

Anthocyanins in Thai rice varieties: distribution and pharmacological significance

Sivamaruthi, B.S., Kesika, P. and *Chaiyasut, C.

Department of Pharmaceutical Sciences, Faculty of Pharmacy, Chiang Mai University, Chiang Mai, Thailand

Article history

Received: 29 April 2017
Received in revised form:
18 July 2017
Accepted: 26 July 2017

Abstract

Anthocyanins are phenolic, water-soluble, predominant flavonoids of plants, and are known for its wide distribution and its pharmacological importance. Almost all the plant sources like vegetables, fruits, cereals, grains are residing with anthocyanins. The type and quantity of the anthocyanins differ based on the species, varieties, cultivars, even the growth stage of the same plant, part of the plant, ethnic and environmental factors. Rice is one of the regular food sources for more than half of the people in the world. The rice cultivars and strains vary among the countries. Apart from the typical, polished, white rice, some of the colored rice varieties are in use. Anthocyanin present in the rice outer layer contributes the color of the rice. The nature, concentration, and distribution of anthocyanins are found to be varied among the rice cultivars. The current review focused on the anthocyanins content of Thai rice varieties and its reported pharmacological significance.

Keywords

Anthocyanins
Thai rice
Pharmacological
importance

© All Rights Reserved

Introduction

Rice commonly consumed food worldwide especially among Asian peoples. The nutritional value and the phytochemical contents were found to be differed among the rice varieties (Goufo and Trindade, 2014; Ujjawal, 2016). The quality of the rice depends on their phytochemical content, which is highly influenced by several factors like geography, irrigation, quality of the fertilizers used, and cultivars, etc. The majority of the chemical constituents of the rice were residing in the rice bran (RB), and endosperm (Pengkumsri *et al.*, 2015a). All components of rice have specific chemopreventive activity (Henderson *et al.*, 2012). The occurrence of γ -oryzanol and phenolic acids, ferulic acid ester, sterol, phytosterols, and carotenoids contributes the RB oil as an effective chemopreventive agent (Lamberts and Delcour, 2008). Rice comprised of the high content of tocopherols (tocotrienols and tocopherols) and γ -oryzanol than that of the other common cereal grains. It is well known that rice consists of anthocyanins, cellulose, lignin, vitamin B, amino acid, and some minerals (Ryan *et al.*, 2011). Anthocyanins are the most important water-soluble pigments that belong to the flavonoid group and are accountable for the different color in plant tissues (Glover and Martin, 2012; Trouillas *et al.*, 2016; Cortez *et al.*, 2017). Anthocyanins extensively occur in several plants,

fruits, vegetables, and are documented by a recent study (Chaiyavat *et al.*, 2016). The fruits, especially berries, are well-known source of anthocyanin. However, it is not affordable to all the people in their daily life. Rice is one of the commonly used staple foods around the world. The distribution of the rice anthocyanins depends on the rice cultivars. The consumption of colored rice varieties is increasing among the people, because of its health benefits. Moreover, rice bran (by-product of rice milling) is considered as an agricultural waste, which are rich in phytochemicals especially anthocyanins. The recent developments in extraction methods of anthocyanins in rice bran, and clinical studies have proven that the rice anthocyanins are cheap and abundant source of potent bioactive compound with antioxidant, anti-inflammatory, and other health promoting properties. The present review focused on the content, and distribution of anthocyanins, specifically in Thai rice varieties. Moreover, the review also glances about the general property of anthocyanins with a particular reference to pharmaceutical values.

Structure of anthocyanins

Anthocyanins are glycosylated polyphenolic compound of anthocyanidins, byproducts of polyhydroxy and polymethoxy 2-phenylbenzopyrylium linked by anthocyanidin attached with variable glycosidic moieties like

*Corresponding author.
Email: chaiyavat@gmail.com

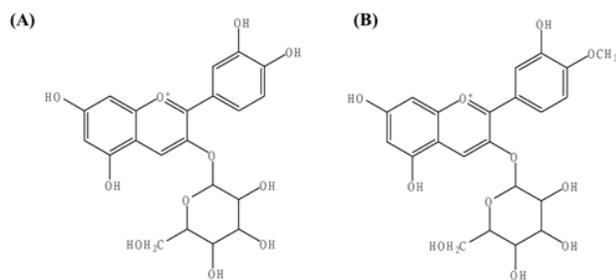


Figure 1. The chemical structure of cyanidin 3-glucoside (A) and peonidin 3-glucoside (B) in rice (Modified from Hu *et al.*, 2003).

arabinose, fructose, galactose, glucose, rhamnose, and xylose at the C3, C5 or C7 locations (Smeriglio *et al.*, 2014). Anthocyanins consist of two benzyl rings and a heterocyclic ring and linked via carbon (3n of C) bridge. Cyanidin (Cy), petunidin (Pt), peonidin (Pn), malvidin (Mv), delphinidin (Dp), and pelargonidin (Pg) are widely present in plants. About seventy percentage of anthocyanidins are Cy, Dp, and Pg, which are non-methylated form of three glycosylated anthocyanidins, and Cy is present in common edible plants (Kong *et al.*, 2003; Castañeda-Ovando *et al.*, 2009; Luciola, 2012). The structure of the commonly occurring rice anthocyanins was represented in Figure 1.

Stability of anthocyanins

The anthocyanins are more vulnerable to degradation, and are easily affected by several physical and biological parameters like pH, temperature, oxygen, light, and enzymes. The stability of the anthocyanins is also attributed by its structure (Figure 2).

The glycone molecules are relatively stable when compared with its aglycone form (with glycosyl units and acyl groups). The hydroxyl and methoxyl groups, and acylation also influence the stability. Glycone forms (anthocyanins) are more stable than its respective aglycone forms (anthocyanidins) (Andersen, 2001; Stintzing and Carle, 2004). In nature, they commonly exist as glycone forms (anthocyanins) for stability purpose (Timberlake and Bridle, 1966).

