International Journal of Applied Chemistry.
ISSN 0973-1792 Volume 12, Number 2 (2016) pp. 129-138

http://www.ripublication.com

Volatile Aroma Compounds of Green Chili Pepper Treated with Different Heat Drying Processes

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Abstract

Green chili pepper (*Capsicum annuum* Linn.) is one of well-known local plants of the northern part of Thailand. It is used for flavoring many traditional foods such as chili paste. This work focused on the effects of heat drying on the volatile aroma compounds of green chili pepper. The heating processes studied were hot air oven (moving bed type), hot oven and tray dryer oven. The extract was obtained using simultaneous steam distillation and extraction by Likens-Nickerson apparatus with dichloromethane as a solvent. The analysis and comparison of aroma composition were done by Gas Chromatography-Mass Spectrometry (GC-MS). It was found that there was the effect of heat treatment on the composition of aroma compounds which were n-hexanal, furfural, 2-hexenal, 2-hexenol, δ-3-carene, α-pinene, δ-3-carene isomer, (E, E)-2, 4 decadienal, 2-methyltridecane, γ-himachalene, (E)-farnesene, pentadecanal and neophytadiene of fresh and heated pepper.

Keywords: Green chili pepper, *Capsicum annuum* Linn., Aroma, Gas Chromatography-Mass Spectrometry

INTRODUCTION

"Nam Prik Noom" or "Green Chili Paste" is very popular in northern Thailand. Its texture is soft and fairly thick, containing some moisture with the natural texture of the vegetables. The taste is mixed harmoniously among saltiness, pungency and sweetness. The spiciness level is from moderate to high. This chili paste is usually eaten with steamed sticky rice and crispy puffed pork rinds (Kab Muu) with fresh or fast-boiled vegetables. The green color signifies the presence of naturally occurring beneficial nutrients. To maintain the natural appearance and quality of the dish, many

treatments of the raw materials are suggested. Drying of green chili pepper (*Capsicum annuum* Linn.) is one of the treatments used in order to keep its naturally-green color and to bring out the flavor of the ingredients.

Green chili pepper, the main ingredient, is scientifically called *Capsicum annuum* Linn. [1]. It is called "Prik Chee Fah" or "Prik Noom" in the Thai language and may also be called "Chili spur pepper". The shape looks like a finger of 4 to 6 inches long with a degree of pungency of about 30, 000 to 60, 000 Scoville units. Capsaicinoids content is about 0.2 to 2 percent, of which capsaicin accounts for about 50 to 70 percent.

There are different drying methods used for preservation of agricultural products [2]. The most popular is drying or dehydrating by solar drying, which is limited to only sunny places and is time-consuming. In order to obtain products appropriate for preservation and faster cooking, some methods using ovens [3] have been applied [4]. Each drying method aims to produce the desired dried or heated green pepper with the desired flavor and appearance.

Drying of the materials can be done using hot oven dryers, freeze dryer or spray dryers. According to hot oven dryers, there are basic hot oven, hot air oven (moving bed type) and tray dryer. In tray dryers, food materials are spread out, generally quite thinly, on trays in which the drying takes place. Heating may be by radiation from heating source through the trays where air flows above the surface of the food materials in the trays. In hot air dryer (moving bed type), the food materials are heated by hot air across the moving bed, which also removes the moist vapors.

The influence of various drying processes on the chemical composition of fruits and vegetables has been reported. Various drying processes were used to dry herbs by Kamel *et al*. [5]. In his work, air, convection oven and microwave were used and the antioxidant activity was studied with the determination of phenols content. The highest loss of chlorophyll was found in the case of the microwave drying method. Air drying at room temperature was found to be the most efficient drying method, followed by oven drying at 70^{o}C when conserving the beneficial bioactive components was considered. Mohd Zainol *et al.* [6] studied the degradation of selected flavonoids caused by different drying methods. However, high temperature was not applied in any of the drying methods. Degradation of flavonoids occurred when freeze-drying, air-drying and vacuum oven-drying were used. Concerning the volatile constituent of green chili pepper, Srisajjalertwaja *et al.* [7] studied the volatile compounds of fresh and baked green chili pepper (*Capsicum annuum* L. var. Jak Ka Pat) at 180, 210 and 250^{o}C. The volatile compounds were identified, and the concentration of each compound in ng/L was determined using 1, 2-dichlorobenzene as the internal standard.

