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EFFECT OF DIFFERENT STABILIZATION METHODS ON THE PROXIMATE COMPOSITIONS OF BREWER'S RICE

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ABSTRACT

Brewer's rice is one of the by-product that is derived from rice milling processes. It has been considered as unutilized materials due to its high susceptibility to lipid oxidation, even though it contained valuable food ingredients. In the present study, the effect of microwave heating, gamma irradiation, and hydrochloric acid (HCl) treatment on Brewer's rice stabilization was investigated. The effect of stabilization method on the free fatty acid (FFA) content and proximate composition of Brewer's rice were monitored during storage at ambient temperature. The FFA content in Brewer's rice increased significantly ($p<0.05$) during storage time for all stabilization methods, except for HCl treatment. No significant ($p<0.05$) effect of stabilization treatment was observed on the protein, fat, and ash contents of Brewer's rice as compared to the control. Microwave and chemical methods significantly ($p<0.05$) reduced the moisture content, but significantly ($p<0.05$) increased the carbohydrate after 16 weeks of storage. Microwave heating was able to reduce the oxidation of Brewer's rice without influencing the proximate composition of Brewer's rice. Therefore, it can be considered as the most suitable stabilization method to inhibit rancidity.

Keywords: *Brewer's rice; oxidation; microwave heating; γ-irradiation; chemical treatment; proximate composition.*

INTRODUCTION

Rice is a staple food for a large part of the world's human population, covering from East and South Asia, the Middle East, Latin America to West Indies. Rice milling process produces many rice-by-products, which was previously been considered as unutilized materials. However, currently there is a significant interest among researchers to converts them into valuable materials. The most significant rice milling by-product is rice bran which had been proven to provide various functional effect including cancer [1] antioxidant activity [2] and hypocholesterolemic effects [3]. Besides rice bran, another by-product of rice mills which contained significant potential properties as rice bran is Brewer's rice. Brewer's rice comprises of a mixture of broken kernels with intact rice germ that is separated during the paddy milling process as it passes through the rotary sieve after the final polishing step. Intact rice germ contains carbohydrate, protein, essential lipids, natural antioxidants such as tocopherols, tocotrienol, oryzanols, vitamin B and minerals, that had been related with health benefits effects [4,5].

Although Brewer's rice is rich in valuable food components, the high susceptibility towards lipid oxidation limits its application as a food ingredient. It usually has a limited shelf life as it could rapidly deteriorate at ambient temperatures during storage leading to development of off-flavor and odors, mainly due to the enzymes, microorganisms, and insects activities which accelerate its deterioration [6]. One of the methods that could prolong Brewer's rice shelf life is by inhibiting the potential sources that could accelerate rancidity. It had been reported that several stabilization methods are able to extend the product shelf life up to 6 months when stored at room temperature [7].

Stabilization methods such as extrusion cooking, chemical treatment, gamma irradiation, and microwave treatment have been reported to be able to prevent deterioration of the by-products [8-10]. Proper stabilization process is able to deactivate enzymes that resulted in rancidity such as lipase and lipoxygenase [11]. Since stabilization could inhibit rancidity and prolong the shelf life, choosing the appropriate methods that enable the preservation of its nutrients composition become more challenging. Hence, the objective of the present study was to compare the effect of different stabilization methods namely microwave heating, γ-irradiation and hydrochloric acid (HCl) treatments on the free fatty acid (FFA) formation and proximate compositions of Brewer's rice.

MATERIALS AND METHODS

Materials

Samples of Brewer's rice were freshly collected from rice mills in Sekinchan, Selangor, Malaysia. The samples were immediately placed into plastic (polypropylene) containers to protect them from direct light. The samples were stored at 4°C prior to analysis. The samples were sieved to remove husks, broken pieces of rice, and other unwanted foreign materials.

Chemicals and Reagents

Hydrochloric acid, sodium hydroxide, sodium sulphate anyhydrous, cuprum sulphate, selenium dioxide, sulphuric acid, boric acid and petroleum ether were purchased from Merck (Germany). Phenolpthalein, methyl red and methylene blue indicators were purchased from Fisher (New Jersey, USA).

