

## Antioxidant Capacity Changes of Bird Chili (*Capsicum frutescens* Linn.) During Hot Air Drying

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### ABSTRACT

The antioxidant capacity of bird chili (*Capsicum frutescens* Linn.) during hot air drying at 70, 100 and 121°C was analyzed by three different methods: ferric-reducing, antioxidant power (FRAP) assay; improved, ABTS, radical cation decolorization assay; and DPPH, free radical scavenging activity, together with the analysis of total phenolic content and browning pigment formation. It was found that total phenolic content might decrease at the beginning of the drying process, but that it would increase when the browning pigments were developed. Phenolic compounds of fresh, red bird chili were less heat stable than the ones of fresh, green bird chili. In addition, the antioxidant capacity of dried bird chili was dependent on the degree of browning and the drying temperature. All the antioxidant capacities of the dried products were higher than for the fresh ones, except after drying at 70°C, when the reducing power, FRAP value, of dried green and red chili was lower than the fresh one, and the values of the free radical scavenging activities, ABTS and DPPH of dried red bird chili did not change.

**Key words:** antioxidant capacity, dried bird chili, phenolic content, browning reaction products

### INTRODUCTION

Bird chili (*Capsicum frutescens* Linn.) is one of two chili types widely used in Thailand. Known in Thai as “Prik Khee Nu”, it is a tiny cone and only 0.75 to 1.5 inches in length, with a value of 50,000-100,000 Scoville units. Chilies are high in vitamin A and C, but low in calories and sodium and contain potassium, magnesium and folic acid. But capsaicinoids (vanillylamides of monocarboxyl acids) which are responsible for the pungency or bite are considered as active compounds in chilies. Capsaicin accounts for about 50% to 70% of the total capsaicinoids. It gives bite, but has no odor. Other bite-contributing components are: 20 to 25% dihydrocapsaicin,

which together with capsaicin provides the fiery notes from the mid-palate to the throat; 7% nordihydrocapsaicin, which is fruity and sweet and has the least-burning sensation; and 1% homocapsaicin and 1% homodihydrocapsaicin, which give a numbing and prolonged burn (Uhl, 2000).

Chilies have been recognized by many cultures around the world for their medicinal qualities. When chilies are eaten, capsaicin stimulates the release of endorphins, which give a pleasurable feeling. Moreover, chilies are believed to: increase circulation; relieve rheumatic pain; treat mouth sores and infected wounds; reduce blood clots; and aid digestion by stimulating saliva and gastric juice flow (Uhl, 2000). Capsaicin has

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been tested by many investigators for its effects on experimental carcinogenesis and mutagenesis. There is no solid evidence showing that chili and capsaicin are carcinogenic in humans. In contrast, many studies reveal substantial antioxidant, antigenotoxic and anticarcinogenic effects of chili extracts and capsaicin (Surh *et al.*, 1998; Prasad *et al.*, 2004). Therefore, capsaicin is suggested as an important dietary phytochemical with antioxidant and chemopreventive activities.

Antioxidant values and the total phenolic content of chili were reported in some previous papers. Pellegini *et al.* (2003) showed that the FRAP and ABTS values were 23.54 mmol Fe<sup>2+</sup> equivalent per kg of fresh weight and 7.62 mmol Trolox equivalent per kg of fresh weight, respectively. Wangcharoen and Morasuk (2007) showed that the FRAP, ABTS and DPPH values were 0.62-2.4, 1.32-6.68, and 0.36-1.23 mg vitamin C equivalent per gram of fresh weight, respectively and total phenolic content was 0.85-3.48 mg gallic acid equivalent per gram of fresh weight.

Both fresh and dried chilies are used as food ingredients or seasonings. They provide not only heat but also flavor, color, and visual appeal to foods. During the heating process, non-enzymatic browning reaction including Maillard reaction, caramelization and chemical oxidation of phenols occur. The antioxidant activity of the Maillard reaction (Manzocco *et al.*, 2001; Yanagimoto *et al.*, 2002; Yilmaz and Toledo, 2005; Osada and Shibamoto, 2006) and caramelization products (Benjakul *et al.*, 2005) have been reported. This paper studied the antioxidant capacity of bird chili during hot air drying at 70, 100 and 121°C by three different methods: ferric-reducing, antioxidant power (FRAP) assay; improved, ABTS, radical cation decolorization assay; and DPPH free radical scavenging activity, together with the total phenolic content and browning pigment formation, with absorbance at 420 nm. The correlations of the % antioxidant

capacity, the total phenolic content and absorbance at 420 nm were analyzed.

## MATERIALS AND METHODS

### Chemicals and instruments

TPTZ (2,4,6-tripyridyl-s-triazine), DPPH (2,2-diphenyl-1-picrylhydrazyl) [Sigma], ABTS (2,2'-azinobis (3-ethylbenzothiazoline-6-sulfonic acid)), Folin-Ciocalteu phenol reagent, ferric chloride, gallic acid, glacial acetic acid, hydrochloric acid, sodium acetate, potassium persulphate, sodium carbonate, and vitamin C [Fluka] were of analytical grade. A hot air oven (TS 8136 of Termaks) was used for the drying process.