The pH is one of the most influencing factors of stability, and color of the anthocyanins. The anthocyanins are more stable in acidic condition than in the alkaline condition. The impact of pH on the color of anthocyanins (chromophore) has been reported from pH 1 to 14. It is known that the anthocyanins are exhibiting four different ionic form in aqueous condition with respective pH such as flavylium cation (pH 1-3), carbinol pseudobases or hemiketals (pH 4-5), quinonoidal base (pH 6-8), and

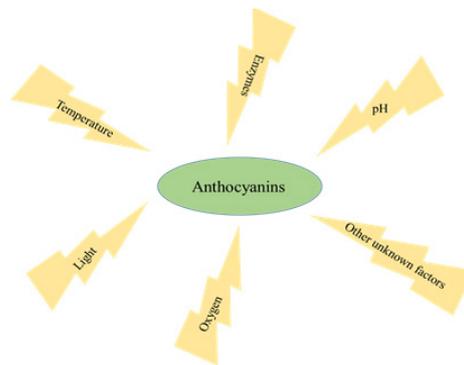


Figure 2. The factors frequently affecting the stability of anthocyanins.

chalcone (pH 7-8). The carbinol form is colorless, whereas chalcone form is more unsteady, and easily breaks into phenolic acid and aldehydes (Fleschhut *et al.*, 2006). The increase in pH reduces the bonding of conjugated heterocyclic ring that leads to open ring formation, and facilitates the degradation. Thus, flavylium cation in acidic condition is more stable, whereas, in alkaline condition, anthocyanins are prevailing as chalcone form, which is certainly susceptible to the degradation.

The high temperature will affect the glycosyl moieties and facilitates the hydrolysis of the glycosidic bond (Adams, 1973). Thermal degradation of anthocyanins has been reported as first order kinetics behavior (Rhim, 2002; Ahmed *et al.*, 2004). For example, strawberries and raspberries extracts, which contains anthocyanins can be stored for a long time under freezing condition (Kalt *et al.*, 1999), or above freezing temperature for a short time (Wang and Stretch, 2001). Anthocyanins are more delicate to a temperature at above 70°C. Sivamaruthi *et al.* (2016) has reported about the degradation of representative anthocyanidins (cyanidin, and peonidin) upon commonly used sterilization methods like microwave, heat, and sonication. The heat exposure (95°C for 2 hr) triggers the degradation of anthocyanins quickly, and about 90% of deformation was reported when compared with the microwave, and sonication methods (Sivamaruthi *et al.*, 2016).

Oxygen is one of the factors in promoting the degradation of anthocyanins. In the combination with temperature, oxygen fastens the anthocyanins degradation, whereas anaerobic condition protects the anthocyanins from decomposition. It is reported that the presence of spare oxygen stimulate the depigmentation in berry juices (Nebesky *et al.*, 1949), and the oxidation of anthocyanins lead to the browning of fruits and vegetables (Jackman *et al.*, 1987).

Although light is an essential factor required for the biosynthesis of pigments, it triggers the anthocyanin degradation faster than oxygen due to

the UV protective nature of anthocyanins. The light activates the flavylum cation to an excited state and leads to degradation (Furtado *et al.*, 1993). Thus, it is advisable to store the anthocyanin-rich food materials, and other formulations in dark at acidic condition (Kearsley and Rodriguez, 1981; Markakis, 1982).

Apart from physical factors, enzymes are the major biological factor that affects the stability of anthocyanins. For example, glycosidases are the destructive force of covalent bond of glycosyl residue in the aglycones (anthocyanidins) and sugar links of glycones (anthocyanin) (Huang, 1956). Moreover, phenolases (phenol oxidases and polyphenol oxidases) and peroxidases could react directly at the phenolic links of anthocyanins, possibly by the oxidation of phenolics and formation of quinines and browning of anthocyanins (Yokotsuka and Singleton, 1997; Garcia-Palazon *et al.*, 2004).

Distribution of anthocyanins in Thai rice cultivars

Thai rice cultivars

The survey of rice varieties in Thailand by the Rice Research Institute (1982-86) documented about 1,500 rice varieties in northeast Thailand (Chaidee and Thongpitak, 1992). Another survey revealed that only 18% of the rice land were occupied by the modern rice varieties during 1990's in Thailand (Rerkasem, 2007). In general, white rice, Hom Mali, Pathumthani fragrant rice, glutinous rice, husked rice, parboiled rice, broken parboiled rice are cultivated in all the part of Thailand and also exporting them to many places around the world (Office of Agricultural Economics, 2010). Only, the traditional rice cultivar, KDML 105, was widely cultivated along with the mutant varieties such as RD 6 and RD 15 (Rerkasem, 2007). In Thailand, many people are consuming glutinous sticky rice as their daily food, especially north and northeast Thai people. Several glutinous rice cultivars are being cultivated and consumed in large quantity, among which following are the most popular cultivars such as Sanpatong, RD6, and RD10 (Keeratipibula *et al.*, 2008).

Major phytochemicals of Thai rice

Several studies have been reported about the phytochemical content of Thai rice cultivars. The major phytochemical constituents of rice are phenolic acids, anthocyanins, tocopherols, and γ -oryzanol. The individual phenolic acids like caffeic acid, chlorogenic acid, protocatechuic acid, p-hydroxybenzoic acid, p-coumaric acid, and syringic acid were studied and recorded in Thai cultivars. The concentration and the presence of phenolic acid were found to be varied depends on the rice strain. Pengkumsri

et al. (2015a) reported the detailed phenolic acid, flavonoids, and anthocyanin content of Chiang Mai Black rice, Mali Red rice, and Suphanburi-1 Brown rice varieties of northern Thailand. The Chiang Mai black rice contains caffeic acid, protocatechuic acid, p-coumaric acid, and syringic acid, whereas, Mali red rice and Suphanburi-1 brown rice varieties have not been reported for the caffeic acid, and p-coumaric acid content, but these varieties were accounted for the presence of either p-hydroxybenzoic acid or chlorogenic acid (Pengkumsri *et al.*, 2015a). About 17.54 ± 0.75 , 17.54 ± 0.88 , and 18.49 ± 1.52 mg of γ -oryzanol per gram of Chiang Mai Black rice, Mali Red rice, and Suphanburi-1 Brown rice bran oil, respectively, were reported (Pengkumsri *et al.*, 2015b). The changes in the phenolic acid content, especially protocatechuic acid, and vanillic acid, of Thai purple rice by different cooking methods were reported (Chatthongpisut *et al.*, 2015).

Anthocyanins content

Black rice (*Oryza sativa* L. indica) is one of the anthocyanins rich rice cultivar, characterized with heavy pigmented outer layer. There are six commonly found aglycones, that covers 95% of total anthocyanins content, such as delphinidin (Dp), pelargonidin (Pg), peonidin (Pn), cyanidin (Cy), malvidin (Mv), and petunidin (Pt) found in rice (Eder, 2000; Kong *et al.*, 2003). The summary of the reported anthocyanin content in Thai rice varieties were tabulated (Table 1). Maisuthisakul and Changchub (2014) reported the anthocyanins content of nine Thai rice varieties namely Kum, Hawm kanya, Hawm nil, Sang yod, Red Jasmine, Hawm Ubon, Jasmine rice 105, Lao tek, and Sin lek. The impact of extraction methods on the yield of the phytochemicals was also reported. The Kum rice cultivar (black rice) noted to possess high anthocyanins content among the other tested samples, and acid hydrolysis method was best in terms of yield.