Stabilization Process of Brewer's Rice

Brewer's rice was subjected to three different stabilization methods, namely microwave, gamma irradiation and HCl treatments. Microwave stabilization was carried out according to the method proposed by Ramezanzadeh et al. [12] with slight modifications. The moisture content of the Brewer's rice was adjusted to 21% from 12% by adding deionized water prior to microwave stabilization. The microwave chamber of microwave oven (Model R-958A, 2450 MHz Sharp Electronic Corp) was preheated at 100 % power for 2 min. The sample (150 g) was placed in a microwaveable plastic container and heated at medium power for 3 min. The sample was allowed to cool at room temperature before it was packed into polyethylene zipper bag.

For the gamma irradiation, the method was carried out according to Sung, [10] with some modifications. The samples (150g) were packed in polyethylene bag and subjected to 1kGy γ-irradiation (^{60}Co) doses at the MINTec-SINAGAMA, Agensi Nuklear Malaysia.

Meanwhile, the HCl treatment was carried out according to the procedure described by Prabhakar and Venkatesh [13] with slight modification. Briefly, 40 ml of hydrochloric acid was sprinkled on 1 kg of Brewer's rice and the rice was thoroughly stirred manually. The samples were packed in polyethylene zipper bag prior to analysis.

Free Fatty Acid Content

All treated Brewer's rice was packed into individual polyethylene zipper bag and stored at ambient temperature. The samples were analyzed for free fatty acid (FFA) content at 0, 4, 8, 12, and 16 weeks of storage. The FFA was determined according to the AOCS official methods (methods 5a-40) [14].

Proximate Analysis

Proximate composition of Brewer's rice was determined at 0 and 16 weeks of storage using standard AOAC methods [15] for protein (Method 992.5), fat (Method 945.16A), moisture (Method 985.14), and ash (Method 920.153). The percent of carbohydrate was by difference, calculated according to Equation 1.

Carbohydrate (%) = [100 – (% protein +% fat+% moisture +% ash)] [1]

Statistical Analysis

were analyzed using the SPSS, version 16.0, (SPSS Inc., Chicago, IL, USA). Data were subjected to analysis of variance (ANOVA) using the General Linear Model and the comparison of means was conducted according to the Duncan multiple range test procedure at $P < 0.05$.

RESULTS AND DISCUSSION

Free Fatty Acid

The effect of different stabilization methods including microwave heating, gamma irradiation and HCl treatments on the free fatty acids content of Brewer's rice during storage were investigated. Figure 1 shows the content of FFA in Brewer's rice during storage at ambient tempeature up to 16 weeks. FFA content increased during storage time for all samples except for sample that was subjected to HCl treatment. The FFA content for control and γ-irradiated samples had increased abruptly from zero day to week 4 of storage followed by a slight increased thereafter up to week 16. The initial FFA content of Brewer's rice was 6.2 – 11.5 %. At week 16, the FFA of the control (66.6%) and γ-irradiated (62.9%) Brewer's rice were significantly ($p<0.05$) higher than the FFA content of other treatments. Similar trend was showed by microwave Brewer's rice. The FFA content tremendouly increased at the early storage period until week 4 and then it gradually increased up to week 16. However, the FFA content at week 16 was 33.7 %, which is significantly ($p<0.05$) lower than the control and γ-irradiated Brewer's rice. No significant ($P<0.05$) difference was observed in the FFA content during initial and week 16 of Brewer's rice treated with HCl treatment. The increment of FFA content in the Brewer's rice that was stabilized by using γ-irradiation was much more higher when compared with that of microwave treatment. The initial FFA content of Brewer's rice stabilized by gamma irradiation was 6.23% and it increased up to ten-folds i.e. 62.87% at week 16. While for microwave stabilization method, the FFA content of Brewer's rice increased from 11.5 % on zero day to 33.7% at week 16.

