Effect of various heat treatment on physical and chemical characteristics of red rice bran (Oryza nivara L.) Rojolele

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Abstract. This research aims to study the effect of various heat treatment on physical and chemical characteristics of red rice bran (Oryza nivara L.) Rojolele. This study used a Completely Randomized Design (CRD) with one-factor variations of heat treatment applied on the bran. The various heat treatments use Oven an hour (80°C and 100°C), Microwave maximum temperature (2 and 5 minutes), and Autoclave 150°C (5 and 10 minutes). Results showed that all heat treatment methods decrease L value. The highest moisture level is on heating by microwave for 2 min. There were no significant difference in the level of ash, fat, and antioxidant activity. The FFA content was decreased by all heating treatment. The fenol level with heating with Oven 80°C an hour was the highest. Among the treatments, Oven an hour at 80°C is the best method. This method produces red rice bran with characteristics of lightness, water content, ash, fat, protein, total phenol, antioxidant activity, crude fiber, and free fatty acid content respectively 49.78; 5.51%; 8.37%; 27.11%; 10.50%; 0.25%; 75.88%; 9.30%; and 13.48%. Red rice bran Rojolele also contains anthocyanin and thiamin obtained from spectroscopy FTIR.

1. Introduction

Red rice (Oryza nivara L.) is a type of rice, that color of red. The red color of rice is caused by the presence of anthocyanins on the outside of the rice seeds. Red rice contains many higher nutritional compound compared to white rice. Red rice has soluble fiber and rich in vitamin B [1]. Nutritional compounds in red rice are 14.38% water, 9.16% protein and 2.5% fat [2].

Rice bran, a natural by-product obtained from the milling process of rice, is the outer layer of rice grains and includes a small portion of starch endosperms [3]. Rice bran generally consists of several pericarp tissues, seed coat, nucelus, aleurome layer, embryo (germ), a little chaff and a little endosperm. The process of rice milling or silting produces 8-18% rice bran [4]. Red rice bran has a high nutritional content there are carbohydrate content of 48.3-50.7%, crude protein 15.7-17.2%, fat 23.3-24.9%, ash 9.2-11.3 %, and moisture content 9.61-14.74% [5]. The high-fat content in rice bran caused it to be able to experience both oxidative and hydrolytic damage [6]. Rancidity in rice bran is caused by enzymes such as lipases, that hydrolyzing fat into fatty acids and glycerol. Free fatty acids are oxidized to peroxide, ketones, and aldehydes causing rancidity [7]. Hydrolytic damage is caused by the interaction of fat with water [8]. Rice bran damage during the storage process due to the formation of free fatty acids from enzymatic reactions. The three free fatty acids that are formed are palmitic acid, oleic acid, and linoleic acid. The free fatty acids formed an oxidative reaction which
causes a rice bran rancidity [9]. One way to increase the stability of rice bran is by using heating treatment.

Rice bran stabilization method can be done by wet heating, dry heating, and microwaves. Wet heating is one of the effective methods for the rice bran stabilization process. Pressure is needed to maintain moisture loss during the heating process. The combination of wet and autoclave pressurization methods was carried out at 1050°C for 5 and 10 minutes [4]. The stabilization method with dry heating using an oven is heated at a temperature of 800°C and 1000°C for 1 hour. Stabilization with the oven causes increased the shelf life of white rice bran and prevents damage from oxidative damage [10].

Another method that can be used for stabilization is a microwave. The use of a microwave to reduce the water content of rice bran so that the water in the material does not interact with fat causes rancidity [11]. Microwave heating aims to activate the lipases so that the enzyme does not interact with the surface of water and oil so that it does not cause damage to the rice bran [9]. Research conducted by Kim et al. (2014) shows that the stabilization of microwave white rice bran can be done with a maximum temperature of 2 and 5 min. This research aims to study the effect of various heat treatment on physical and chemical characteristics of red rice bran (Oryza nivara L.) Rojolele.

2. Materials and Methods

2.1 Materials

The red rice bran (Oryza nivara L.) Rojolele was provided by Abdi Bumi Lestari Farmers Group, Karangpandan Village, Karanganyar Regency. The materials used for chemical analysis were purchased from Merck (Germany) and Sigma-Aldrich (USA). The tools used for chemical analysis are weigh bottles (Pyrex), porcelain crucibles, ovens (Memert UNB 400), desiccators (AS ONE), ignition furnaces (Necraft), clamps, analytical balance sheets (Ohaus), kjeldahl flasks, measuring cups (Pyrex), measuring cup, water bath (Memert), vortex, test tube, rotary evaporator (KNF RC 600), UV-Vis spectrophotometer (Spectronic 20 D+), spectrophotometer IR (Shimadzu IRPrestige 21), and Chromameter (Konika Minolta CR-400).

