Advances in Engineering Research, volume 205
Proceedings of the 3rd Green Development International Conference (GDIC 2020)

Chemical Properties of Ground Red Chili Based on *Dihydrocapsaicin* at Different Heating Process

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ABSTRACT

Heating process of ground red chili can affect chemical compound of dihydrocapsaicin that can caused less spicy. The objective of this research was to determine the effect of heating process of ground red chili based on the chemical compund of dihydrocapsaicin, and also moisture and vitamin C. Research was conducted on using a completely randomized design of ground red chili processed at different heating temperature of 70^{o}C, 75^{o}C, 80^{o}C, 85^{o}C and 90^{o}C for 10 minutes. Extraction of dihydrocapsaicin was done using ethanol as solvent, while high liquid chromatography (HPLC) was used for separation, identification and quantitation of the components. Vitamin C and moisture content of ground red chili was also determined; it could be affect the chemical compound of dihydrocapsaicin. Result showed that heating process at different temperatures affected the chemical properties of ground red chili based on dihydrocapsaicin , water and vitamin C content. The processing ground red chili processed at temperature of 90^{o}C resulted in the highest dihydrocapsaicin, water content and lower vitamin C of 62.91 µg/g, 73.01%, and 94.6 mg/100g respectively. Heating process of ground red chili processing affected chemical compound of dihydrocapsaicin, moisture and vitamin C.

***Keywords**: ground red chili, heating process, extraction, dihydrocapsaicin, vitamin C.*

1. INTRODUCTION

Red chili (Capsicum annum L) is one of the leading horticultural vegetable commodities, which can be consumed both fresh and processed. Ground red chili is red chili processing as semi-solid product, still have intact seeds that are not crushed and it needs processing to consume it, so it can be said to be a semi-finished product.

Red chili processing in food industry has been potentially demand. It is about 40 percents of red chili harvesting in Indonesia are used for food industry and household such as chili sauce, dried chili, chili oil, chili powder, oleoresin and ground red chili. Spiciness is very important in these products mainly for consumtion and industrial red chili processing.

Spiciness is mainly characteristics of chili. It has different levels of spiciness which stated in the Scoville Heat Unit (SHU) based on their varieties and kinds of chilies [1]. The level of spiciness of chilies in SHU units consists of no spicy (0-700) SHU, slightly spicy (700-3000) SHU, moderately spicy (3000-25,000) SHU, spicy (25,000-70,000) SHU and very spicy (> 80,000) SHU [2].

The spicy taste of chilies comes from the content of capsaicinoid compounds consisting of capsaicin (69%), dihydrocapsaicin (22%), nordyhidrocapsaicin (7%) and homodyhidrocapsaicin and homocapsaicin (1%). Capsaicin and dihydrocapsaicin, which are the dominant molecules, account for about 90% of the total capsaicinoids in chilies [3]. Dihydrocapsaicin is a lipophilic odorless compound that is colorless, soluble in dimethyl sulfoxide and ethanol, and is easily damaged by the oxidation process.

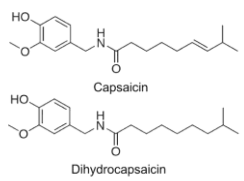

Figure 1. Structure of capsaicin and dihydrocapsaicin

The difference between capsaicin ($C18H27NO3$) and dihydrocapsaicin ($C18H29NO3$) is in carbon chain (R) that is bonded with amida group at capsaicinoid base compound. Capsaicin is 69% of capsaicinoid compound in chili, it is higher than dihydrocapsaicin and another capsaicinoid compound (Iwai et al., 1979[4]: Renate et al., 2014)[5]. The spiciness level of capsaicin and dihydrocapsaicin are 16,1.000.000 SHU and 15,1.000.000 SHU respectively [5].

Heating process such as roasting, boiling has been affected dihydrocapsaicin compound. Roasted Habanero peppers had higher dihydrocapsaicin content compared to the treatment of fresh and boiled chilies of 727.3 ± 39.0 µg ; 463.4 ± 48.1µg and 419.20 ± 51.0 µg, respectively [3]. It was also found that the boiling process reduced the dihydrocapsaicin content compared to fresh peppers. Heating in this food product requires conditions to reduce oxidation-oxidation reactions caused by the presence of oxygen which can reduce quality of dihydrocapsaicin compounds. Heating process of red chili puree at the temperature of 80o C for 10 minutes resulted in the lowest capsaicin degradation and was very effective compared to other heating times in milled red chilies [5].The heating temperature to obtain these conditions is 80o C to 90o C which is heated for 8-10 minutes [6]. Heating process of chili puree at a temperature of 50-90o C experienced degradation of the capsaicin compound, from 559 µg of fresh chili puree to 441 µg after heating. At 85o C, the capsaicin compound was degraded by 19.1% [7] Research on dihydrocapsaicin on chili preparations is still rarely carried out therefore it is necessary to conduct research based on dihydrocapsaicin on chili processing.

