhang, Lv, Pan & Fan, 2012). Alternatively, degradation of complex anthocyanins for example, degradation of keracyanin to cyanidin-3-glucoside by direct oxidative and/or through the action the oxidizing enzyme such as polyphenoloxidase (PPO) causing more degraded smaller molecule anthocyanins. Since FIR drying temperature (40 ºC) was in the range of the optimum temperature (40-50 ºC) of PPO (Lv et al., 2017; Vetrova et al., 2019).

Tables 4.12 Changes in anthocyanin contents (µg/g dw) of pigmented Thai rice grains as affected by FIR and HA treatments.

Samples	Anthocyanin contents (µg/g dw)							Total (µg/g dw)
	Keracyanin	Malvin	Dephinidin	Cyanidin-3-glucosides	Pelargonidin-3-glucoside	Malvidin	Dephinidin-3-glucoside	
Hom Nil								
Unheated	18.29±0.02^{a}	2.66±0.04^{a}	10.11±0.03^{b}	60.45±0.13^{b}	12.11±0.11^{b}	4.00±0.03^{b}	7.56±0.04^{a}	115.18±4.45
FIR drying	9.44±0.03^{b}	1.72±0.01^{b}	17.52±0.08^{a}	195.70±0.13^{a}	13.27±0.10^{a}	5.13±0.03^{a}	5.98±0.03^{b}	248.76±5.78
HA drying	6.69±0.03^{c}	1.71±0.01^{b}	4.52±0.05^{c}	29.09±0.11^{c}	8.98±0.04^{c}	1.77±0.02^{c}	4.98±0.03^{c}	57.74±3.68
Mali Dang								
Unheated	5.75±0.40^{a}	0.91±0.01^{a}	ND	18.98±0.03^{b}	3.21±0.07^{b}	1.04±0.02^{b}	1.11±0.01^{a}	31.00±3.17
FIR drying	3.99±0.05^{b}	0.56±0.01^{b}	0.56±0.01^{a}	25.76±0.04^{a}	4.11±0.07^{a}	1.57±0.03^{a}	0.67±0.01^{b}	37.22±4.10
HA drying	1.63±0.04^{c}	0.54±0.02^{b}	ND	9.11±0.03^{c}	2.19±0.07^{c}	0.68±0.01^{c}	0.54±0.01^{c}	14.69±2.71
Riceberry								
Unheated	9.77±0.07^{a}	2.01±0.01^{a}	3.31±0.03^{b}	50.23±0.15^{b}	50.11±0.09^{b}	3.98±0.03^{b}	6.89±0.06^{a}	126.30±4.61
FIR drying	6.52±0.04^{b}	1.37±0.01^{b}	9.78±0.08^{a}	64.71±0.14^{a}	50.34±0.11^{a}	4.96±0.03^{a}	4.11±0.03^{b}	141.79±5.11
HA drying	4.54±0.09^{c}	1.39±0.01^{b}	1.00±0.01^{c}	26.78±0.10^{c}	28.99±0.10^{c}	1.44±0.01^{c}	3.87±0.01^{c}	68.01±3.02

The anthocyanin compounds were not detected in all polished rice samples. Values are expressed as mean ± standard deviation (n = 3). Means with different letters in the same rice variety as affected by different drying methods were significantly different at the level $p < 0.05$. No, not detected.