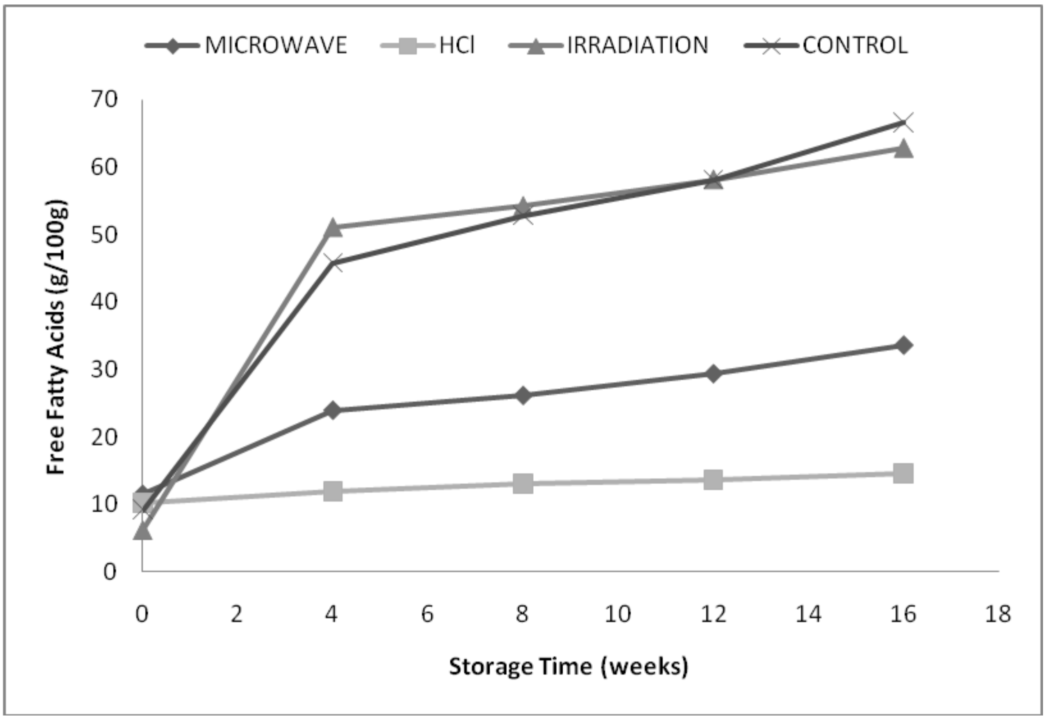

Fig. 1: The free fatty acids content of treated Brewer's rice and the control during storage at ambient temperature (27±2°C).

The removal of bran layer from the endosperm during the rice milling process disrupted the cells causing the lipids in the bran to come into contact with highly reactive lipases enzyme resulting in the rapid hydrolysis of the triglycerides of the oil into glycerol and FFA. Further oxidation which naturally occur in the presence of oxygen molecules and lipoxygenase resulted in the enzymantic rancidity of the food [9, 6]. Several stabilization methods using thermal treatment such as microwave heating and blanching, and chemical stabilization method have been found to inactivate the lipase and lipoxygenase and prolong the shelf life of rice bran and sweet corn [9, 12,11].

In this study, the increased in the FFA content of the control sample during storage indicated that the activities of lipases and lipoxygenase are high in the unstabilized Brewer's rice. The FFA content increased to 66.6 % from 9.2% at week 16. Similar observation was reported in other rice mill by-products. Malekian et al. [9] found that the FFA content in untreated rice bran increased from 2.5% to 48.0% for sample packed in polythylene zipper bags and 54.3% for vacuum packed samples over 16 weeks of storage at ambient temperature. The rapid development of hydrolytic rancidity in unstabilized rice bran causes the product to be unsuitable for human consumption [17, 9]. The amount of FFA for human consumption should not exceed 10 % FFA and 5 % FFA in bran oil and bran, respectviely [17]. Thus, unstabilized Brewer's rice can be considered as not fit for human consumption as it is succeptible for lipid oxidation.