Heating process can affect decreasing moisture and vitamin C content. Heating process of food can reduce oxidation reaction of vitamin C. Vitamin C or ascorbic acid is antioxidant and dissolved compound on food. Vitamin C is also effective to formed Reactive Oxygen Species (ROS) formation and free radical [8]. Food processing can loss high vitamin C due to chemical degradation.

2. METHODS

Material used in this study were fresh curly red chilies obtained from Sebapo Village, Muaro Jambi Regency, Jambi Province. The criteria of red chillies were good, clean, ripe dark as well as additional materials used salt, citric acid, and sodium benzoate. Materials for analysis were starch indicator 1%, iodine solution 0.01 N, ethanol p.a 96%, standard dihydrocapsaicin pure. The instrument of HPLC (High Performance Liquid Chromatography), and vial tube. The experimental design in this study used a completely randomized design (CRD) with five heating temperature treatments of 70, 75, 80, 85, and 90 oC and two replication.

Processing of ground red chili [5], curly red chilies were sorted and separated from the stalks. The next step was weighing 250 grams, then washing and blanching at 80° C for 3 minutes. The red chilies were then crushed using a chili grinding machine, when grinding it was added citric acid, benzoic acid and salt of 0.5%, 0.05% and 6% respectively. Then the ground red chilies were put into sterilized jar bottles.

The next, the ground red chili were heated in a water bath containing 2/3 of the height of the jar. Heating was done by adjusting the heating temperature according to the treatment temperature (70,75, 80, 85, and 90 oC) and the ground chili samples were put in a bottle cap opened and placed in a waterbath. The next step is to wait for the milled chili samples to reach the temperature according to the treatment, after the temperature is reached, the heating time was calculated for 10 minutes. Samples then were immediately closed and removed from the water bath for further analysis.

Sample extraction [1], the ground red chilies were weighed as much as ± 3.5 g, then these were put into a 50 mL pyrex tube, added ethanol 96% of then the tube was closed with a cover (line cap, not airtight). The sample was then stirred using a vortex for 10 seconds, then the tube was placed in a water bath at 70ºC for 4 hours, and it was stirred using vortex every hour. Samples then were removed and placed at room temperature to be cooled. The cooled sample was then centrifuged to obtain the supernatant. The supernatant obtained was transferred into a vial tube with a capacity of 20 mL (supernatant volume 10 mL, if less, a few mL of 96% ethanol are added).

Standard curve creation, standard solution of dihydrocapsaicin was injected into the HPLC tool to obtain peak areas. The results of sample readings on the HPLC can be seen on the monitor screen, which is then a graph of the calibration curve for the standard concentration of dihydrocapsaicin.

Dihydrocapsaicin analysis, the supernatant obtained from sample extraction was then analyzed using HPLC by injecting it into the HPLC. The analysis results showed that the peak height and retention time were used to calculate the dihydrocapsaicin levels.

$$\text{Dihydrocapsaicin } (\mu g/\ ml)\ bb = \frac{Dihydrocapsaicin\ in\ sampel}{weight\ of\ samples\ (g)}$$

Water content

Samples of ground red chili were weighed as much as 2 grams in a cup that has been dried and the weight was known. Then the ground red chilies were put in the oven at 105 ºC for 3 - 5 hours. Furthermore, it was cooled in a desiccator until it reaches room temperature, then it was weighed. The ground red chilies were heated again in the oven for 30 minutes, cooled in a desiccator and weighed.

The treatment was repeated until the weight becomes constant.