4.2.8 Changes in γ-oryzanol and tocopherol

Many studies have reported that γ-oryzanol, isolated from various natural sources (particulally rice bran oil), exhibits the potential for human health benefits (Butsat & Siriamornpun, 2010; Surh & Koh, 2014). Furthermore, γ-oryzanol is an effective antioxidant in reducing the risk of anti-inflammatory activity, the incidence of tumour and platelet aggregation inhibition (Lerma-Garcia, Herrero-Martinez, Simó-Alfonso, Mendonça & Ramis-Ramos, 2009). Changes of FIR drying on the γ-oryzanol and tocopherols contents of pigmented brown and polished rice grains are shown in Table 4.12. When compared between the unpolished and polished samples, regardless the thermal treatment, polished samples had significantly ($p<0.05$) lower content of γ-oryzanol compared to unpolished samples in all varieties. For comparison in two drying treatments, all unheated-unpolished pigmented rice cultivars were the best source of γ-oryzanol compared to dried samples. The amount of γ-oryzanol ranged from 1.07 mg/g in hot-air treated polished rice to 4.58 mg/g in unprocessed pigmented brown rice. The unprocessed pigmented brown rice of all varieties were the best source of γ-oryzanol (4.23– 4.58 mg/g) while the polished pigmented rice varieties ranged from 1.07 to 1.87 mg/g. Both of brown and polished pigmented rice varieties decreased slightly ($p < 0.05$) after FIR and HA treated, respectively. Most samples decreased slightly ($p < 0.05$) after FIR and HA treatments, respectively. Our results indicate that drying leads to degradation of γ-oryzanol content in pigmented rice varieties. Previously, the reduction of γ-oryzanol content was also observed in rice bran dried by FIR and HA (Wanyo, Meeso, & Siriamornpun, 2014). There was also a reduction for unpolished rice after any of the thermal processes (Lerma-Garcia, Herrero-Martinez, Simó-Alfonso, Mendonça & Ramis-Ramos, 2009). This study demonstrated that the levels of bioactive compounds including γ-oryzanol in plant samples decreased, increased or remained unchanged depending on the type of processing.

When compared between the unpolished and polished samples, regardless the thermal treatment, all unpolished samples had significantly ($p<0.05$) higher contents of α- and γ-tocopherol compared to polished rice (Table 4.2). For comparison in two drying treatments, an increase in α-tocopherol content was found in Hom Nil (50%), Mali

Dang (49%) and Riceberry (47%) unpolished rice varieties after FIR treatment, while in HA dried rice grains α-tocopherol content decreased to 22% (Hom Nil), 19% (Mali Dang) and 21% (Riceberry). FIR drying could affect the levels of Tocol compounds (tocopherols or vitamin E and tocotrienols), which are classified as lipid-soluble antioxidants, with great potential to scavenge free radicals, to inhibit cholesterol oxidation in biological membranes and to reduce lung cancer risk (Lerma-Garcia et al., 2009). The α- and γ-tocopherol contents differed as a result of heat processing of the pigmented unpolished and polished rice. The increase of temperature led to a higher degradation of the tocopherols by heat in food processing such as cooking, roasting and drying (Surha & Koh, 2014; Zigoneanu, Williams & Sabliov, 2008). In our present study, the conditions of hot air drying using a higher temperature (60 °C) than FIR combined with hot air (40 °C) resulted in an decrease of tocopherol content. Previous study also showed that 40°C was not high enough to cause α-tocopherol degradation (Zigoneanu, Williams & Sabliov, 2008). FIR dried samples had greater levels of γ-tocopherol compared to those of unheated samples, while HA drying did not affect the amounts of γ-tocopherol of both unpolished and polished samples. Similar results were found in rice bran treated by FIR: the α- and γ-tocopherol contents were increased significantly which were 17% and 2%, respectively (Wanyo, Meeso, & Siriamornpun, 2014).

The tocopherols are major and important forms of vitamin E. They exist as a structure of a chromanol ring of 16 carbons; differences between the positions of methyl groups give the variations of α-, γ-, δ-, and β-tocopherols. They are a family of fat-soluble phenolic compounds. Phenolic groups in the chromanol ring help to reduce electrons of free radicals (Benzie & Strain, 1996). Thus, the tocopherol contents increased similarly to the phenolic compounds as affected by FIR drying. The heat of FIR rays transfers smoothly to the centre of cell plants without damaging the composition of surface materials (Lee et al., 2006). Many antioxidants in plants are most frequently present in a covalently bound form as insoluble polymers, so if this bonding is not strong, FIR treatment could liberate and activate low-molecular-weight natural antioxidants in plants, such as the α-, γ-, tocopherols in rice bran (Wanyo, Meeso, & Siriamornpun, 2014). FIR may possess the ability to cleave covalent bonds and release more bioactive compounds such as phenolic compounds, thus increasing

the contents of bioactive compounds (Lee et al., 2006). However, we speculate that the method of drying both for HA and FIR dryings, may have a significant effect on the internal structure of the grain, which may increase the yield of extraction of some components, including the bioactive ones (Haard & Chism, 1996).