It is interesting to note that the HCl stabilization method is able to control the formation of FFA in brewers rice. The FFA content in the Brewer's rice as stabilized through HCl treatment showed an increament only from 10.28% during intial stage of storage up to 14.58% within 16 weeks storage period. The present study showed that HCl treatment could effectively inhibited the formation of FFA in the Brewer's rice as compared to the other stabilization methods. Addition of hydrochloric acid to the Brewer's rice resulted in a low pH enviroment which is unsuitable for lipase to react with its substrate. Similar obeservation was reported by Prabhakar and Venkatesh [13], whereby HCl treatment was able to stabilize rice bran. They observed that the FFA content during initial stages and after 51 days storage at ambient temperature was in the range of 3.0–9.3%. The optimum pH condition for lipase in rice bran is known to be at 7.5-8.0. Addition of HCl decreased the pH and inhibit the lipase activity (Figure 1).

Microvawe stabilized Brewer's rice contained significantly ($P<0.05$) lower FFA content as compared to the γ-irradiated and control samples. The lower FFA indicated that the rate of enzymatic oxidation in Brewer's rice was low. Microwave heating inactivated the enzymes that caused rancidity such as lipases and lipoxygenases through the internal heating of food particles within the microwave cavity. The cavity makes the dipolar water molecules in the samples excited by the electromagnetic waves, resulting in enhancement of kinetic energy along with the friction and produces an even heat distributiont throughout the samples [9]. However, in the present study, the microvawe treatment was not able to completely inhibit these lipases and, hence, the rancidity process still continues. This implied that a longer heating time or heating at higher power is required to completely inactivate the lipases. The increment of FFA in irradiated samples during the storage period may due to the radiolysis of glycerides by γ-irradiation itself and enzymatic hydrolysis of glycerides by lipases. Similar observation was reported by Shin and Godber [18] whereby a greater loss of phospholipids and formation FFA of rice bran were observed when γ-irradiation was increased from 5 to 15 kGy. It can be deduced that the application of γ-irradiation in food product even at lower doses also could accelerate lipid oxidation.

This sudy demonstrated that HCl treatment could effectively inhibit lipase activity in Brewer's rice and retard the lipid oxidation, since no significant ($P>0.05$) changes in FFA content was observed during the storage period. Microwave stabilization method also showed considerable efficiency in inhibiting the lipid oxidation of Brewer's rice since the FFA content was significantly ($P<0.05$) lower than the control on week 16. In contrast, γ-irradiation showed similar lipid oxidation pattern as the control sample. Eventhough, HCl treatment could effectively inhibit lipid oxidation, microwave method is more applicable to be used for food application due to its energy efficiency.

Proximate Composition

The effect of different stabilization methods on the proximate composition of Brewer's rice at week 0 and week 16 were compared with the control (Figures 2-6).