Vitamin C

Using Iodometric method, samples of ground red chili were weighed as much as 10 grams into a 100 ml measuring flask and add aquadest to the mark. Then the mixture was filtered to separate the phytrate. After that, 5 ml of ground red chili filtrate was taken and put in 125 ml Erlenmeyer. It was added starch indicator 1% and aquadest of 2 ml and 20 ml respectively and then was titrated with iodine solution of 0.01 N until dark blue. The percentage of vitamin C was calculated using the formula:

$$\text{Vitamin C (mg/100 gr)} = \frac{ml\ iod\ x\ 0{,}88x\ FP}{bsample\ weight}\ x\ 100$$

3. RESULTS

Extraction and quantitation steps were carried-out in duplicate for each sample. The standard solutions used for the calibration curve were regularly injected at intervals between sample injections to confirm the retention times. The chromatograms shown in Figures 2 and 3 correspond to a standard and extracted solution, respectively; they reveal that dihydrocapsaicin is eluted at 6.41 min.

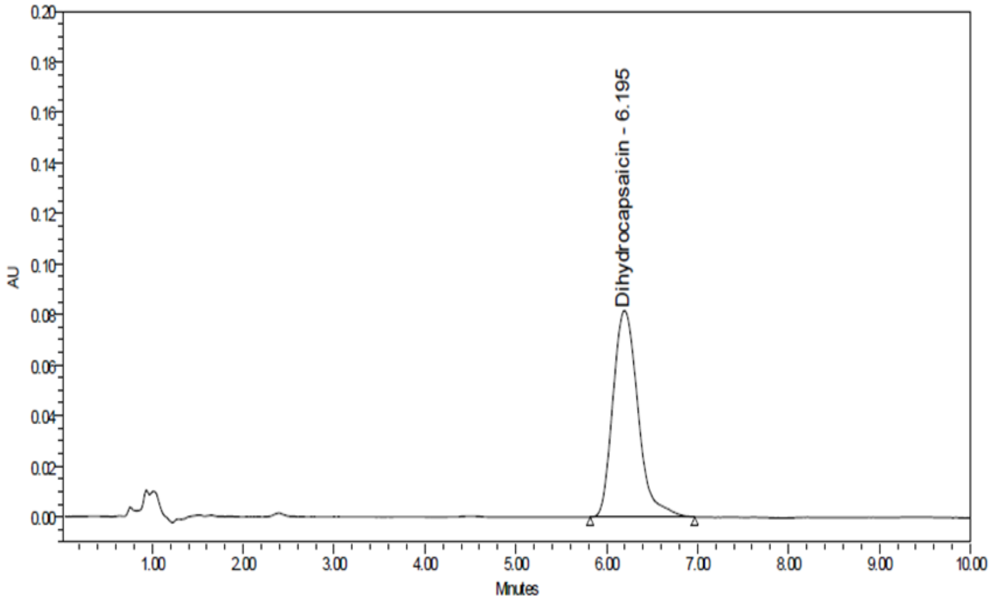

Figure 2. Chromatogram of the standard solution corresponding to 100 μg/g of dihydrocapsaicin (conditions: column Betasil C18 (150 × 4.6 mm × 3 μm), mobile phase: H2O/CH3CN, 50:50 v/v, flow rate: 1.5 mL/min, UV detection at 222 nm).

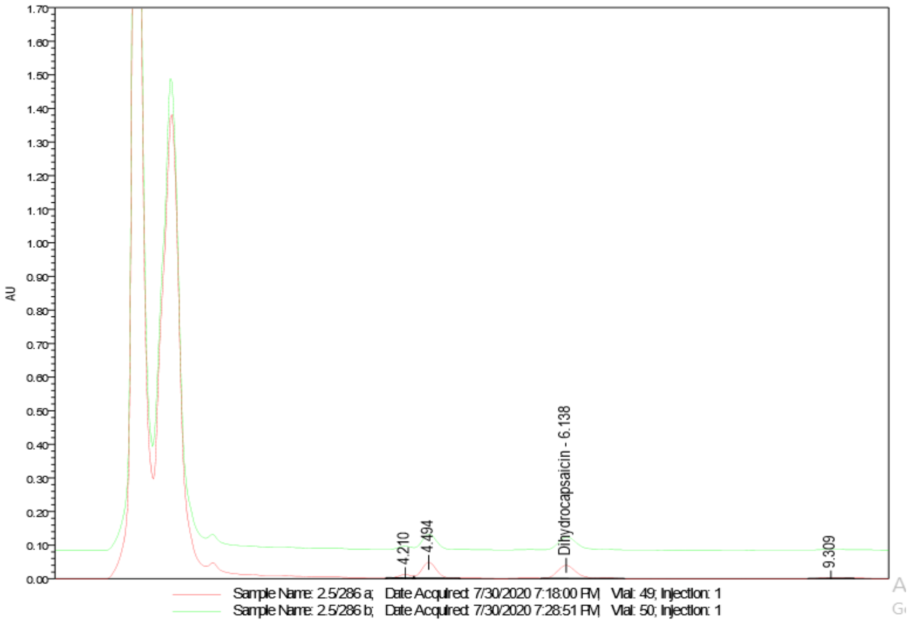

Figure 3. Chromatogram of the ground red chili extract solution corresponding to 100 µg/g of dihydrocapsaicin with heating process of 90 °C