The compounds responsible for flavor in cooked or heated green chili pepper, especially capsaicinoids, were reported [8]. The aroma of *Capsicum annuum* is due to both fresh plant compounds and compounds that develop after the period of storage or processing [9, 10].

OBJECTIVE

This work aims to study the effects of different drying processes on the aroma of the chili pepper. A novel drying method, hot air oven (moving bed type), was used to dry the green pepper in order to get an acceptable product to be used to prepare foods, especially chili paste. The method of drying was expected to give the product of a good aroma while retaining its natural properties. We also aimed to do the analysis of volatile aroma of the products dried using hot air oven (moving bed type), hot oven and tray dryer oven. The method used for the analysis was GC-MS, and the extracts were obtained by steam distillation and extraction in a solvent, dichloromethane.

METHODOLOGY

Materials:

Green chili pepper(*Capsicum annuum* Linn. Var. Yok Siam) cultivated in Pai district, Mae Hong Son province and available in Chiang Mai local markets was used in this study.

Laboratory Analysis:

Heat drying of green chili pepper:

Three different heat drying ovens-hot air oven (moving bed type, in-house constructed, Department of Chemistry, Faculty of Science, Chiang Mai University, Thailand), hot oven (Binder ED Series, Binder Inc., New Yolk, USA), and tray dryer oven (HT02 S/N 02-433;Technotrans International CO., LTD., Tokyo, Japan)-were used for heat drying of the green chili pepper. The drying temperature of 5-kg batches of chili peppers were 60, 70 and 80^{o}C for hot-air oven, 100^{o}C for hot oven, and 80^{o}C for air blowing tray dryer oven. The times needed to reach constant weight of the specimens so as to have completed drying were 11, 10, 9, 11, and 15 hours, respectively.

Extraction of volatile aroma compounds:

Simultaneous steam distillation and extraction (SDE) was carried out using the Likens-Nickerson apparatus. Redistilled dichloromethane was employed as a solvent. For each extraction, 100 g of chopped dried chili pepper was homogenized with 500 ml of distilled water and charged in a 2.5 L round bottom sample flask. Another 250 ml round bottom flask was filled with 150 ml of dichloromethane. The temperature of both flasks was brought to the boiling point of the sample and dichloromethane. The temperature of the circulating water system was operated at 4^{o}C. Distillation was stopped 2 hours after condensation commenced while the solvent extraction was continued for a further 15 min. The extract was subsequently concentrated to 5 ml by solvent evaporation and to 0.5 ml under a stream of analytical grade nitrogen gas. In order to dry the extract, anhydrous sodium sulfate was applied.

GC-MS Analysis:

An Agilent 19091 S-433E gas chromatograph-mass spectrometer equipped with an FID detector was used for the analysis. Volatile aroma compounds were separated on

non-polar fused silica capillary column HP-5 (5% phenyl methyl siloxane, Agilent 19091 J-413) measuring 30.0 m x 0.25 mm coated with 0.25 µm film thickness. Carrier gas (nitrogen) was applied at a flow rate of 1 ml/min (split ratio: 50:1). The column temperature program was 70ºC for 14 min and then programmed to 270ºC at 10ºC/min. Injection volume was 1 µL. The identification of the volatile aroma compounds was done by comparing the mass spectrum with the known compounds in the database library.

RESULT AND DISCUSSION

Chromatograms of the volatile aroma compounds of dried chili peppers are shown in Figure 1 (a) to (f). The results of the compound identification for each sample are shown in Table 1. The extract of fresh green chili pepper obtained is a yellowish green liquid with a fresh green and pungent odour. Five compounds were found with an unknown as shown in Figure 1 (a).