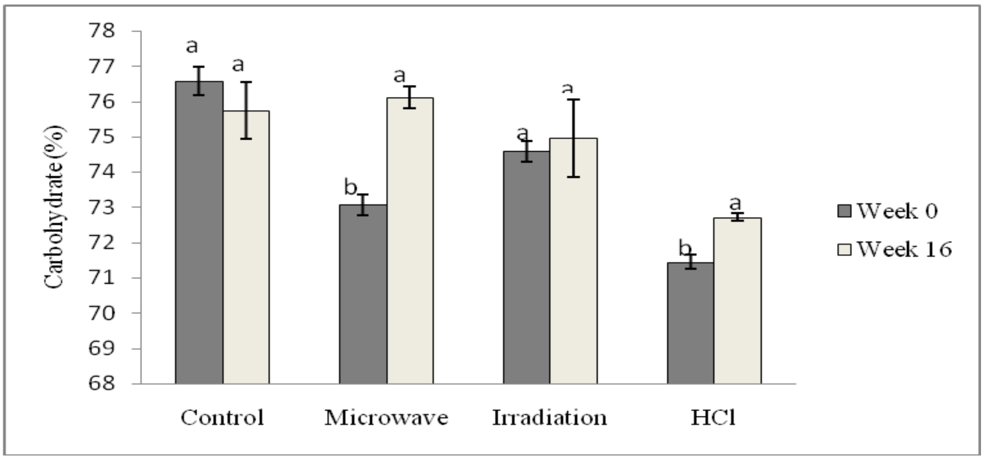

Fig. 2:The carbohydrate content of treated and untreated Brewer's rice during storage at ambient temperature (27±2°C). (Data represents mean ± standard deviation. Means followed by different letters in the same stabilization methods (a,b) are significantly different at (P<0.05).

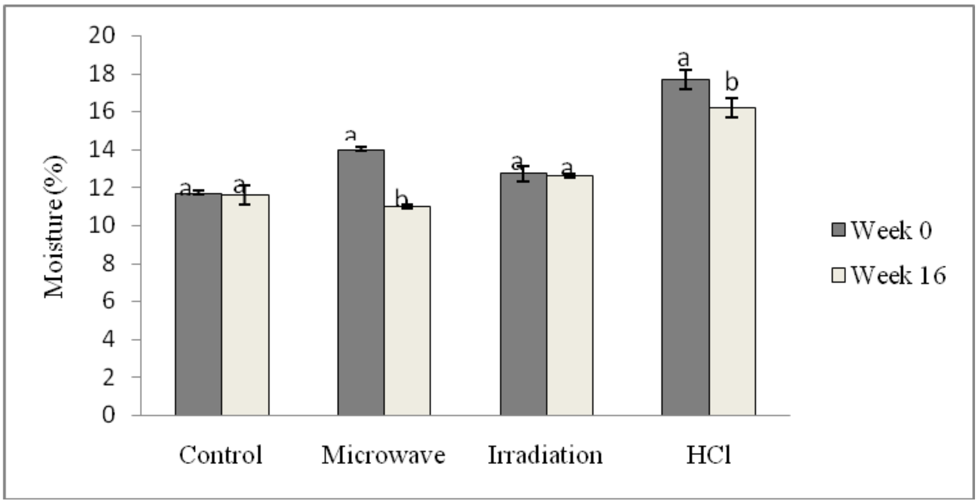

Fig. 3: The moisture content of treated and untreated Brewer's rice during storage at ambient temperature (27±2°C). (Data represents mean ± standard deviation. Means followed by different letters in the same stabilization methods (a,b) are significantly different at (P<0.05).

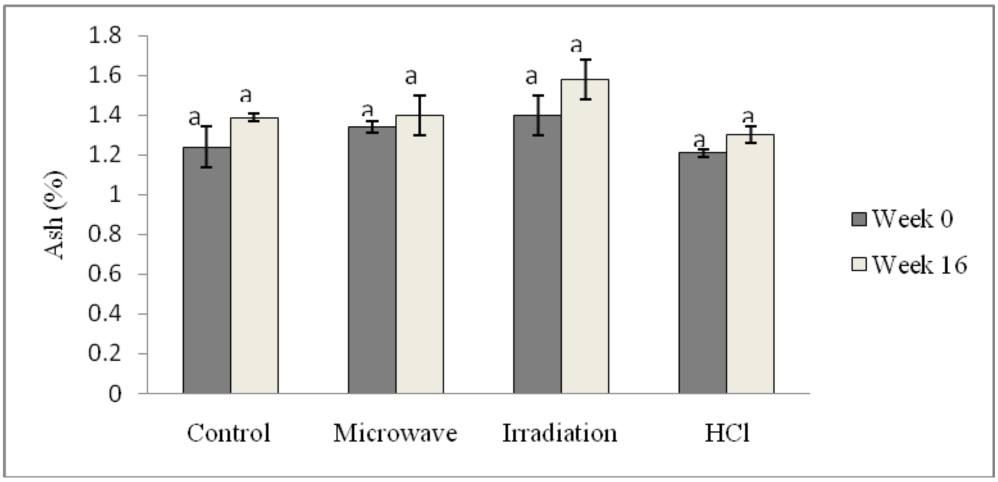

Fig. 4: The ash content of treated and untreated Brewer's rice during storage at ambient temperature (27±2°C). (Data represents mean ± standard deviation. Means followed by different letters in the same stabilization methods (a,b) are significantly different at (P<0.05).