The anthocyanin content and antioxidant ability of three Thai rice varieties, namely, Phitsanulok 2 (non-pigmented rice), Niew Dam (glutinous black rice), and Hom Nil (black non-waxy rice) were reported with respect to soaking and germination time. The content of anthocyanins varied from 1.09 ± 0.75 to 10.80 ± 5.20 , 17.89 ± 12.20 to 103.45 ± 10.03 , and 3.22 ± 1.75 to 10.89 ± 3.64 mg/100g of Phitsanulok 2, Niew Dam, and Hom Nil rice, respectively (Sutharut and Sudarat, 2012). Another study also suggested that the Niew Dam rice contains the maximum amount of naturally occurring anthocyanin (109 mg/100g rice) (Sompong *et al.*, 2011).

Riceberry is a cross breed of Hom Nil rice

Table 1. Summary of reported anthocyanins content in Thai rice cultivars.

Cultivar / strain	Anthocyanins content	Remarks	References
1000-11-2-26	~ 2 / 26 µg/mL of extract	Pn-3-glu/Cy-3-glu content	Pitija et al., 2013
BC2F7#62-56 Black Rose	0.77 ± 0.0 mg/g fresh weight 0.06 ± 0.01 mg/L of extract	Cy-3-glu content monomeric anthocyanin content	Daiponmak et al., 2010 Suwannalert and Rattanachitthawat, 2011
Chiang Mai Black rice	5.69 ± 0.28 mg/g of extract (Cy-3-glu); 11.46 ± 0.57 mg/g of extract (Pn-3-glu)	Cy-3-glu, Pn-3-glu content in rice bran	Pengkumsri et al., 2015a
Hawm kanya	~40 / 140 mg/g of db	TAC (S/AH method)	Maisuthisakul and Changchub, 2014
Hawm nil	~45 / 151 mg/g of db	TAC (S/AH method)	Maisuthisakul and Changchub, 2014
Hawm Nil	1.08 ± 0.06 mg/ L of extract	monomeric anthocyanin content	Suwannalert and Rattanachitthawat, 2011
Hawm Ubon	~30 / 75 mg/g of db	TAC (S/AH method)	Maisuthisakul and Changchub, 2014
Hom Nil Ngok	0.262 ± 0.3 mg/mL of extract	TAC	Kitisin et al., 2015
Hom Nil Phayao	0.375 ± 0.0 mg/mL of extract	TAC	Kitisin et al., 2015
Hom Nil rice	3.32-1.89 mg/100 g of rice	Total anthocyanins content (TAC) in germinated rice	Sutharut and Sudarat, 2012
Hom Nil Tai Tai	1.038 ± 1.3 mg/mL of extract	TAC	Kitisin et al., 2015
Hom Nil Thinnakorn	1.365 ± 0.9 mg/mL of extract	TAC	Kitisin et al., 2015
Jaowdam208	54.34 ± 4.1 mg Mal. Eq/100 g of rice	TAC	Chakuton et al., 2012
Jaowdam209	42.38 ± 17.2 mg Mal. Eq/100 g of rice	TAC	Chakuton et al., 2012
Jasmine rice 105	~20 / 60 mg/g of db	TAC (S/AH method)	Maisuthisakul and Changchub, 2014
KDML 105	1.31 ± 0.1 mg/g fresh weight	Cy-3-glu content	Daiponmak et al., 2010
Kham	1.35 ± 0.0 mg/g fresh weight	Cy-3-glu content	Daiponmak et al., 2010
Khamdoisaket	9.95 ± 0.4 mg/g fresh weight	Cy-3-glu content	Daiponmak et al., 2010
Khao Hom Nin BD	2.43 / 16.01 µg/mL of extract	Pn-3-glu/Cy-3-glu content	Pitija et al., 2013
Khao Hom Nin BT	7.36 / 34.40 µg/mL of extract	Pn-3-glu/Cy-3-glu content	Pitija et al., 2013
Khao Hom Nin BT No. 3	~ 4 / 24 µg/mL of extract	Pn-3-glu/Cy-3-glu content	Pitija et al., 2013
Klam	7.36 ± 0.26 mg/L of extract	monomeric anthocyanin content	Suwannalert and Rattanachitthawat, 2011
Kum	~220 / 430 mg/g of db	TAC (S/AH method)	Maisuthisakul and Changchub, 2014
Lao tek	~15 / 40 mg/g of db	TAC (S/AH method)	Maisuthisakul and Changchub, 2014
Leum Phua	36.94 ± 0.97 mg/L of extract	monomeric anthocyanin content	Suwannalert and Rattanachitthawat, 2011
Mali Nil Surin No. 6	64.50 ± 0.2 mg/100 g of rice	TAC in Raw rice	Chatthongpisut et al., 2015
Mali Nil Surin No. 6	40.90 ± 0.3 mg/100 g of rice	TAC (Cooked rice by electric cooker)	Chatthongpisut et al., 2015
Mali Nil Surin No. 6	20.30 ± 0.1 mg/100 g of rice	TAC (Cooked rice by autoclave)	Chatthongpisut et al., 2015
Mali Nil Surin No. 6	11.00 ± 0.1 mg/100 g of rice	TAC (Cooked rice by microwave)	Chatthongpisut et al., 2015
Mali Nil Surin No. 6	492 µg/g of db (raw rice)	Cy-3-glu content	Chatthongpisut et al., 2015
Mali Nil Surin No. 6	~ 200 µg/g of db (raw rice)	Pn-3-glu content	Chatthongpisut et al., 2015
Mali Red rice	ND	Cy-3-glu; Pn-3-glu content in rice bran	Pengkumsri et al., 2015a
Mali-dang2-206	ND	TAC	Chakuton et al., 2012
Mun Poo HPM	0.111 ± 0.0 mg/mL of extract	TAC	Kitisin et al., 2015
Mun Poo Phayao	0.309 ± 0.0 mg/mL of extract	TAC	Kitisin et al., 2015
Mun Poo Pink	0.028 ± 0.0 mg/mL of extract	TAC	Kitisin et al., 2015
Neawdan1-202	9.23 ± 2. mg Mal. Eq/100 g of rice	TAC	Chakuton et al., 2012
Neawdan2-203	9.02 ± 3.8 mg Mal. Eq/100 g of rice	TAC	Chakuton et al., 2012
Neawdan53	1045.12 ± 4.4 mg Mal. Eq/100 g of rice	TAC	Chakuton et al., 2012
Niaw Dam Pleuak Khao	137.41 ± 16.66 / 11.07 ± 0.97 mg/100 g of DM	Cy-3-glu / Pn-3-glu content	Sompong et al., 2011
Niaw Dam Pleuak Dam	19.39 ± 0.09 / 12.75 ± 0.51 mg/100 g of DM	Cy-3-glu / Pn-3-glu content	Sompong et al., 2011
Niew Dam	17.89-99.53 mg/100 g of rice	TAC in germinated rice	Sutharut and Sudarat, 2012
Niew Dam Doi Hang	5.172 ± 0.6 mg/mL of extract	TAC	Kitisin et al., 2015
Niew Dam Phayao	1.247 ± 0.3 mg/mL of extract	TAC	Kitisin et al., 2015
Pa-mia97	2.10 ± 2.0 mg Mal. Eq/100 g of rice	TAC	Chakuton et al., 2012
Phitsanulok 2	1.09-10.83 mg/100 g of rice	TAC in germinated rice	Sutharut and Sudarat, 2012
Red Jasmine	~15 / 80 mg/g of db	TAC (S/AH method)	Maisuthisakul and Changchub, 2014
Riceberry	1.03 ± 0.1 mg/g fresh weight	Cy-3-glu content	Daiponmak et al., 2010
Sang yod	~20 / 95 mg/g of db	TAC (S/AH method)	Maisuthisakul and Changchub, 2014
Sang Yod Phattalung	0.128 ± 0.0 mg/mL of extract	TAC	Kitisin et al., 2015
Sang Yod Songkla	0.097 ± 0.0 mg/mL of extract	TAC	Kitisin et al., 2015
Sin lek	~20 / 70 mg/g of db	TAC (S/AH method)	Maisuthisakul and Changchub, 2014
Sin lek	1.02 ± 0.0 mg/g fresh weight	Cy-3-glu content	Daiponmak et al., 2010
Suphanburi-1 Brown rice	ND	Cy-3-glu; Pn-3-glu content in rice bran	Pengkumsri et al., 2015a
ULR012	~ 5.60 mg/g of grain	anthocyanin contents (average) [#]	Somsana et al., 2013
ULR017	~ 5.58 mg/g of grain	anthocyanin contents (average) [#]	Somsana et al., 2013
ULR038	~ 4.35 mg/g of grain	anthocyanin contents (average) [#]	Somsana et al., 2013
ULR046	~ 7.10 mg/g of grain	anthocyanin contents (average) [#]	Somsana et al., 2013
ULR238	~ 7.16 mg/g of grain	anthocyanin contents (average) [#]	Somsana et al., 2013
ULR239	~ 5.88 mg/g of grain	anthocyanin contents (average) [#]	Somsana et al., 2013
ULR291	~ 5.68 mg/g of grain	anthocyanin contents (average) [#]	Somsana et al., 2013
Wongwan98	9.02 ± 0.9 mg Mal. Eq/100 g of rice	TAC	Chakuton et al., 2012