The results from the GC-MS analysis of the extract from different heat-processed green chili peppers gave more additional compounds. The extract of the hot air oven (moving bed type) dried pepper gave very similar profiles with eight peaks of known compounds as shown in Figure 1 (b, c and d). The identified compounds are listed in Table 1. Moreover, the chromatogram of the hot oven drying process shows not much difference from the results of hot air oven (moving bed type) drying with six identified compounds and an unknown as shown in Figure 1(e) and Table 1. However, the chromatogram of tray drying oven heating shows a decrease of a known compound, furfural, with six identified compounds as also shown in Figure 1(f) and Table 1.

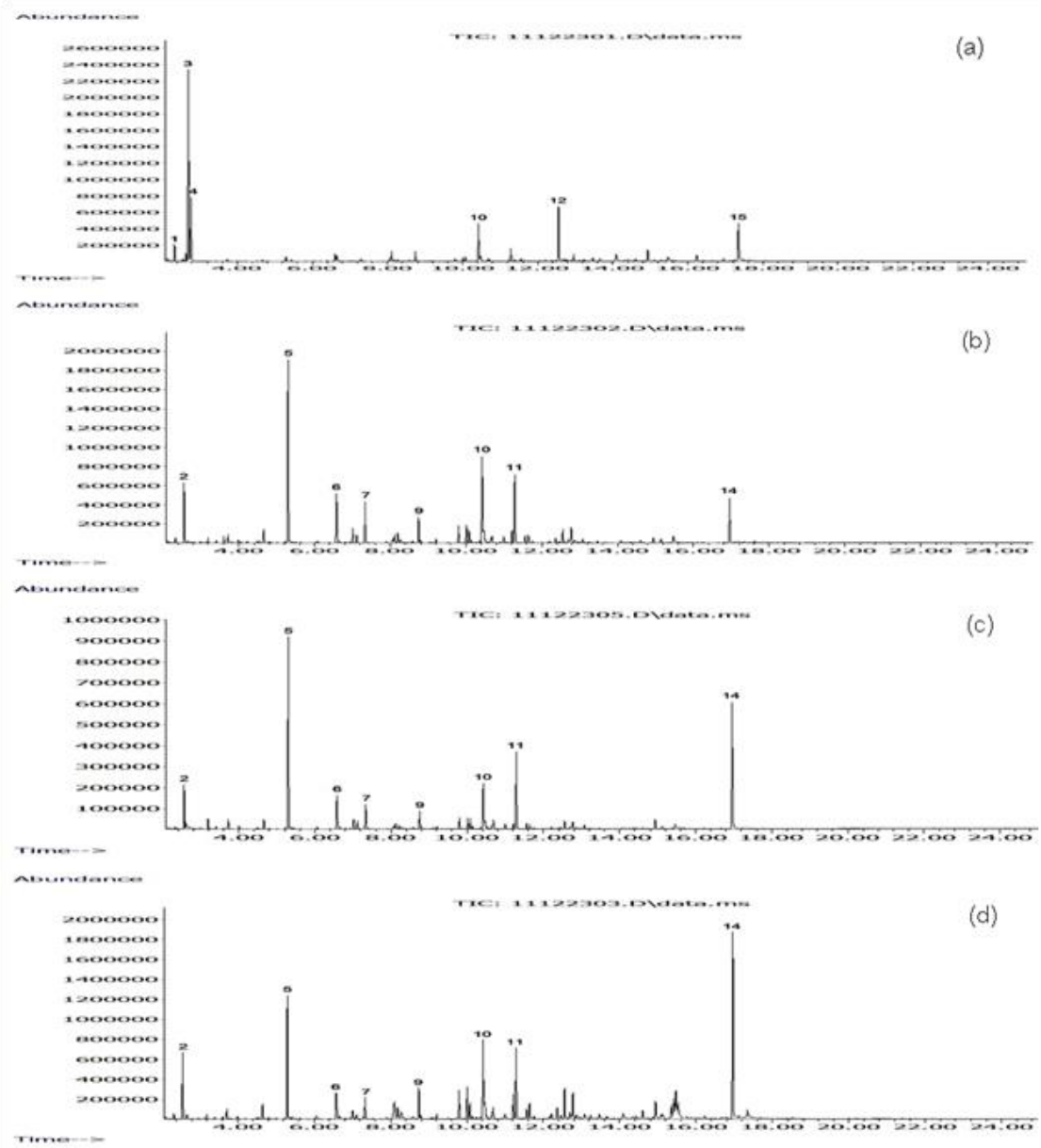
The dominant volatile aroma compounds that are found in fresh green chili pepper and seem to decrease in heated pepper are n-hexanal, 2-hexenol and 2-hexenal. These compounds are usually found in fresh vegetables and fruits such as green tea, mulberry leaves, apples, kiwis, peaches, strawberries, tamarinds and fresh chilies.