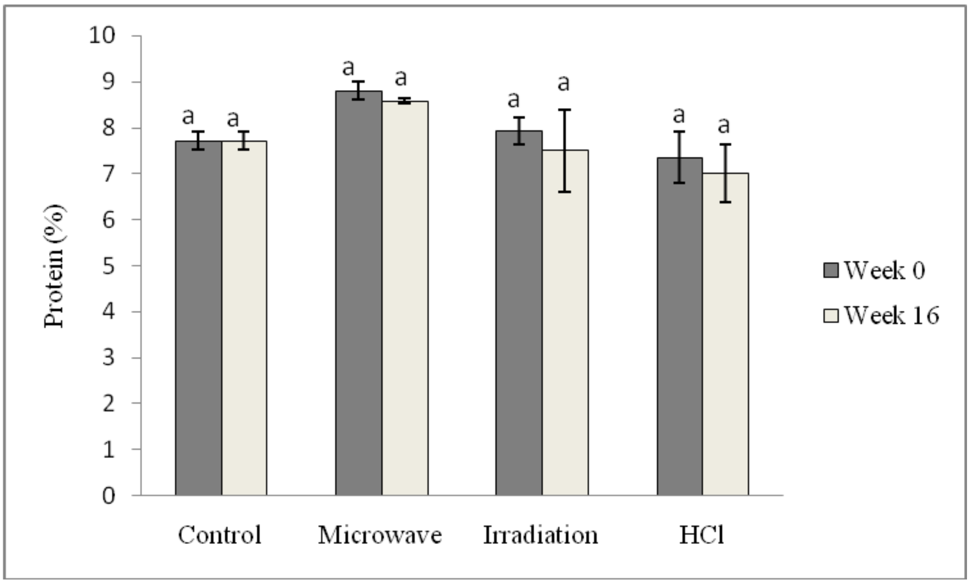

Fig. 5: The crude protein content of treated and untreated Brewer's rice during storage at ambient temperature (27±2°C). (Data represents mean ± standard deviation. Means followed by different letters in the same stabilization methods (a,b) are significantly different at (P<0.05).