ND: Not detected; S/AH: Soaking / acid hydrolysis method; db: Dry basis; Cy-3-glu: Cyanidin-3-glucoside; Pn-3-glu: Peonidin-3-glucoside; mg Mal. Eq.: mg malvidin equivalent; DM: dry matter; #average of anthocyanin contents in rice cultivated at different environmental conditions

and Khao Dawk Mali 105, and it is recognized for possessing high content of peonidin and cyanidin (66.76 and 150.81 mg/100g of rice, respectively) (Jittorntrum *et al.*, 2009). The impact of salt stress on the anthocyanins content of Riceberry, Kham, Khamdoisaket, KDML 105, Sinlek, and BC2F7#62-56 varieties were reported. The concentration of cyanidin-3-glucoside of Khamdoisaket and KDML105 increased considerably after 60mM of salt treatment, whereas slight or no significant changes were witnessed in Riceberry, Kham and Sinlek, and BC2F7#62-56 (Daiponmak *et al.*, 2010).

The ethanolic extract of some of the Thai rice varieties (Mun Poo Phayao, Mun Poo Pink, Mun Poo HPM, Sang Yod Phattalung, Sang Yod Songkla, Niew Dam Phayao, Niew Dam Doi Hang, Hom Nil Ngok, Hom Nil Tai Tai, Hom Nil Thinnakorn, Hom Nil Phayao) were studied for determining the anthocyanins content, and the average concentration of anthocyanins were found to be varied from 0.636 ± 0.393 to 1.428 ± 0.985 mg GAE/mL extract. To the maximum of 2.849 ± 0.104 mg GAE/mL extract of total anthocyanins was recorded in Mun Poo Pink (Kitisin *et al.*, 2015).

The influence of cooking strategies and changes in the anthocyanin content of the Thai purple rice was reported. The total anthocyanins content was 64.5 ± 0.2 mg/100g of raw rice, 40.9 ± 0.3 , 20.3 ± 0.1 , and 11.0 ± 0.1 mg/100g of rice cooked using rice cooker, autoclave and microwave, respectively. The major anthocyanins in Thai purple rice were found as 3-glucosides of peonidin and cyanidin (Chatthongpisut *et al.*, 2015). The results revealed that the quality of the rice regarding anthocyanins was demolished by the regular cooking processes, especially by microwaves. The 3-glucosides of peonidin and cyanidin content of Mali Nil Surin No.6 rice was about 200 μ g/g dry weight and 492 μ g/g dry weight, respectively. The Mali Nil Surin No.6 rice strain was superior to black rice, *O. sativa* L. japonica var. SBR (Hiemori *et al.*, 2009) and Korean black rice cultivars namely, Sinnongheugchal and Sintoheugmi (Surh and Koh, 2014) regarding peonidin-3-glucoside content. About 41.7% and 74.2% of degradation of 3-glucosides of peonidin and cyanidin were reported in Thai purple rice upon cooking processes. The studies suggested that peonidin-3-glucoside is relatively stable than cyanidin-3-glucoside against temperature mediated damages (Hiemori *et al.*, 2009; Chatthongpisut *et al.*, 2015).

Chakuton *et al.* (2012) documented the anthocyanin content of commonly used eight colored local Thai rice cultivars such as Neawdan53, Pamiya97, Wongwan98, Neawdan1-202, Neawdan2-203,

Malii-dang2-206, Jaowdam208, and Jaowdam209. The Leum Phua, Klam, Hawm Nil, and Black Rose cultivars were subjected to the phytochemical analysis, and the study found that Leum Phua has a high concentration of anthocyanin, phenolic compounds than that of the other tested varieties (Suwannalert and Rattanachitthawat, 2011).