4.2.9 Changes in the content and composition of amino acids

Amino acids are one of the important nutrients in rice (Liu, Zheng & Chen, 2017). However, there has been no report on changes in this class of compound by drying methods especially by FIR. Ten amino acids were identified in pigmented unpolished and polished rice after processing (Figure 4.4). When compared between the unpolished and polished samples, regardless the thermal treatment, almost all polished samples had significantly ($p<0.05$) lower contents of amino acids compared to unpolished samples in all varieties. The highest values of almost all amino acids, except valine, were obtained in Riceberry unpolished rice. Mostly, eight amino acids namely, lysine, histidine, leucine valine, arginine, isoleucine, methionine and threonine, decreased after the polishing of rice. Valine was only detected in the unpolished samples and disappeared in polished Hom Nil rice. The greatest losses for methionine (an essential amino acid) after milling were observed with 83% loss in Riceberry (purple) followed by Mali Dang (red) (82% loss). In Riceberry, lysine and arginine decreased to 89% and 82%, respectively. Phenylalanine and tryptophan were not significantly different (at $p>0.05$) in Hom Nil and Mali Dang, respectively. Similarly, previous study has reported the reduction of methionine (9%-29 %), lysine (12%-15%) and threonine (9%), while phenylalanine and tryptophan were not significantly different (at $p>0.05$) in milled rice depending on rice varieties and degree of milling. They explained that the decrease in amino acid was largely attributed to variety differences however the reduction of protein content was mostly affected milling instead of the distribution pattern of amino acid (Liu, Zheng & Chen, 2017).

Decreases in amino-acid content after drying methods were found in all pigmented rice varieties (Fig. 4.4). Compared to unheated samples, the polished Mali Dang rice was found to sustain the greatest loss, involving three amino acids.

Tables 4.13 Changes in γ-oryzanol and tocopherols (mg /g dw) of pigmented Thai rice as affected by FIR and HA.

Samples	γ-Oryzanol (mg /g dw)		α-Tocopherol (mg /g dw)		γ- Tocopherol (mg /g dw)	
Khao Dawk Mali 105	Brown	Polished	Brown	Polished	Brown	Polished
Unprocessed	3.52±0.01^{a}	1.46±0.04^{a}	25.17±0.08^{b}	11.54±0.05^{b}	3.02±0.04^{b}	0.37±0.02^{b}
FIR drying	3.02±0.01^{b}	1.16±0.04^{b}	37.41±0.11^{a}	15.51±0.07^{a}	3.25±0.01^{a}	0.66±0.01^{a}
HA drying	2.69±0.06^{c}	0.80±0.01^{c}	19.70±0.27^{c}	8.67±0.11^{c}	3.06±0.01^{b}	0.35±0.01^{b}
Hom Nil						
Unprocessed	4.58±0.01^{a}	1.87±0.02^{a}	30.54±0.11^{b}	16.73±0.18^{b}	5.13±0.02^{b}	0.66±0.01^{b}
FIR drying	4.17±0.01^{b}	1.46±0.04^{b}	45.82±0.05^{a}	20.87±0.10^{a}	5.70±0.08^{a}	0.97±0.04^{a}
HA drying	2.97±0.02^{c}	1.26±0.04^{c}	23.60±0.17^{c}	10.05±0.05^{c}	5.17±0.07^{b}	0.67±0.01^{b}
Mali Dang						
Unprocessed	4.23±0.01^{a}	1.73±0.00^{a}	31.14±0.06^{b}	17.05±0.04^{b}	5.34±0.08^{b}	0.84±0.02^{b}
FIR drying	4.03±0.01^{b}	1.33±0.02^{b}	45.37±0.16^{a}	21.02±0.01^{a}	5.97±0.03^{a}	1.08±0.02^{a}
HA drying	3.32±0.08^{c}	1.07±0.04^{c}	24.46±0.06^{c}	10.20±0.05^{c}	5.36±0.07^{b}	0.77±0.07^{b}
Riceberry						
Unprocessed	4.44±0.14^{a}	1.73±0.01^{a}	30.86±0.11^{b}	16.84±0.22^{b}	5.16±0.01^{b}	0.71±0.05^{b}
FIR drying	4.04±0.03^{b}	1.32±0.02^{b}	44.73±0.14^{a}	22.07±0.03^{a}	5.60±0.02^{a}	0.92±0.02^{a}
HA drying	3.24±0.04^{c}	1.12±0.02^{c}	23.97±0.16^{c}	10.23±0.05^{c}	5.20±0.02^{b}	0.69±0.02^{b}