2.2 Methods

2.2.1. Preliminary Treatment of Red Rice Bran

Red rice bran before analysis was screened through a 60-mesh sieve to have a uniform particle size.

2.2.2. Stabilization by Various Heat Treatment (Oven, Microwave, and Autoclave)

Stabilization by heat treatment using an oven refers to the research of Kim et al., (2014) [10]. Red rice bran was transferred into shallow pans and spread uniformly in a layer of about 0.5 cm thickness. The pans were then placed in an oven at 80 and 100°C for 1 h. Heat treatment using a microwave begins with the addition of distilled water to a moisture content of 20% [10]. Before heating the rice bran, the microwave is heated at maximum temperature for 3 min to get a stable temperature and effective heating. Rice bran was transferred into shallow pans and spread uniformly in a layer of about 1.5 cm thickness and covered with plastic wrap then heated using a maximum temperature (120°C) for 2 min and 5 min [9]. Autoclave heating was carried out with 1 cm rice bran thickness wrapped in a filter cloth then heated at a 105°C pressure of 1 atm for 5 min and 10 min. The sample is then dried with a cabinet dryer at 50°C for 1 hour. All heat treated samples were sealed polyethylene bags and then stored in a freezer at -20°C until analysis.

2.2.3 Method of Analysis

Chemical analysis was conducted on water content by thermogravimetric method [12], ash content by dry ignition method [12], fat content by the Soxhlet extraction method [12], protein content by micro-Kjeldahl method [12], carbohydrate content by difference method [12], crude fiber content [12], antioxidant activity by DPPH immersion method [13], total phenol by the folin-ciocalteu method [13], free fatty acids by gravimetric method [10] and structure FTIR functional group [14]. The physical analysis was conducted on the form of color values were measures using a chromameter [15].
3. Results and Discussion

3.1 Effects of Various Heat Treatment on Color of Red Rice Bran

The color analysis conducted using chromameter to get the value of L*, a*, and b*. Then the \(^{\circ}\)Hue was calculated with the formula \(^{\circ}\)Hue = \(\text{arc tan} (b*/a*)\). The color values of various heat treatment samples are shown in Table 1.

| Treatment | \(L^*\) | \(a^*\) | \(b^*\) | \(^{\circ}\)Hue |
|-----------|--------|--------|--------|--------------|
| Control   | 50.45±0.06\(^{d}\) | 13.85±0.06\(^{d}\) | 15.50±0.12\(^{f}\) | 46.30±0.00\(^{e}\) |
| F\(_1\)   | 49.78±0.15\(^{c}\) | 13.18±0.10\(^{bc}\) | 14.35±0.17\(^{c}\) | 46.13±0.17\(^{e}\) |
| F\(_2\)   | 49.38±0.29\(^{d}\) | 13.23±0.10\(^{c}\) | 14.13±0.13\(^{e}\) | 45.83±0.25\(^{d}\) |
| F\(_3\)   | 46.38±0.19\(^{c}\) | 14.60±0.12\(^{e}\) | 13.75±0.13\(^{d}\) | 42.75±0.17\(^{c}\) |
| F\(_4\)   | 46.20±0.14\(^{c}\) | 14.53±0.05\(^{c}\) | 13.30±0.20\(^{c}\) | 42.73±0.13\(^{c}\) |
| F\(_5\)   | 43.48±0.13\(^{b}\) | 12.73±0.15\(^{a}\) | 10.03±0.24\(^{a}\) | 41.15±0.17\(^{b}\) |
| F\(_6\)   | 43.15±0.13\(^{a}\) | 13.05±0.06\(^{b}\) | 10.30±0.12\(^{a}\) | 40.75±0.13\(^{a}\) |

Values with different superscripts within the same column are significantly different (p<0.05). F\(_1\) = 80°C oven for 1 h; F\(_2\) = 100°C oven for 1 h; F\(_3\) = microwave 2 min maximum temperature; F\(_4\) = microwave 5 min maximum temperature; F\(_5\) = 5 min of autoclave temperature 105°C; F\(_6\) = 10 min of autoclave temperature 105°C.

The redness of red rice brand after microwave heat treatment (2 min and 5 min) increases but decreased by heating the oven (80°C and 100°C) and autoclave (5 min and 10 min). Yellowness decreased in all samples. The values of \(a^*\) and \(b^*\) in the sample, were significantly different from the control. The lightness (\(L^*\)) of red rice bran after all various heat treatment decreased. Similarly, the decreased in lightness (\(L^*\)) of white rice bran with increased in heat temperature has been reported by Aliva and Silva, 1999 [16] and Kim et all, 2004 [10]. The heat treatment induce formation some products from the Maillard reaction [10].