In fresh Habanero chili (*Capsicum chinense* Jack), 2-hexanal was found and decreased when ripening occurred [11]. The formation of n-hexanal, 2-hexenol and 2-hexenal is known to be results of lipase and lipoxygenase enzymes action on linoleic and linolenic unsaturated fatty acids followed by reduction of alcohols to aldehydes and isomerization reactions [12]. γ-Himachalene is a sesquiterpene found in Habanero chili. Pentadecanal, which was found in Cachucha chili [13], is a long chain aldehyde with a high boiling point. Both volatiles are still retained in heat processing pepper, but a few were found in the case of tray drying oven treated pepper.

δ-3-Carene, α-pinene, δ-3-carene isomer, 2-methyltridecane and (E)-farnesene were all found in genus *Capsicum* [11, 14]. (E, E)-2, 4-Decadienal is an alkadienal compound that may result from the degradation of fatty acids, especially the omega-3 fatty acids, and was identified in pepper fruits of *Capsicum annuum* [15]. These compounds remained in heat drying chili peppers while n-hexanol, 2-hexenal and 2-hexenol were lost. Neophytadiene was reported to be present in *Capsicum annuum* L. var. acuminatum [16]. The compound was identified in all heat-treated samples. Neophytadiene may be derived from the hydrolysis of chlorophyll and dehydration of

phytol, released especially under gentle drying conditions [17]. The degradation of chlorophyll to neophytadiene is shown in Figure 3 [18].

During leaf senescence and fruit ripening, the green color is degraded due to the breakdown of chlorophyll to colorless products. The early steps of the chlorophyll catabolic pathway consist of four enzymatic activities [19]. Furfural, an aroma responsible for producing a caramel-like odour, may be produced by the heating of carbohydrates. Furfural and neophytadiene were not detected in the work of Srisajjalertwaja *et al*. [7] in either fresh or baked green chili pepper. These two compounds may be the result of heat drying processes except for furfural in the tray drying sample. In addition, these compounds were not found in fresh chili pepper.