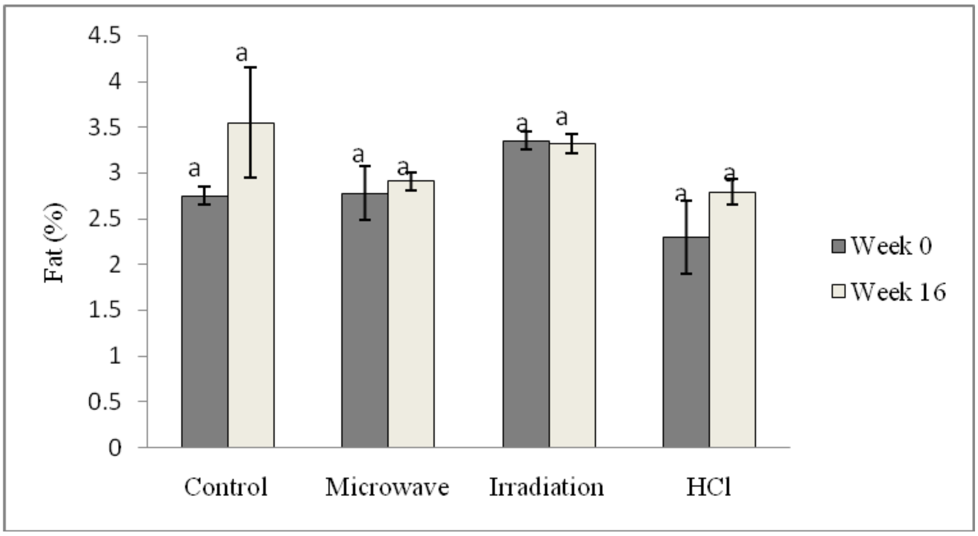

Fig. 6: The crude fat content of treated and untreated Brewer's rice during storage at ambient temperature (27±2°C). (Data represents mean ± standard deviation. Means followed by different letters in the same stabilization methods (a,b) are significantly different at ($P<0.05$).

The result of the study showed that the stabilization methods studied caused significant ($P<0.05$) increased the carbohydrate content and significant ($P<0.05$) reduction in the moisture content of Brewer's rice at week 16 as compared to the control (Figures 2-3). However, all the studied stabilization methods studied did not significantly ($P>0.05$) changed the ash, protein and fat contents of Brewer's rice (Figures 4-6).
Figure 2 shows the carbohydrate content of brewers rice in the control and stabilized samples during 16 weeks of storage. The carbohydrate content for all stabilized Brewers rice was significantly ($P<0.05$) higher on week 16 as compared to week 0 except for the γ-irradiated and control samples. The carbohydrate content of microwaved and chemical stabilized Brewer's rice increased significantly ($P<0.05$) from an initial value of 73.1% to 76.1% and 71.5% to 72.7%, respectively.

Proximate composition is one of the important nutritional value for food to be considered as raw material for food products. It represents the content of major macrocomponents of food. Generally, rice contained high percentage of carbohydrate followed by protein and fat. In the present study, the carbohydrate content of the microwaved and HCl treated samples were significantly ($P<0.05$) reduced prior to stabilization process at week 0. In contrast, the carbohydrate content in the microwaved stabilized Brewer's rice was found to increase significantly ($P<0.05$) with storage time, however no significant different was observed with that of the control at week 16.

Figure 3 showed that the moisture content of microwave stabilized (14%) and chemical stabilized Brewer's rice (17.7%) was higher compared to the control (11.7%) in week 0, but it was significantly ($P<0.05$) decreased to 11% and 16.2%, respectively after 16 weeks of storage. The higher moisture content on zero day of microwaved stabilized samples was due to the addition of water to the sample which increases the moisture content to 21.0% prior to microwave heating. Similarly, for the chemically treated sample, the addition of hydrochloric acid at the begining of experiment increased the moisture content. Reduction of moisture content in microwave stabilized sample was due to the the microwave treatment. During microwave process, water molecules undergo rotation and absorb microwave energy, resulting in an increase in temperature and thereby reduction in moisture content [19, 9].

In general, no significant ($P>0.05$) changes in protein, fat and ash content as compared with control was observed as illustrated in Figures 4, 5 and 6, respectively. These findings were in agreement with the earlier findings of Malekian et al. [9[who reported that microwave stabilization did not significantly change the contents of protein and fat in rice bran, even after 16 weeks of storage at ambient temperature. It can be deduced that stabilization of Brewer's rice by microwave heating, γ-irradiation and chemical treatment had little effect on the nutritional composition of the by-product.

CONCLUSIONS

Microwave and HCl treatments significantly ($P<0.05$) inhibited the lipases activity in Brewer's rice. All the stabilization methods did not significantly ($P>0.05$) influenced the the proximate composition of Brewer's rice. Results of this study showed that chemical stabilization method could prevent the formation of FFA without affecting the proximate compositions of Brewer's rice against rancidity. However, due to restriction of HCl application in food industry, microwave stabilization method is the most suitable method to be used in stabilizing the Brewer's rice. Microwave able to reduce FFA formation and significantly ($P<0.05$) retained its nutritional components. Furthermore, microwave treatment could be used in the food technology due to its energy-efficiency and rapidity. The nutritious stabilized Brewer's rice can be further processed into other food products or food ingredients.

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