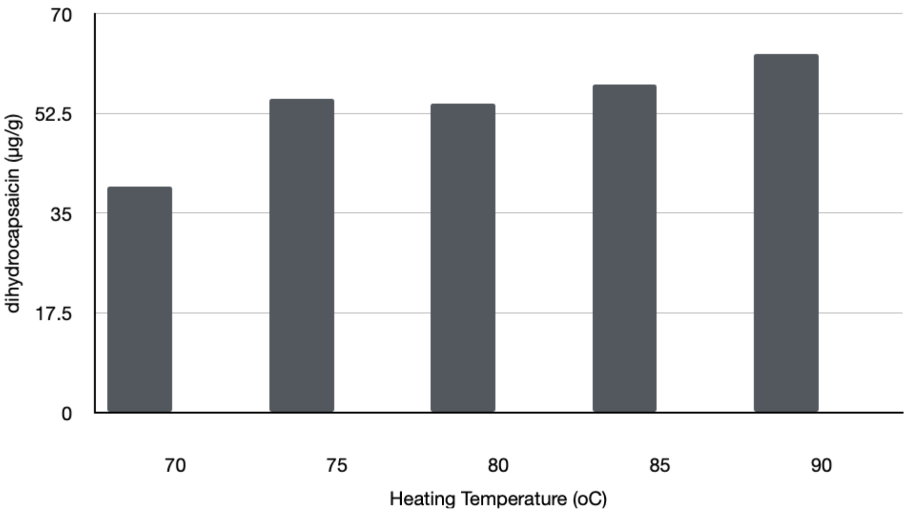

Figure 4. Dihydrocapsaicin of ground red chili with heating temperature process

3.1. Water Content

Water content of ground red chili with heating temperature of 70 until 90 °C could be seen in Table 1. The heating temperature treatment affected the moisture content of ground red chilies.

Table 1. Water content of ground red chilies with heating temperature treatment

Heating Temperature °C	Water Content (%)
70	74.23 a
75	74.20 a
80	73.57 ac
85	73.15 c
90	73.01 c

Note: The numbers followed by the same lowercase letter show no significant difference at the 5% level according to the DMRT test.

3.2. Vitamin C

Vitamin C of ground red chili with heating temperature of 70 until 90 °C could be seen in Table 2. The heating temperature treatment significantly affected the vitamin C content of ground red chilies.

Table 2. Vitamin C of ground red chilies with heating temperature treatment

Heating Temperature °C	Vitamin C (mg/100 gr)
70	134.25 d
75	127.60 c
80	114.40 bc
85	105.60 ab
90	94.60 a

Note: Figures followed by different lowercase letters show significant differences at the 5% level according to the DNMRT test.

4. DISCUSSION

The dihydrocapsaicin compounds in this study were clearly identified using commercially available standard dihydrocapsaicin compounds using HPLC. Capsaicinoid compound analysis has been carried out using several methods. HPLC is the most efficient technique of some existing methods, which can separate compounds quickly and free from a mixture of complex and bonded organic compounds. The result of the HPLC reading against the dihydrocapsaicin standard produces a standard curve.

The chromatogram shown in figure 3 show that in sample of dihydrocapsaicin, ground red chilies were detected at each retention time of 6,138 minutes. The chromatogram obtained in the analyzed sample only dihydrocapsaicin was detected, so this show good separation and there is no disturbance at the dihydrocapsaicin peak that causes other compounds to be detected.

Figiure 4 showed that the increasing heating temperature process of ground red chili had been increased the dihydrocapsaicin of the ground red chili. The heating process of 90 oC of ground chili resulted the highest content of dihydrocapsaicin of 62.91 µg/g with the level of spiciness of 1012.851 SHU. The results also showed that the content of dihydrocapsaicin was directly proportional to the SHU produced. Handoko and Yeni [9] state that the SHU produced is directly proportional to the capsaicin content obtained. The SHU produced in this study ranged from 638,043-1012,851 which is at a slightly spicy level different from dihydrocapsaicin [9]. Capsaicin has a spicy level of chili pepper. Ahmed et al. [10] stated that chilies which have a slightly spicy taste are also very popular in making salads and pickles.