Some of the genetically related Thai black rice varieties (Khao Hom Nin BT, Khao Hom Nin BD, Khao Hom Nin BT No. 3, and 1000-11-2-26.) were assessed for the anthocyanins content, and the results indicated that the major anthocyanins and its levels were ranging from 16.01–34.40 μ g/mL (cy-3-O-gluc) and 2.43–7.36 (pe-3-O-gluc) μ g/mL. The strain Khao Hom Nin BT exhibited the high content of anthocyanin than that of the other tested samples (Pitija *et al.*, 2013).

Sompong *et al.* (2011) detailed about the anthocyanins distribution among the Thai black, and red rice varieties such as Niaw Dam Pleuak Dam, Niaw Dam Pleuak Khao, Bahng Gawk, Niaw Dawk Yong, Niaw Look Pueng, Haek Yah, Niaw Lan Tan and Sung Yod Phatthalung. Obviously, the black rice varieties Niaw Dam Pleuak Khao, and Niaw Dam Pleuak Dam were recognized for possessing high content of anthocyanins (19.39 ± 0.09 - 137.41 ± 16.66 mg/100g of rice).

Seven promising Thai black indigenous rice varieties such as ULR012, ULR017, ULR038, ULR046, ULR238, ULR239, and ULR291 were studied in detail for determining the anthocyanin content upon changes in environmental conditions. The results indicated that the average anthocyanins concentration were recorded in ULR012, ULR017, ULR038, ULR046, ULR238, ULR239, and ULR291, respectively with tested environmental influences (Somsana *et al.*, 2013). We have reported the phytochemical and anthocyanin content of three Thai rice strains namely Mali Red rice, Chiang Mai Black rice, and Suphanburi-1 Brown rice cultivars with different extraction methods. The results indicated that Chiang Mai Black rice have the maximum amount of phytochemicals, anthocyanins, and bioactivities than that of the other tested samples (Pengkumsri *et al.*, 2015a).

Pharmacological importance of anthocyanins

Health promoting properties of anthocyanins from dietary sources are beneficial for human health (Figure 3, Table 2). The anthocyanins are recognized for its several health benefits such as free radical scavenger, anti-inflammatory, anti-cancer, anti-obesity, anti-diabetes candidate, and also for the cardio protective nature, antimicrobial property,

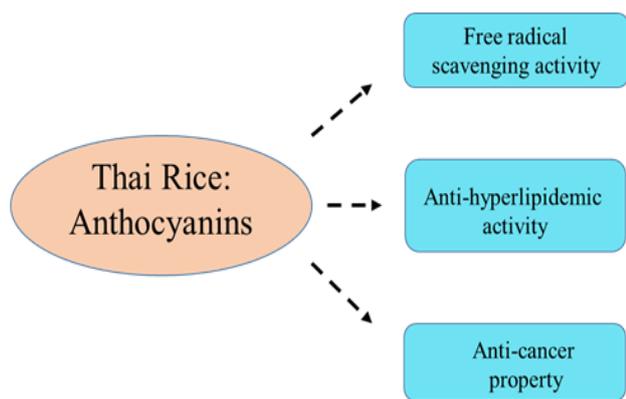


Figure 3. The reported pharmacological importance of anthocyanins of Thai rice cultivars.

etc. (He and Giusti, 2010; Pojer *et al.*, 2013; Reis *et al.*, 2016). Yao *et al.* (2013) investigated the role of anthocyanins of black rice in controlling the cholesterol levels *in vitro* conditions. They revealed that 3-glucosides of cyanidin and peonidin in the black rice extract effectively reduced the absorption of cholesterol in Caco-2 cells (Yao *et al.*, 2013). Yu group studied the protective role of anthocyanins of black rice against the breast cancer using the human breast cancer cells that are positive for human epidermal growth factor receptor 2. They evidenced that the anthocyanins of black rice exhibited metastasis inhibition ability both *in vitro* and *in vivo* models (Luo *et al.*, 2014). Yu group also revealed that anthocyanins of black rice suppress the activation of RAS/RAF/MAPK signaling pathway players to inhibit the metastasis in the human breast cancer cells (Chen *et al.*, 2015). Another study by Chung group showed that anthocyanins of black rice exhibited anti-metastasis ability by inhibiting the activation of NF- κ B and PI3K/Akt pathway players in human oral cancer cells (Fan *et al.*, 2015). Shimoda group have reported that intake of anthocyanin rich purple rice extract (single dose: 25 mg) effectively reduced the raise of postprandial blood sugar that occurs after the consumption of 200g rice ball by the healthy human subjects (Shimoda *et al.*, 2015).

Many studies have been reported on the benefits of anthocyanins isolated from the rice varieties of Thailand (Table 1). Sangkitikomol *et al.* (2010) has reported the health promoting properties (antioxidant and anti-hyperlipidemic activity) of Thai black sticky rice using HepG2 cells. The Thai black sticky rice extract that is rich in anthocyanins reduced the oxidative stress and regulated the expression of low-density lipoprotein receptor gene in HepG2 cells (Sangkitikomol *et al.*, 2010).

Leardkamolkarn *et al.* (2011) reported the chemopreventive properties of the Thai rice (Riceberry)

Table 2. Health promoting properties of anthocyanin of Thai rice.

S. No	Beneficial effects	Thai Rice	Reference
1	Antioxidant activity	Thai black sticky rice	Sangkitikomol <i>et al.</i> , 2010
		Leum Phua	Suwannalert and Rattanachitthawat, 2011
		Thai Black rice	Pitija, 2013
		Thai purple rice	Chatthongpisut <i>et al.</i> , 2015
2	Anti-carcinogenic activity	Riceberry	Leardkamolkarn <i>et al.</i> , 2011
		Payao purple rice	Banjerdpongchai <i>et al.</i> , 2013
		Thai purple rice	Chatthongpisut <i>et al.</i> , 2015
3	Anti-hyperlipidemic activity	Thai black sticky rice	Sangkitikomol <i>et al.</i> , 2010
4	Improvement in learning and memory impairment	Thai Black sticky rice	Kangwan <i>et al.</i> , 2015

bran using Caco-2, MCF-7, and HL-60 cells. The methanolic extract of Riceberry bran showed anti-cancer properties, which was mainly due to the presence of peonidin-3-glucoside and cyanidin-3-glucoside (Leardkamolkarn *et al.*, 2011). Similarly, the 3-O-glucosides of peonidin and cyanidin was reported as the major anthocyanins of Thai black rice, and the extract of Thai black rice bran showed high antioxidant activity (Pitija, 2013). Leum Phua (unpolished Thai rice) exhibited a high content of total phenolic content, anthocyanin content, and antioxidant activity when compared with the other varieties of Thai rice namely, Black Rose, Hawm Nil, and Klam (Suwannalert and Rattanachitthawat, 2011).