3.2 Effects of Various Heat Treatment on Chemical Properties of Red Rice Bran

The proximate characteristics of the heat-treatment red rice bran sample are shown in Table 2.

| Treatment | Water (%wb) | Ash (% db) | Fat (% db) | Protein(% db) | Carbohydrate (% db) |
|-----------|-------------|------------|------------|---------------|---------------------|
| Control   | 10.29±0.32\(^{c}\) | 7.90±0.65\(^{a}\) | 28.55±0.34\(^{b}\) | 9.75±0.17\(^{b}\) | 42.34±0.87\(^{e}\) |
| F\(_1\)   | 5.51±0.23\(^{b}\) | 8.37±0.66\(^{b}\) | 27.11±0.27\(^{b}\) | 10.50±0.08\(^{d}\) | 48.19±0.96\(^{f}\) |
| F\(_2\)   | 4.13±0.22\(^{a}\) | 8.87±0.24\(^{b}\) | 26.24±0.15\(^{a}\) | 10.38±0.13\(^{d}\) | 50.23±0.45\(^{d}\) |
| F\(_3\)   | 12.51±0.17\(^{f}\) | 7.90±0.32\(^{a}\) | 32.39±0.35\(^{d}\) | 9.48±0.10\(^{a}\) | 35.97±0.44\(^{a}\) |
| F\(_4\)   | 8.60±0.36\(^{d}\) | 8.70±0.24\(^{b}\) | 27.40±0.38\(^{b}\) | 10.10±0.34\(^{c}\) | 44.40±0.79\(^{d}\) |
| F\(_5\)   | 11.36±0.20\(^{f}\) | 7.89±0.31\(^{a}\) | 28.80±0.66\(^{c}\) | 9.35±0.17\(^{a}\) | 41.16±0.27\(^{b}\) |
| F\(_6\)   | 8.05±0.31\(^{c}\) | 7.79±0.42\(^{a}\) | 27.22±0.18\(^{b}\) | 10.10±0.08\(^{c}\) | 46.13±0.44\(^{e}\) |

Values with different superscripts within the same column are significantly different (p<0.05). F\(_1\) = 80°C oven for 1 h; F\(_2\) = 100°C oven for 1 h; F\(_3\) = microwave 2 min maximum temperature; F\(_4\) = microwave 5 min maximum temperature; F\(_5\) = 5 min of autoclave temperature 105°C; F\(_6\) = 10 min of autoclave temperature 105°C.

Table 2 shows that the differences in heat treatment methods an effect on the water content of red rice bran. The highest water content was found in F\(_3\) treatment (12.51%). This is due to the raw red rice bran was first adjusted to 21% by adding deionized water. Water added to the rotation process and absorb microwave energy cannot be completely evaporated. The maximum rice bran water content is 12% [17]. The differences in heat treatment methods also effect on the ash content of red rice bran. The
stabilized red rice bran has an ash content of 7.79% - 8.87%. The maximum ash content of rice bran flour is 10% [17]. The ash content obtained was not significantly different from the control. High-temperature heating cannot remove the mineral content contained in bran [4].

The differences in heat treatment methods also effect on the protein content of red rice bran. The protein content of rice bran flour is at least 8% [17]. Decreased protein content caused by a decrease in water content of rice bran. When the water content is decreased, it will reduce the possibility of chemical reactions such as oxidation, deamination, denaturation, and aggregation. In high water content, the protein content in the ingredients becomes unstable and degraded. Increased chemical reactions due to increased water content cause conformation of the flexibility of the protein molecule. The lower of water content in a material, the possibility of a chemical reaction can decrease. Protein damage reactions can be minimized by reducing the moisture content of the ingredients [18]. According to SNI 01-4439-1998, the fat content of rice bran flour is at least 3%. Non-stabilized control rice bran and stabilized rice bran have fat content greater than 3%. The highest fat content was found in F3. The increase in fat content is caused by a disturbance in the fat complex and protein or fat and carbohydrates so that the opening of the bond is due to heating in a short time. Decrease in fat content in microwave heating for 15 minutes due to triglyceride decomposition by releasing free fatty acids and volatile components that provide aroma, at a longer duration of heating [19].