Values are expressed as mean ± standard deviation (n = 3). Means with different letters in the same column were significantly different at the level $p < 0.05$.

FIR-dried rice, respectively, displayed 99% loss in isoleucine, 80% in lysine and 75% in phenylalanine, with respect to amino acid reductions. The greatest decrease was for HA-treated rice: 89% in methionine and less severe decreases for some other amino acids. The effects of FIR and HA dryings were not significant ($p > 0.05$) in rice samples with respect to threonine in three dry-treated samples. Methionine was sensitive to HA, while eight amino acids showed greater sensitivity to FIR than HA. In this present study indicate that the decreases in amino-acid composition also depended on the drying methods and on the varieties of rice studied.

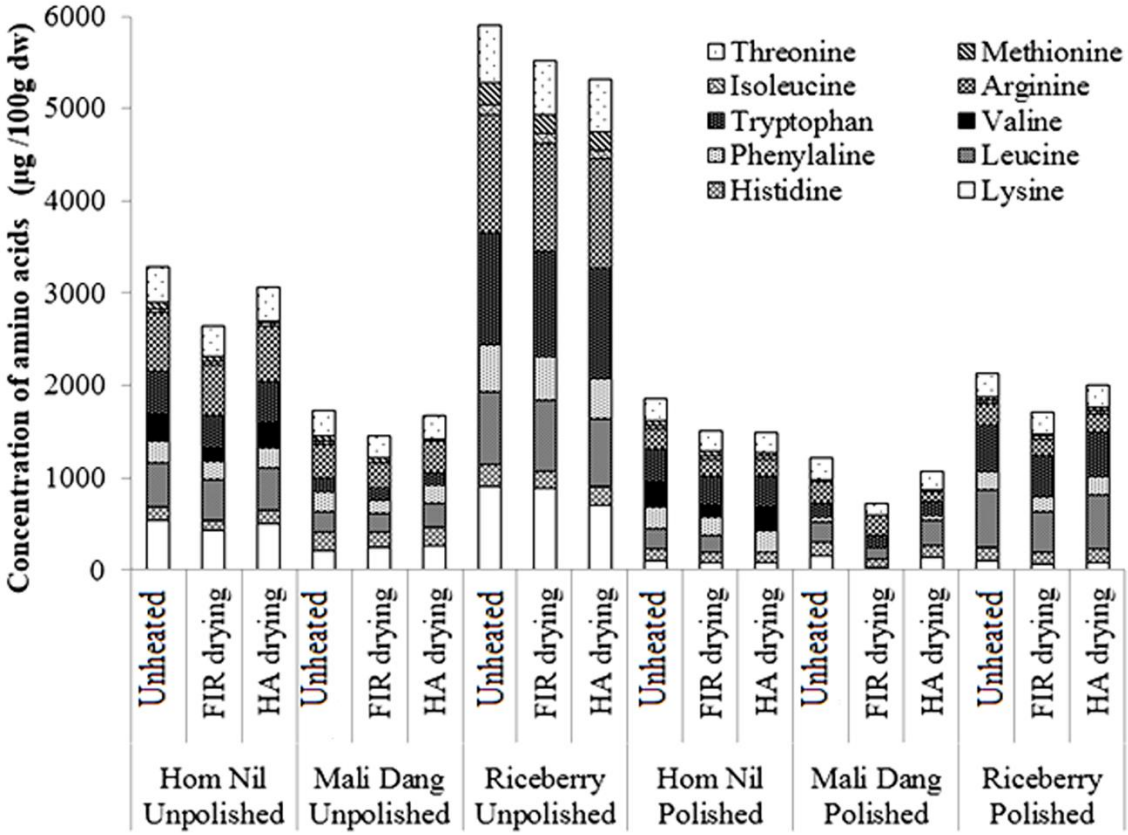


Figure 4.19 The effects of FIR and HA dryings on amino acids (µg /100g dw) in pigmented Thai rice. Each value is the mean ± the standard deviation (n = 3).

Moreover, we observed that after rice was processed by either of the heat methods, the content of amino acid in polished dried rice was more depleted than for unpolished dried rice. This result suggests that the external layer of plant seeds may protect the inner components from some processes (Bors, Michel & Stettmaier, 2001).

Similar results for thermal effects on amino-acid composition have been reported by Coimbra, Nunes, Cunha and Guine (2011), who found decreases in the amounts of amino acids such as lysine (25%) and alanine (40%) in sun dried pears. Drying might contribute to the Maillard reaction, thus leading to the destruction of amino acids (Moreno, Molina, Olano & López-Fandiño, 2003). This present study provides important indications about reductions in amino-acid composition due to the combined processing of polishing and drying for conventional rice. Furthermore, thermal drying methods can be expected to cause reductions in the amino acid content of all pigmented rice varieties. Nevertheless, the external layer of pigmented rice cultivars may help to protect the destruction of amino acids in the endosperm of rice from heat.

4.3 Results and discussions of experiment 3

Product development from pigmented Thai rice as functional food (Riceberry jam)