Banjerdpongchai *et al.* (2013) reported the anti-carcinogenic activity of purple rice of Payao, Thailand. The methanolic extract of Payao purple rice showed the cytotoxic effect on human HepG2 cells by inducing apoptosis via the mitochondrial pathway. The extract also exhibited synergistic effect by increasing the cytotoxic effect of vinblastine (Banjerdpongchai *et al.*, 2013). Chatthongpisut *et al.* (2015) reported the anticancer activity of Thai purple rice using human colon cancer cells. The methanolic extract of cooked (sterilization) Thai purple rice showed high antioxidant and anti-proliferative activity on Caco-2 cells (Chatthongpisut *et al.*, 2015). Suttajit group investigated the health promoting property of anthocyanin extracted from black sticky rice of Payao, Thailand and revealed that the anthocyanin of Thai black rice extract effectively enhanced the learning and memory in cerebral-

ischaemia mice model (Kangwan *et al.*, 2015).

Recommended dosage of anthocyanins

The recommended daily dosage for the consumption of anthocyanins by humans differ among the countries. Italy, New Zealand, and Korea have been prescribing the anthocyanins as medicine. Whereas in Japan and U.S.A, anthocyanins are recognized as a health supplement. Based on the *in vivo* studies, acceptable daily consumption of anthocyanins is 2.5 mg/kg of body weight (Clifford 2000; He and Giusti, 2010). As per the Japan Health Food and Nutrition Food Association, 29 mg of anthocyanins per day is the recommended dose for human consumption (Yamamoto *et al.*, 2013).

Conclusion

Several studies have been reported about the phytochemical content of Thai rice cultivars and its changes upon different processing conditions, and environmental changes. Whereas, the biological activity of Thai rice extract, especially anthocyanins, are poorly reported when compared to other rice varieties. Recent studies have revealed the health beneficial effects of Thai rice anthocyanins like antioxidant, anti-carcinogenic and anti-hyperlipidemic activity. Anthocyanin of Thai black glutinous rice has also been reported for its role in effectively improving the learning and memory impairment. Further detailed study on anti-inflammatory, anti-diabetes, and anti-obesity properties of Thai rice and its active phytochemicals are required to explore the natural remedies for the diseases, and metabolic disorders.

Acknowledgments

All the authors thankfully acknowledge the Faculty of Pharmacy and Chiang Mai University, Chiang Mai for the essential support. BSS also gratefully acknowledges the CMU Post-Doctoral Fellowship.

References

- Adams, J. B. 1973. Thermal degradation of anthocyanins with particular reference to the 3-glycosides of cyanidin. I. In acidified aqueous solution at 100° C. *Journal of the Science of Food and Agriculture* 24(7): 747-762.
- Ahmed, J., Shivhare, U. S. and Raghavan, G. S. V. 2004. Thermal degradation kinetics of anthocyanin and visual colour of plum puree. *European Food Research and Technology* 218(6): 525-528.
- Andersen, O. M. 2001. Anthocyanins. In *Encyclopedia of Life Sciences (ELS)*. London: John Wiley and Sons. doi:10.1038/npg.els.0001909.
- Banjerdpongchai, R., Wudtiwai, B. and Sringarm, K. 2013. Cytotoxic and apoptotic-inducing effects of purple rice extracts and chemotherapeutic drugs on Human cancer cell lines. *Asian Pacific Journal of Cancer Prevention* 14(11): 6541-6548.
- Castañeda-Ovando, A., Pacheco-Hernández, M., Paez-Hernández, M. E., Rodríguez, J. A. and Galán-Vidal, C. A. 2009. Chemical studies of anthocyanins: a review. *Food Chemistry* 113: 859-871.
- Chaidee, S. and Thongpitak, P. 1992. Local rice variety cultivation situation in 17 provinces of Northeast Region. Ubon Rice Research Center, Rice Research Institute, Department of Agriculture, Thailand. (In Thai.) p. 238.
- Chaiyasut, C., Sivamaruthi, B. S., Pengkumsri, N., Sirilun, S., Peerajan, S., Chaiyasut, K. and Kesika, P. 2016. Anthocyanin profile and its antioxidant activity of widely used fruits, vegetables, and flowers in Thailand. *Asian Journal of Pharmaceutical and Clinical Research* 9(6): 218-224.
- Chakuton, K., Puangpronpitag, D. and Nakornriab, M. 2012. Phytochemical content and antioxidant activity of colored and non-colored Thai rice cultivars. *Asian Journal of Plant sciences* 11(6): 258-293.
- Chatthongpisut, R., Schwartz, S. J. and Yongsawatdigul, J. 2015. Antioxidant activities and antiproliferative activity of Thai purple rice cooked by various methods on human colon cancer cells. *Food Chemistry* 188: 99-105.
- Chen, X. Y., Zhou, J., Luo, L. P., Han, B., Li, F., Chen, J. Y., Zhu, Y. F., Chen, W. and Yu, X. P. 2015. Black Rice Anthocyanins Suppress Metastasis of Breast Cancer Cells by Targeting RAS/RAF/MAPK Pathway. *Biomed Research International* 2015: 414250. doi: 10.1155/2015/414250.
- Clifford, M. N. 2000. Anthocyanins-nature, occurrence and dietary burden. *Journal of the Science of Food and Agriculture* 80: 1063-1072.
- Cortez, R., Luna-Vital, D. A., Margulis, D. and Gonzalez de Mejia, E. 2017. Natural pigments: Stabilization methods of anthocyanins for food applications. *Comprehensive Reviews in Food Science and Food Safety* 16(1): 180-198.
- Daiponmaka, W., Theerakulpisut, P., Thanonkao, P., Vanavichit, A. and Prathepha, P. 2010. Changes of anthocyanin cyanidin-3-glucoside content and antioxidant activity in Thai rice varieties under salinity stress. *ScienceAsia* 36: 286-291.
- Eder, R. 2000. Pigments. In Nolle, L. M. L. (Ed). *Food Analysis by HPLC*, p. 845-880. Monticello, NY: Marcel Dekker.
- Fan, M. J., Wang, I. C., Hsiao, Y. T., Lin, H. Y., Tang, N. Y., Hung, T. C., Quan, C., Lien, J. C. and Chung, J. G. 2015. Anthocyanins from black rice (*Oryza sativa* L.) demonstrate antimetastatic properties by reducing MMPs and NF-κB expressions in human oral cancer CAL 27 cells. *Nutrition and Cancer* 67(2): 327-338.