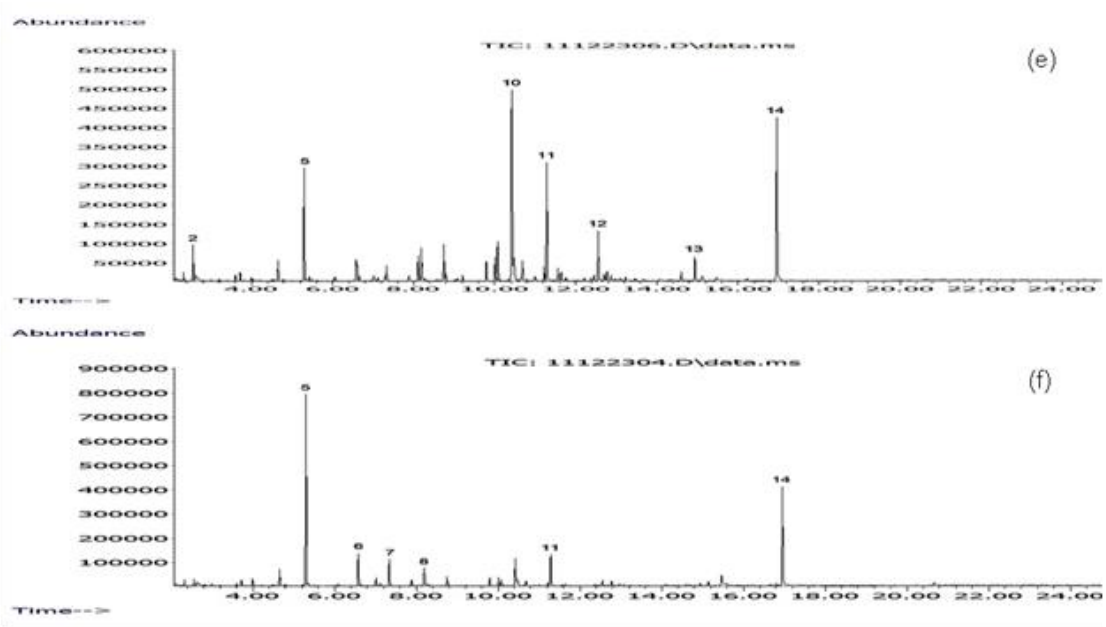


Figure 1. Chromatograms of green chili pepper volatile aroma compounds (a) fresh (b) hot air oven (moving bed type) 60ºC (c) hot air oven (moving bed type) 70ºC (d) hot air oven (moving bed type) 80ºC (e) hot oven 100ºC (f) tray dryer oven 80ºC.

Table 1. Volatile aroma compounds of fresh and dried green chili pepper

Retention time(min.) (Peak No.)	Compounds	Fresh	Hot air oven	Hot oven	Tray dryer oven
2.34(1)	n-Hexanal	✓	-	-	-
2.56(2)	Furfural	-	✓	✓	-
2.70(3)	2-Hexenal	✓	-	-	-
2.77(4)	2-Hexenol	✓	-	-	-
5.30(5)	δ-3-Carene	-	✓	✓	✓
6.58(6)	α-Pinene	-	✓	-	✓
7.34(7)	δ-3-Carene isomer	-	✓	-	✓

8.19(8)	(E, E)-2, 4-Decadienal	-	-	-	✓
8.75(9)	2-methyltridecane	-	✓	-	-
10.42(10)	γ-himachalene	✓	✓	✓	-
11.29(11)	(E)-Farnesene	-	✓	✓	✓
12.56(12)	Pentadecanal	✓	-	✓	-
14.94(13)	Unknown	-	-	✓	-
16.96(14)	Neophytadiene	-	✓	✓	✓
17.35(15)	Unknown	✓	-	-	-

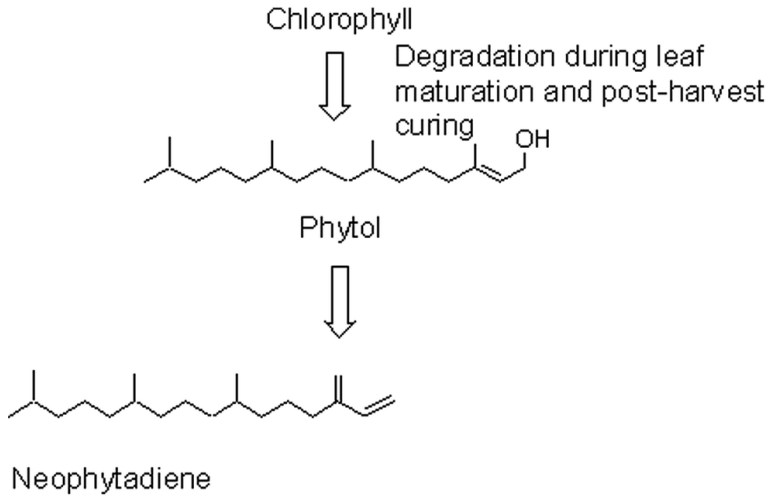


Figure 3. Degradation of chlorophyll to neophytadiene.