The pigmented pericarp rice varieties in this study had high amounts of phenolic antioxidants including anthocyanins that have been recognized as health enhancing cereal due to their antioxidant capability. Additionally, the change in amount of these compounds is also affected by drying processing as Far-infrared radiation drying and Hot air drying. The polyphenol in rice are mainly from the pericarp, which is obtained during rice milling process. The application of FIR increased the levels of total phenolic, flavonoids and anthocyanin contents in all rice samples, as well as tocopheols when compared to HA and raw samples. Similarly, FIR also increased the functional properties of antioxidant by scavenging DPPH radical and reducing power. In this studty, Riceberry brown or unpolished rice variety as dried by FIR contains high content of the bioactive compound especially, anthocyanin (pelargonidin), phenolic acid (protocatechuic acid and vanillic acid of bound form) and antioxidant activity. Currently, it also was promoted to plant and consume in our country. Many products of Riceberry rice were developed considerably. Therefore, we developed product of Riceberry brown rice as treated by FIR to be Riceberry jam, which was functional food product from rice.

4.3.1 Evaluation of chemical, physical and sensory properties

4.3.1.1) Chemical measurements; Measurement of peroxide value (PV)

Peroxide value (PV) is a measure of the amount of peroxides and hydroperoxides formed in the initial stages of lipid oxidation. PV is one of the most widely used tests for the analysis of oxidative rancidity in oils and fats. However, only the evaluation of peroxides on the storage is not sufficient to evaluate the product quality or efficiency of thermal treatment. Therefore the secondary products of lipid oxidation using K270 analysis should be further performed. In this present study, the oxidation degree on Riceberry product samples was determined by measuring PV in the absence at ambient temperature. A significant difference ($p < 0.05$) in PV was observed between the unprocessed or control and the samples with different stored time. FIR drying had produced slightly high PV compared to the unprocessed. The PVs of fresh jam was slightly increased from the beginning of the storage period, indicating initial process of oxidation. The PV of the stored 30 day of jam reached a maximum value of 2.65 meq oxygen/kg (Table 4.11).