Heating process can reduce up to 50% or increase 26 times the capsaicinoid content in chilies (Ahmed et al., 2002)[7]. The results of capsaicin research in the last few years on capsaicinoid compounds, show that there is degradation of capsaicin compounds due to the heating process ([11][5][12]). In this research indicated that the compounds of dihydrocapsaicin increases with increasing heating temperature. The increase in capsaicinoid content, in this case dihydrocapsaicin, according to Harrison and Haris [6] is due to the breakdown between capsaicinoid compounds and other compounds in the placenta.

Capsaicin compounds were degraded due to the heating process, and argued that this was due to the heat process that caused the capsaicin compound to undergo a molecular change into other compounds, which were not identified as capsaicin compounds [13]. Heating puree chilies at a higher temperature of 90oC causes the capsaicin structure to change, where the hydrophobic bonds are substituted quickly compared to lower heating temperatures. As a result, the capsaicin analog compound formed is different [5].

The substrate that plays a role in the synthesis of capsaicin is vanillylamine and its fatty acid derivatives which produce 2-44% are various types of capsaicin analogues. [14]. The availability of capsaicin was influenced by the interaction between the ripening stage of the fruit and the heating process, while the availability of dihydrocapsaicin was influenced by the interaction of fatty acids, the ripening levels and the heating process [11]. Heating affects the content of compounds that cause spicy taste, this is due to changes in the permeability and susceptibility of chilies during the heating process, thereby triggering the release of capsaicinoid compounds. The decrease or increase in the ratio of capsaicin and dihydrocapsaicin is probably due to differences in heat resistance of the two capsaicinoid compounds [11]. Harrison and Haris [6] also observed decreased capsaicin and increased dihydrocapsaicin after canning and cooking of jalapeno peppers. The results of other studies only found a slight change in the concentration of capsaicinoids in several types of peppers after heating, which resulted in the retention of capsaicinoids during the heat process, one of which depends on the type of heating and temperature [10].

Table 1 shows that the water content of groud red chilies with a heating temperature was not significantly different, it was of 73.01 - 74.23%. The higher temperature in processing resulted the water content of ground red chilies decreases. Heating process causes more water to evaporate so that the water content in the material is getting smaller. This evaporation is also caused by the difference in vapor pressure between the water in the material and the water vapor in the air. The water vapor pressure in the material is generally greater than the air vapor pressure so that the mass transfer of water from the material to the surrounding air occurs. Until now, there is no quality standard for ground chili, so it still refers to the quality standard of chili sauce. Chili sauce that can be accepted organoleptically has a water content of less than 83.3%, so the moisture content in this study was 74.23%, can be accepted organoleptically.

Table 2 showed that each heating temperature has a significant effect on the content of vitamin C. The results of this study showed that ground red chilies contain vitamin C ranging from 94.6-134.25 mg/100 g. The highest content of vitamin C was 134.25 mg/100 g at a heating temperature of 70o C, while the lowest vitamin C was 94.6 mg/100g at a heating temperature of 90o C. The results also showed that the higher of heating temperature, the vitamin C levels decreased, this is in accordance with the statement of Hok et al [8] that the higher the heating temperature will cause a decrease in vitamin C levels. Renate [5] stated that the decrease in vitamin C levels in the heating process is due to the fact that vitamin C is the most unstable vitamin that is soluble in water and is very easily damaged by heating. Vitamin C is also very easily oxidized and the heating process can also accelerate the oxidation reaction of vitamin C.

5. CONCLUSIONS

Reseach concluded that heating process of ground red chili processing affected chemical compound of dihydrocapsaicin, moisture and vitamin C. The processing ground red chili processed at temperature of 90ºC resulted in the highest dihydrocapsaicin content, water content and lower vitamin C of 62.91 µg/g, 73.01%, and 94.6 mg/100g respectively.

ACKNOWLEDGMENT

The Author would like to thanks to the Deanship of Scientific Research at University for funding the work through the research group project No. B/727/UN21.18/PT.01.03/2020 Tanggal 07 Mei 2020

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