The drying temperatures used for chili peppers were 60, 70 and 80ºC for hot air oven, 100ºC for hot oven and 80ºC for tray dryer oven. As for the times needed to reach constant weight of the specimens so as to have completed drying of each process, these were 11, 10, 9, 11 and 15 hours, respectively. The time of drying as well as the process used may affect the composition of the aroma compounds. High contact temperature may cause the compounds such as neophytadiene and furfural to be formed by heat. This is not in the case of tray drying, though, because this process requires the longest drying time of. The tray drying process is not sufficient to have

high contact temperature as expected due to the circulation of air. The hot air oven at 60^{o}C seems to be the most suitable way because most of the fresh pepper aroma compounds were retained. Likewise, the pleasant baking odour for enhancing the odour of green pepper chili paste was produced. The evidence is shown by comparing the hot-air oven to hot oven and tray dryer oven products as illustrated in Figure 4 (a, b and c). Drying with hot air oven is therefore found to be the best way to give a desired product. The formation of neophytadiene occurred while the natural composition remained intact.

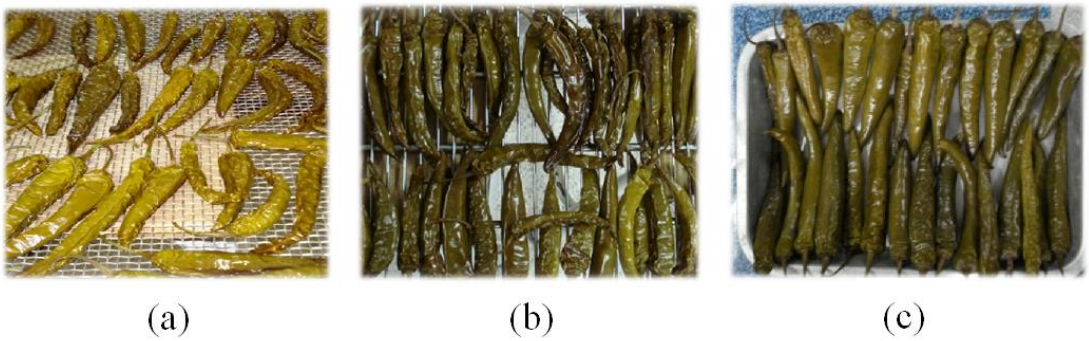


Figure 4. Comparison of dried chili pepper, (a) Hot air oven 60^{o}C (b) Hot oven 100^{o}C and (c) Tray dryer oven 80^{o}C.

CONCLUSION

In conclusion, the volatile aroma compounds found were n-hexanal, furfural, 2-hexenal, 2-hexenol, δ-3-carene, α-pinene, δ-3-carene isomer, (E, E)-2, 4-decadienal, 2-methyltridecane, γ-himachalene, (E)-farnesene, pentadecanal and neophytadiene in fresh and heated pepper. After the heating process, fresh green odour, n-hexenal, 2-hexenal and 2-hexenol decreased. Other aroma compounds-δ-3-carene, α-pinene, δ-3-carene isomer, (E, E)-2, 4 decadienal, 2-methyltridecane, γ-himachalene, (E)-farnesene and pentadecanal-were retained. Furfural and neophytadiene were produced. Tray dryer heat processing did not give furfural, and the product was considered to be insufficient. On the other hand, hot-air oven processing at 60^{o}C was determined to be the appropriate way of heat drying.

ACKNOWLEDGEMENTS

The authors would like to express their deepest gratitude to Rajamangala University of Technology Lanna Chiang Mai, Chiang Mai, Thailand, for the shared funding as well as the laboratories of the Department of Chemistry and the Department of Industrial Chemistry, Faculty of Science, Chiang Mai University for all the materials and facilities provided.

REFERENCES

[1] Wangcharoen, W. and Morasuk, W., 2007, "Antioxidant capacity and phenolic content of chilies, Kasetsart J. (Nat. Sci.), pp. 41, 561 –569.

[2] Topuz, A., Dincer, C., Ösdemir, K.S., Feng, H. and Kushad, M., 2011, "Influence of different drying methods on carotenoids and capsaicinoids of paprika (cv. Jalapeno)", Food Chemistry, 129(3), pp. 860-865.

[3] Surbkar, R., 2013, "Dehydration technology", The Journal of KMUTNB, 23(2), pp. 500-512.