Tables 4.14 Effect of storage time on peroxide value of Riceberry rice variety (meq Oxygen / kg)

Riceberry rice variety	P.V. (meq)
Flour (unprocessed)	1.99 ± 0.00^{d}
FIR dried flour	2.04 ± 0.02^{c}
Jam (0 day)	2.39 ± 0.04^{b}
Jam (30 day)	2.65 ± 0.02^{a}

Values are expressed as mean ± standard deviation (n = 3). Means with different letters in the same column were significantly different at the level $p < 0.05$.

4.3.1.2) Physical measurements; Colorimetric parameters

Colour is a psychological property of food products that effects to the enjoyment of eating. Temperature during drying is one of the causes of colour degradation in dehydrated products (Lozano and Ibarz, 1997). Colour parameters of Riceberry rice jam as made from FIR dried rice compared to fresh jam and stored jam are shown in Table 4.12. Overall, when compared with flour, a smaller decrease in L and b values of the fresh jam than those of stored jam was observed. Further, stored jam product showed a larger decrease in L and b values. The total colour difference

ΔE, which is a combination of parameters L-, a- and b-values, is a colorimetric parameter extensively used to characterize the variation of colours in food during processing.

Tables 4.15 Colour parameters of Riceberry rice product

Riceberry rice product	Colour parameters			
	L*±S.D	a*±S.D	b*±S.D	ΔE
Flour	27.83± 0.83[a]	1.65 ± 0.21[a]	-5.15± 0.51[a]	-
Jam (0 day)	25.97 ± 0.38[b]	1.18 ± 0.07[b]	-3.78 ± 0.26[b]	3.46[b]
Jam (30 day)	23.81 ± 0.71[b]	1.18 ±0.05[b]	-3.13± 0.33[c]	4.01[a]

Values are expressed as mean ± standard deviation (n = 3). Means with different letters in the same column were significantly different at the level $p < 0.05$.

The results presented in this work suggest that the change in ΔE of fresh jam as treated by FIR drying were smaller as compared to stored jam. As the colour of fresh jam appears to be more like flour this may imply that this drying method can preserve bioactive compounds and activities. The colour changes in Riceberry rice jam caused by the thermal may be due not only the non-enzymatic browning reaction, but also to the destruction of pigments present in the flour. Degradation of certain bioactive compounds in the flour tissues might be related to decreasing bioactivity of the jam.

4.3.1.3) Sensory evaluation

The 9-point hedonic scale, also known as degree-of-liking scale, is the most common hedonic scale for measuring product liking by consumers. The Sensory evaluation of Riceberry rice flour, Riceberry rice jam and the stored jam are shown in (Table 4.13). Riceberry rice flour had higher values of hedonic scale in the part of smell, colour, sweetness and overall liking than did Riceberry rice jam and stored jam.

4.3.1.4) Analysis of bioactive compounds.

Phenolic compounds are widely distributed in fruits and vegetables (Li et al., 2006), which have received considerable attention, due to their potential

antioxidant activities and free-radical scavenging abilities, which potentially have beneficial implications in human health (Li et al., 2006; Lopez-Velez et al., 2003). The soluble and bound TPC of Riceberry rice flour, Riceberry rice jam and the stored jam are shown in (Table 4.14). Riceberry rice flour had higher values of TPC, than did Riceberry rice jam and stored jam. Thermal processing has been reported to have both adverse and favorable effects on TPC. Losses in TPC by thermal processing have been reported by many studies, mostly in vegetables (Roy et al., 2007; Chan et al., 2009). Flavonoid compounds are the most common and widely distributed group of plant phenolic compounds that are characterized by a benzo-y-pyrone structure, which is ubiquitous in fruits and vegetables. We found that the Riceberry flour contained the highest soluble and bound flavonoid content, followed by the Riceberry rice jam and the stored jam (Table 4.14). The anthocyanin content was also shown in Table 4.11. We found that the Riceberry flour contained (0.68 mg /g dw) the highest the anthocyanin content, followed by the Riceberry rice jam (0.45 mg /g dw) and the stored jam. (0.32 mg /g dw)