The level of bran carbohydrate of red rice bran Rojolele ranged between 35.97% - 50.23%. The highest carbohydrate levels were found in F2. The process of heating and drying causes an increase in the carbohydrate of red rice bran. Carbohydrate increase is caused by a decrease in other components in the ingredients.

| Treatment | Phenolic Compound (%) | Antioxidant Activity(%) | Crude Fiber (%) | Free Fatty Acid (FFA) (%) |
|-----------|-----------------------|-------------------------|----------------|-------------------------|
| Kontrol   | 0.22±0.002c           | 73.90±0.11ab            | 10.63±0.19d    | 17.89±0.52e            |
| F1        | 0.25±0.005e           | 75.88±0.21b             | 9.30±0.14c     | 13.48±0.00f            |
| F2        | 0.24±0.004f           | 73.93±1.02ab            | 9.40±0.27c     | 11.80±0.12d            |
| F3        | 0.16±0.008c           | 74.98±2.23ab            | 7.83±0.25b     | 16.41±0.35d            |
| F4        | 0.13±0.003c           | 75.93±1.02b             | 6.45±0.24b     | 8.04±0.17a             |
| F5        | 0.05±0.002b           | 75.10±1.80b             | 7.85±0.13b     | 13.47±0.12c            |
| F6        | 0.03±0.002a           | 72.85±2.02a             | 6.50±0.16b     | 12.24±0.69b            |

Values with different superscripts within the same column are significantly different (p<0.05). F1 = 80°C oven for 1 h; F2 = 100°C oven for 1 h; F3 = microwave 2 min maximum temperature; F4 = microwave 5 min maximum temperature; F5 = 5 minif autoclave temperature 105°C; F6 = 10 minif autoclave temperature 105°C.

Rice bran contains many unique bioactive compounds, such as tocopherols, tocotrienols, phytosterols, ferulic acids and gammarayzanol, Loypimai et al., 2009 [20]; Sharma et al., 2004 [21] that have various health-beneficial effects on glucose metabolism, lipid profiles, and blood pressure Cicero and Derosa, 2005 [22]; Shirakawa et al., 2006 [23]. The highest content of phenol red bran rice was found in F1 (0.25%). This value is higher than control. The content of phenol compounds is very sensitive and more susceptible to degradation. The most important phenol degradators are temperature, oxygen, and light. Increasing temperature will cause damage to most phenolic compounds. Increased temperature and heating time can decrease the total phenol content in the material [24]. The treatment of stabilization using oven at 800C that showed the greatest phenol yield. Similarly, the increased in tocil of white rice bran in dry heating (800C) has been reported by Kim et all, 2004 [10].

The antioxidant activity of red rice bran Rojolele ranged from 72.85% - 75.93%. The antioxidant activity of all samples was not significantly different from control. The stabilized white rice bran then extracted, also obtained the results of antioxidant activity which was not significantly different from...
the control [25]. The level of crude fiber ranged from 10.63% - 6.45%. The stabilization process causes a decrease in crude fiber content. Decreased levels of crude fiber caused by softening of the fiber structure, so that in testing the addition of acid-base can dissolve several parts of the fiber [26]. The highest free fatty acid content is found in the control sample. The stabilization process using an oven, microwave and autoclave can inhibit enzymatic activity. The content of oleic fatty acids in white rice bran was higher than that of stabilized white rice bran using microwave and stored for 4 months with storage treatment using plastic and in cold temperatures. White rice bran-free fatty acids control about 20% and white rice bran stabilized using microwave less than 10% [9]. The increase in free fatty acids for the control sample was much higher than sample with various heat treatment, indicating that the various heat treatments were effective in retarding the enzyme degradation. Similarly result also has been reported by Kim et all (2004) in stabilization of white rice bran.

In this study, the FTIR method was used to determine the bioactive compounds contained in brown rice bran. FTIR results showed that the red rice bran Rojolele contained anthocyanin and thiamin (data not shown). The treatment of stabilizing red rice bran using various heat treatment does not eliminate the anthocyanin and thiamin content in the rice bran. Stabilized rice bran with various heating methods has anthocyanin and thiamin content which is almost the same with control. The best stabilization process is determined by Sullivan et al. method [27]. The results showed that Oven an hour at 80ºC is the best method, with a weight of 0.809 (data not shown). A heating method using an Oven temperature of 800C for 1 hour is the best method because it show a high value of quality the red rice bran Rojolele.

4. Conclusion
The results showed that all heat treatment methods decrease L value. The highest moisture level is on heating by microwave for 2 min. There were no significant difference in the level of ash, fat, and antioxidant activity. The FFA content was decreased by all heating treatment. The fenol level with heating with Oven 80ºC an hour was the highest. Among the treatments, Oven an hour at 80ºC is the best method. This method produces red rice bran with characteristics of lightness, water content, ash, fat, protein, total phenol, antioxidant activity, crude fiber, and free fatty acid content respectively 49.78%; 5.51%; 8.37%; 27.11%; 10.50%; 0.25%; 75.88%; 9.30%; and 13.48%. Red rice bran Rojolele also contains anthocyanin and thiamin obtained from spectroscopy FTIR.

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