[4] Rabeta, M.S. and Vithyia, M., 2013, "Effect of different drying methods on the antioxidant properties of *Vitex negundo* Linn. Tea", International Food Research Journal, 20(6), pp. 3171-3176.

[5] Kamel, S.M., Thabet, H.A. and Algadi, E.A., 2013, "Influence of drying process on the functional properties of some plants", Chemistry and Materials Research, 3(7), pp. 1-8.

[6] Mohd Zainol, M.K., Abdul-Hamid, A., Abu Bakar, F. and Pak Dek, S., 2009, "Effect of different drying methods on the degradation of selected flavonoids in *Centella asiatica*", International Food Research Journal, 16, pp. 531-537.

[7] Srisajjalertwaja1, S., Apichartsrangkoon, A., Chaikham, P., Chakrabandhu1, Y., Pathomrungsiyounggul, P., N. Leksawasdi, W. Supraditareporn and Hirun, S., 2012, "Color, Capsaicin and Volatile Components of Baked Thai Green Chili(*Capsicum annuum* Linn. var. Jak Ka Pat)", Journal of Agricultural Science, 4(12)**,** pp. 75-84.

[8] Leng, T.W., Idayu Muhamad, I., Abang Zaidel, D.N. and Khairuddin, N., 2013, "Evaluation of capsaicinoids extracts as bioactive substance for antimicrobial films. Jurnal Teknologi (Sciences and Engineering), 64(2), pp. 69-74.

[9] Luning, P.A., D. Yuksel, D., de Vris, R.V. and Roozen, J.P., 1995, "Aroma changes in fresh bell peppers(*Capsicum annuum*) after hot-air drying", Journal of Food Science, 60 (6), pp. 1269 – 1276.

[10] Reinecius, G., 2013, "Source Book of Flavors", Springer Science& Business Media, New York, pp. 139-154.

[11] Pino, J., Gonzalez, M., Ceballos, L., Yah, A.R.C., Aguirre, J.T., Morero L.L. and Duch., E.S., 2007, "Characterization of total capsaicinoids, colour and volatile compounds of Habanero chilli pepper (*Capsicum chinense* Jack.) cultivars grown in Yucatan" Food Chemistry, 104, pp. 1682-1686.

[12] Fauconnier, M.L. and Marlier, M., 1997, "Fatty acid hydroperoxides pathways in plants. A Review", GrasasyAceites, 48(1), pp. 30-37.

[13] Pino, J., V.Fuentes and O. Barrios, O., 2011, "Volatile constituents of Cachucha peppers (*Capsicum chinense* Jacq.) grown in Cuba", Food Chemistry, 125, pp. 860-868.

[14] Forero, M.D., Quijano, C.E. and Pino, J.A., 2008, "Volatile compounds of chile pepper (*Capsicum annuum* L. var. *glabriusculum*) at two ripening stages", Flavour Fragrance, 24, pp. 25-30.

[15] Kevrešan, Ž. S., Hrabovski, N. Č, Kuhajda, K.N., Dukić, N.M. and Saka, M.B., 2009, "Essential oil composition of fresh and dried pepper fruits (*Capsicum annuum* L.)", Food & Feed Research, 36(1-2), pp. 29-34.

[16] Conforti, F., Statti G.A. and Menichini, F., 2007, "Chemical and biological variability of hot pepper fruits (*Capsicum annuum* L. var. acuminatum) in relation to maturity stage", Food Chemistry, 102, pp. 1096–1104.

[17] Belitz, H.D. and Grosch, W., 1999, "Food Chemistry", 2nd edition, Springer-Verlag, New York, p 912.

[18] Changgook, L., Younghoon, L., Jae-Gon, L. and Buglass, A. J., 2015, **"**Development of a reduced pressure headspace solid-phase microextraction-gas chromatography/mass spectrometric (rpHSSPME-GC/MS) method and application to aroma analysis**",** Analytical Methods, 7, pp. 6504-6513.

[19] Hörtensteiner, S., 2006, "Chlorophyll degradation during senescence", Annu Rev Plant Biol, 57, pp. 55-77.