DPPH scavenging activity and FRAP values of soluble and bound of two differentl stored time of Riceberry rice jam and Riceberry rice flour are shown in Table 4.11 Riceberry flour contained the highest soluble and bound flavonoid content, followed by the Riceberry rice jam and the stored jam. Similar results were found in FRAP (Table 4.14). The Riceberry flour contained the highest soluble and bound flavonoid content, followed by the Riceberry rice jam and the stored jam. The result indicate that the thermal process of food processing can decrease the properties of naturally occurring antioxidants so that the overall antioxidant activity decreases or remains unchanged (Tomaino et al., 2005)

Tables 4.16 Sensory evaluations of Riceberry rice product

Riceberry rice product	Sensory evaluations					
	smell	colour	flavor	touch	sweetness	Overall liking
Jam (0 day)	6.69±0.02[a]	6.95±0.56[a]	5.79±0.16[a]	6.47±0.45[a]	6.92±0.01[a]	6.85±0.03[a]
Jam (30 day)	6.32±0.16[b]	5.82±0.61[b]	5.63±0.43[a]	6.49±0.56[a]	6.58±0.01[b]	6.84±0.01[a]

Values are expressed as mean ± standard deviation (n = 3). Means with different letters in the same column were significantly different at the level $p < 0.05$.

Tables 4.17 Total phenolic, flavonoid and total anthocyanin contents, antioxidant capacity of Riceberry rice product

Rice variety	Total phenolic content (mg GAE/g dw)		Total flavonoid content (mg RE/g dw)		DPPH (% inhibition)		FRAP (µmol FeSO4/g DW)		Total anthociyanin content (mg /g dw)
Riceberry	Soluble	Bound	Soluble	Bound	Soluble	Bound	Soluble	Bound	
Flour	63.82±1.38[a]	15.95±0.01[a]	3.89±0.07[a]	2.19±0.04[a]	80.46±0.49[a]	30.46±0.43[a]	53.86±0.17[a]	62.16±0.40[a]	0.68±0.01[b]
Jam (0 day)	40.3±1.04[b]	14.84±0.02[b]	1.76±0.06[b]	1.55±0.04[b]	59.77±0.42[b]	29.67±0.45[b]	39.66±0.37[b]	45.66±0.27[b]	0.45±0.01[b]
Jam (30 day)	35.93±0.10[c]	10.48±0.04[c]	1.61±0.01[c]	1.21±0.06[c]	42.20±0.87[c]	12.20±0.64[c]	35.04±0.60[c]	44.04±0.54[c]	0.32±0.01[b]

Values are expressed as mean ± standard deviation (n = 3). Means with different letters in the same column were significantly different at the level $p < 0.05$.

CHAPTER 5

Conclusion

Our results demonstrated the significant positive and negative impacts of FIR and HA treatments on bioactive compounds being retained for three pigmented rice varieties.

The objectives of the present study included as follows:

1. To investigate bioactive compounds in pigmented and starch digestibility of pigmented Thai rice

2. To investigate the effect of FIR drying on bioactive compounds in pigmented Thai rice varieties.

3. To develop product from selected pigmented Thai rice/ by products as functional food

The findings of the present thesis can be concluded as follows:

5.1 The starch digestion kinetic studies presented in this paper indicate that Thai pigmented rice varieties have lower digestibility than a control white Thai rice variety. The concentration of maltose at the end of the digestion displayed higher values in both flour and purified starch of white rice compared to purple and red rice. There was no effect observed on the rate of digestion. There was a significant difference among the six pigmented rice varieties in polyphenol and anthocyanin content, gelatinization behavior, as well as starch structure in pigmented rice. This data indicates that a combination of differences in starch structure and the inhibitory effects of polyphenols contribute to the reduced starch digestion rates observed for pigmented rice's.