- Fleschhut, J., Kratzer, F., Rechkemmer, G. and Kulling, S. E. 2006. Stability and biotransformation of various dietary anthocyanins *in vitro*. *European Journal of Nutrition* 45(1): 7-18.
- Furtado, P., Figueiredo, P., das Neves, H. C. and Pina, F. 1993. Photochemical and thermal degradation of anthocyanidins. *Journal of Photochemistry and Photobiology A: Chemistry* 75(2): 113-118.
- Garcia-Palazon, A., Suthanthangjai, W., Kajda, P. and Zabetakis, I. 2004. The effects of high hydrostatic pressure on β -glucosidase, peroxidase and polyphenoloxidase in red raspberry (*Rubus idaeus*) and strawberry (*Fragaria* \times *ananassa*). *Food Chemistry* 88(1): 7-10.
- Glover, B. J. and Martin, C. 2012. Anthocyanins. *Current Biology* 22(5): R147-R150
- Goufo, P. and Trindade, H. 2014. Rice antioxidants: phenolic acids, flavonoids, anthocyanins, proanthocyanidins, tocopherols, tocotrienols, γ -oryzanol, and phytic acid. *Food Science and Nutrition* 2(2): 75-104.
- He, J. and Giusti, M. M. 2010. Anthocyanins: natural colorants with health-promoting properties. *Annual Review of Food Science and Technology* 1: 163-187.
- Henderson, A. J., Ollila, C. A., Kumar, A., Borresen, E. C., Raina, K., Agarwal, R. and Ryan, E. P. 2012. Chemopreventive properties of dietary rice bran: Current status and future prospects. *Advances in Nutrition: An International Review Journal* 3(5): 643-653.
- Hiemori, M., Koh, E. and Mitchell, A. E. 2009. Influence of cooking on anthocyanins in black rice (*Oryza sativa* L. japonica var. SBR). *Journal of Agricultural and Food Chemistry* 57(5): 1908-1914.
- Hu, C., Zawistowski, J., Ling, W. and Kitts, D. D. 2003. Black rice (*Oryza sativa* L. indica) pigmented fraction suppresses both reactive oxygen species and nitric oxide in chemical and biological model systems. *Journal of Agricultural and Food Chemistry* 51(18): 5271-5277.
- Huang, H. T. 1956. The Kinetics of the Decolorization of Anthocyanins by Fungal "Anthocyanase". *Journal of the American Chemical Society* 78(11): 2390-2393.
- Jackman, R. L., Yada, R. Y., Tung, M. A. and Speers, R. 1987. Anthocyanins as food colorants-a review. *Journal of Food Biochemistry* 11(3): 201-247.
- Jittorntrum, B., Chunhabundit, R., Kongkachuichai, R., Srisala, S. and Visetpanit, Y. 2009. Cytoprotective and cytotoxic effects of rice bran extracts on H₂O₂-induced oxidative damage in human intestinal Caco-2 cells. *Thai Journal of Toxicology* 24(2): 92-100.
- Kalt, W., Forney, C. F., Martin, A. and Prior, R. L. 1999. Antioxidant capacity, vitamin C, phenolics, and anthocyanins after fresh storage of small fruits. *Journal of Agricultural and Food Chemistry* 47(11): 4638-4644.
- Kangwan, N., Pintha, K., Preedapirom, W., Tantipaiboonwong, P., Chumphukam, O. and Suttajit, M. 2015. Learning and memory enhancing effects of anthocyanin in black rice extract on cerebral ischaemia in mice. *ScienceAsia* 41: 315-321.
- Kearsley, M. W. and Rodriguez, N. 1981. The stability and use of natural colors in foods: anthocyanin, β -carotene and riboflavin. *International Journal of Food Science and Technology* 16(4): 421-431.
- Keeratipibula, S., Luangsakulb, N. and Lertsatchayarn, T. 2008. The effect of Thai glutinous rice cultivars, grain length and cultivating locations on the quality of rice cracker (arare). *LWT - Food Science and Technology* 41(10): 1934-1943.
- Kitisin, T., Saewan, N. and Luplertlop, N. 2015. Potential anti-inflammatory and anti-oxidative properties of Thai colored-rice extracts. *Plant Omics Journal* 8(1): 69-77.
- Kong, J. M., Chia, L. S., Goh, N. K., Chia, T. F. and Brouillard, R. 2003. Analysis and biological activities of anthocyanins. *Phytochemistry* 64(5): 923-933.
- Kushwaha, U. K. S. 2016. Black rice: Research, history and development. 1st ed. Switzerland: Springer International Publishing. doi:10.1007/978-3-319-30153-2.
- Lamberts, L. and Delcour, J. A. 2008. Carotenoids in raw and parboiled brown and milled rice. *Journal of Agricultural and Food Chemistry* 56(24): 11914-11919.
- Leardkamolkarn, V., Thongthep, W., Suttiarporn, P., Kongkachuichai, R., Wongpornchai, S. and Wanavijitr, A. 2011. Chemopreventive properties of the bran extracted from a newly-developed Thai rice: The Riceberry. *Food Chemistry* 125: 978-985.
- Lucioli, S. 2012. Anthocyanins: mechanism of action and therapeutic efficacy. In Capasso, A. (Ed). *Medicinal plants as antioxidant agents: Understanding their mechanism of action and therapeutic efficacy*, p. 27-57. India: Research Signpost.
- Luo, L. P., Han, B., Yu, X. P., Chen, X. Y., Zhou, J., Chen, W., Zhu, Y. F., Peng, X. L., Zou, Q. and Li, S. Y. 2014. Anti-metastasis activity of black rice anthocyanins against breast cancer: analyses using an ErbB2 positive breast cancer cell line and tumoral xenograft model. *Asian Pacific Journal of Cancer Prevention* 15(15): 6219-6225.
- Maisuthisakul, P. and Changchub, L. 2014. Effect of extraction on phenolic antioxidant of different Thai rice (*Oryza Sativa* L.) Genotypes, *International Journal of Food Properties* 17(4): 855-865.
- Markakis, P. 1982. Stability of anthocyanins in foods. In Markakis, P. (Ed). *Anthocyanins as food colors*, p. 163-178. New York: Academic Press Inc.
- Nebesky, E. A., Esselen, W. B., Connell, M., John, E. and Fellers, C. R. 1949. Stability of color in fruit juices. *Journal of Food Science* 14(3): 261-274.
- Office of Agricultural Economics (OAE), Ministry of Agriculture and Cooperatives (Thailand). 2010. Retrieved on July 21, 2016 from OAE Website http://www.oae.go.th/main.php?filename=index__EN
- Pengkumsri, N., Chaiyasut, C., Saenjum, C., Sirilun, S., Peerajan, S., Suwannalert, P., Sirisattha, S. and Sivamaruthi, B. S. 2015a. Physicochemical and antioxidative properties of black, brown and red rice varieties of northern Thailand. *Food Science and*