5.2 Changes in the contents and compositions of total phenolic and flavonoid of soluble and bound form, antioxidant activities (DPPH and FRAP) of soluble and bound form, total anthocyanin content and composition, γ-oryzanol and tocopherol and amino acids of pigmented brown and polished rice grains as affected by HA and FIR treatments.

The soluble TPC of unprocessed pigmented brown rice was higher than that polished rice. For the pigmented brown rice grains, the soluble and bound TPC also increased after FIR treatment in all varieties. After FIR radiation, the present concentration of the soluble TPC from Hom Nil, Mali Dang and Riceberry rice increased significantly up to 18, 10 and 7.5%, respectively; while hot air significantly decreased the contents of total phenolic in all varieties. The TFC of pigmented brown rice grains as treated by FIR and HA drying was significantly higher than those of polished rice. The pigmented brown and polished rice grains as radiated by FIR had the highest TFC while, hot air dried pigmented rice grains had the lowest TFC. The highest value of TAC was observed in FIR dried samples, followed by unprocessed and HA dried samples of all rice varieties. While, the pigmented polished rice of all varieties were not detected. The antioxidant activities of the pigmented brown and polished rice grains, as affected by different treatments, were determined by DPPH radical scavenging and FRAP assays. This indicated that the difference in antioxidant activities of rice grains depending on pericarp color. In all treatments of pigmented rice, the percent inhibition of DPPH ranged from 23 to 87%. After FIR radiated, the highest antioxidant activity as determined by DPPH radical scavenging was observed for brown and polished pigmented rice with FIR irradiation. However, the inhibition of DPPH radical scavenging was found lowest in hot air dried grain of all rice varieties when compared with unprocessed and FIR treated samples. Similarly, we found that the concentration of antioxidant activity as determined by FRAP was increased by the FIR treatment in all varieties of rice grains. In the case of HA drying, the antioxidant activities were significantly decreased when compared with unprocessed samples of all rice varieties. The results indicated FIR radiation increased antioxidant activities (DPPH and FRAP).

Our results have demonstrated the significant positive and negative impacts of FIR and HA treatments on bioactive compounds being retained for three pigmented rice varieties. We emphasized that the application of FIR increased the levels of total phenolic, flavonoids and anthocyanin contents in all rice samples, as well as tocopherols when compared to HA and unheated samples. Similarly, FIR also increased the functional properties of antioxidants by scavenging DPPH radical reducing power. Moreover, FIR also remarkably enhanced the contents of aglycone

flavonoid (quercetin) and aglycone anthocyanin (delphinidin) including monoglycone of cyanidin -3-glucoside due to the deglycosylation of glycone flavonoids (like rutin) and glycone anthocyanins (like dephinidin-3-glucoside and keracyanin) present in pigmented rice grains. In contrast, both FIR and HA methods, together with polishing, resulted inconsiderable decreases in amino-acid content. However, FIR might cause the release of bioactive compounds, therefore increasing the availability of bioactive compounds for pigmented rice. This study suggests that besides their drying function, HA and FIR may have a significant effect on the internal structure of the grain, which may increase the yield of extraction of some components. Therefore, the optimization of drying methods could be the way for enhancing the nutritional value and functional properties of optimize consumer health benefits.

Additionally, our results have also indicated that the polishing lose phytochemicals beneficial to health. Therefore, polished rice products may have sensory quality but lower nutritional quality. This research provides important evidence in support of health benefits of consuming unpolished rice. The results are expected to be helpful for the food, nutraceutical and pharmaceutical industries.

5.3 Product development from pigmented Thai rice as functional food (Riceberry jam) were investigated in the evaluation of chemical, physical and sensory properties including analysis of bioactive compounds of Riceberry rice flour, Riceberry rice jam and the stored jam are indicated that Riceberry flour contained the highest bioactive compound and antioxidant activity, followed by the Riceberry rice jam and the stored jam., However most of these contents were decreased during stored time for 30 day. Similar results were found in the evaluation of chemical and physical except sensory properties that shown the same overall liking in both of fresh Riceberry jam and stored Riceberry jam.

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