- Technology (Campinas) 35(2): 331-338.
- Pengkumsri, N., Chaivasut, C., Sivamaruthi, B. S., Saenjum, C., Sirilun, S., Peerajan, S., Suwannalert, P., Sirisattha, S., Chaivasut, K. and Kesika, P. 2015b. The influence of extraction methods on composition and antioxidant properties of rice bran oil. *Food Science and Technology (Campinas)* 35(3): 493-501.
- Pitija, K., Nakornriab, M., Sriseadka, T., Vanavichit, A. and Wongpornchai, S. 2013. Anthocyanin content and antioxidant capacity in bran extracts of some Thai black rice varieties. *International Journal of Food Science and Technology* 48: 300-308.
- Pojer, E., Mattivi, F., Johnson, D. and Stockley, C. S. 2013. The case for anthocyanin consumption to promote human health: A review. *Comprehensive Reviews in Food Science and Food Safety* 12(5): 483-508.
- Reis, J. F., Monteiro, V. V., de Souza Gomes, R.2., do Carmo, M. M., da Costa, G. V., Ribera, P. C. and Monteiro, M. C. 2016. Action mechanism and cardiovascular effect of anthocyanins: a systematic review of animal and human studies. *Journal of Translational Medicine* 14(1): 315. doi:10.1186/s12967-016-1076-5.
- Rerkasem, B. 2007. Having your rice and eating it too: a view of Thailand's green revolution. *ScienceAsia* 33(S1): 75-80.
- Rhim, J. W. 2002. Kinetics of thermal degradation of anthocyanin pigment solutions driven from red flower cabbage. *Food Science and Biotechnology* 11(4): 361-364.
- Ryan, E. P., Heuberger, A. L., Weir, T. L., Barnett, B., Broeckling, C. D. and Prenni, J. E. 2011. Rice bran fermented with *Saccharomyces boulardii* generates novel metabolite profiles with bioactivity. *Journal of Agricultural and Food Chemistry* 59(5): 1862-1870.
- Sangkitikomol, W., Tencomnao, T. and Rocejanasaroj, A. 2010. Effects of Thai black sticky rice extract on oxidative stress and lipid metabolism gene expression in HepG2 cells. *Genetics and Molecular Research* 9(4): 2086-2095.
- Shimoda, H., Aitani, M., Tanaka, J. and Hitoe, S. 2015. Purple Rice Extract Exhibits Preventive Activities on Experimental Diabetes Models and Human Subjects. *Journal of Rice Research* 3(2): 137. doi:10.4172/2375-4338.1000137.
- Sivamaruthi, B. S., Pengkumsri, N., Saelee, M., Kesika, P., Sirilun, S., Peerajan, S. and Chaivasut, C. 2016. Impact of physical treatments on stability and radical scavenging capacity of anthocyanidins. *International Journal of Pharmacy and Pharmaceutical Sciences* 8(1): 162-167.
- Smeriglio, A., Monteleone, D. and Trombetta, D. 2014. Health effects of *Vaccinium myrtillus* L.: Evaluation of efficacy and technological strategies for preservation of active ingredients. *Mini-Reviews in Medicinal Chemistry* 14(7): 567-584.
- Sompong, R., Siebenhandl-Ehn, S., Linsberger-Martin, G. and Berghofer, G. E. 2011. Physicochemical and antioxidative properties of red and black rice varieties from Thailand, China and Sri Lanka. *Food Chemistry* 124: 132-140.
- Somsana, P., Wattana, P., Suriharn, B. and Sanitchon, J. 2013. Stability and genotype by environment interactions for grain anthocyanin content of Thai black glutinous upland rice (*Oryza sativa*). *SABRAO Journal of Breeding and Genetics* 45(3): 523-532.
- Stintzing, F. C. and Carle, R. 2004. Functional properties of anthocyanins and betalains in plants, food, and in human nutrition. *Trends in Food Science and Technology* 15(1): 19-38.
- Surh, J. and Koh, E. 2014. Effects of four different cooking methods on anthocyanins, total phenolics and antioxidant activity of black rice. *Journal of the Science of Food and Agriculture* 94(15): 3296-3304.
- Sutharut, J. and Sudarat, J. 2012. Total anthocyanin content and antioxidant activity of germinated colored rice. *International Food Research Journal* 19(1): 215-221.
- Suwannalert, P. and Rattanachitthawat, S. 2011. High levels of phytochemicals and antioxidant activities in *Oryza sativa*-unpolished Thai rice strain of Leum Phua. *Tropical Journal of Pharmaceutical Research* 10(4): 431-436.
- Timberlake, C. F. and Bridle, P. 1966. Effects of substituents on the ionization of flavylum salts and anthocyanins and their reactions with sulfur dioxide. *Chemistry and Industry* 2: 1965-1966.
- Trouillas, P., Sancho-García, J.C., De Freitas, V., Gierschner, J., Otyepka, M. and Dangles, O. 2016. Stabilizing and modulating color by copigmentation: Insights from theory and experiment. *Chemical Reviews* 116(9): 4937-4982.
- Wang, S. Y. and Stretch, A. W. 2001. Antioxidant capacity in cranberry is influenced by cultivar and storage temperature. *Journal of Agricultural and Food Chemistry* 49(2): 969-974.
- Yamamoto, M., Yamaura, K., Ishiwatari, M. and Ueno, K. 2013. Difficulty for consumers in choosing commercial bilberry supplements by relying only on product label information. *Pharmacognosy Research* 5(3): 212-215.
- Yao, S.L., Xu, Y., Zhang, Y.Y. and Lu, Y.H. 2013. Black rice and anthocyanins induce inhibition of cholesterol absorption in vitro. *Food and Function* 4(11): 1602-1608.
- Yokotsuka, K. and Singleton, V. L. 1997. Disappearance of anthocyanins as grape juice is prepared and oxidized with PPO and PPO substrates. *American Journal of Enology and Viticulture* 48(1): 13-25.