### Sample extraction

Fresh green and red bird chili (*Capsicum frutescens* Linn.), Prik Khee Nu, were purchased from fresh markets. The edible portion of the fresh samples was homogenized using a blender. Two grams of blended, fresh samples were transferred into a 25 cm × 150 cm tube and then were dried at 70, 100, and 121°C. Sample tubes were collected 10 times during the drying period. The sample extraction method used by Leong and Shui (2002) was modified. Ten ml of a solvent (60% (v/v) of 95% ethanol) was added to the collected sample tube. The extraction was done using a vortex mixer for 1 min and the mixture was filtered through a Whatman filter paper no 1. The filtrate was adjusted to 10 ml with deionized water and then was used for all assays including FRAP, ABTS, DPPH, total phenolic content and the formation of browning pigments (absorbance at 420 nm). Extracts of blended, fresh green and red bird chili were prepared for comparison and the weight change during the drying process also was recorded.

### Ferric-reducing antioxidant power (FRAP) assay

FRAP, a method for measuring the total reducing power of electron-donating substances, was assessed according to Benzie and Strain (1999). Briefly, 6 ml of working FRAP reagent (0.1 M acetate buffer : 0.02 M FeCl<sub>3</sub>:0.01 M 2,4,6-tripyridyl-s-triazine (TPTZ) = 10:1:1) prepared daily was mixed with 20 ml of extract sample. The absorbance at 593 nm was recorded after a 30-min incubation at 37°C. Absorbance increases were calculated as a FRAP value for comparison with the fresh sample. Vitamin C (0 - 15 µg) was used as a standard.

### ABTS radical cation decolorization (ABTS) assay

The method, based on the ability of antioxidant molecules to quench the long-lived ABTS radical cation (ABTS<sup>•+</sup>), of Re *et al.* (1999) was modified. The ABTS<sup>•+</sup> was produced by reacting 7 mM ABTS stock solution with 2.45 mM potassium persulphate (final concentration) and allowing the mixture to stand in the dark at room temperature for 12-16 h before use. The ABTS<sup>•+</sup> solution was diluted with deionized water and 95 % ethanol (1:1) to an absorbance of 0.70 (± 0.02) at 734 nm. Next, 20 µl of the extract was mixed with 6 ml of diluted ABTS<sup>•+</sup> solution. The decrease of absorbance was recorded at 1 min after mixing. Absorbance decreases were calculated as ABTS value for comparison with the fresh sample. Vitamin C (0 - 20 µg) were used as a standard.

### DPPH free radical scavenging activity (DPPH)

The method of Brand-Williams *et al.* (1995), based on the reduction of the DPPH radical solution in the presence of hydrogen-donating antioxidants, was used with some modifications. Initially, a 0.8 mM DPPH radical solution in 95% ethanol was prepared. Using deionized water and 95 % ethanol (1:1), 100 µl of the extract was diluted to 5.4 ml before 0.6 ml of the DPPH radical solution was added and shaken vigorously. The

decrease of absorbance was recorded at 1 min after mixing. Absorbance decreases were calculated as DPPH values for comparison with the fresh sample. Vitamin C (0 - 40 µg) was used as a standard.

### Total phenolic content (TPC)

The Folin-ciocalteau micro method of Waterhouse (n.d.) was used. Deionized water was used to dilute 60 µl of the extract to 4.8 ml and 300 µl Folin-ciocalteau reagent was added and shaken. After 8 min, 900 µl of a 20% sodium carbonate was added and mixed. the solution was left at 40°C for 30 min, before reading the absorbance at 765 nm. Absorbance increases were calculated as total phenolic content for comparison with the fresh sample. Gallic acid (0-50 µg) was used as a standard.

**Values of FRAP, ABTS, DPPH, and TPC** (mg standard equivalent per gram of dried weight)

*Value.of.FRAP,ABTS,DPPH,and.TPC* =

$$\frac{[SA - BA]}{Slope} \times [10 / U]$$

$$\frac{[2]}{[1,000]}$$

where: SA = sample absorbance for FRAP value and TPC or absorbance decrease of sample for ABTS and DPPH values

BA = blank (no extract) absorbance for FRAP value and TPC or absorbance decrease of blank for ABTS and DPPH values (extract was substituted by deionized water for blank)

Slope = slope of standard curve

[10/U] = total volume of extract (10 ml) / Used volume of extract (ml)

[2] = weight of blended sample (g)

MC = % moisture content of sample / 100

[1,000] = factor for changing µg to mg

### Change of antioxidant capacity, TPC, and weight (%)

*Change.of.antioxidant.capacity,TPC,and.weight =*

$$\frac{\text{Value.of.collected.sample}}{\text{Value.of.blended.fresh.sample}} \times 100$$

### The formation of browning pigment

The formation of browning pigments for all extracts was determined by the official method (ADOGA, 1976), with the measurement of absorbance at 420 nm for each diluted extract.

### Statistical analysis

The experiment was repeated three times and was conducted on separate marketing purchases (triple measurements for each marketing purchase). The bivariate correlations between the percentage of antioxidant capacity, total phenolic content and absorbance at 420 nm were analyzed.

## RESULTS AND DISCUSSION

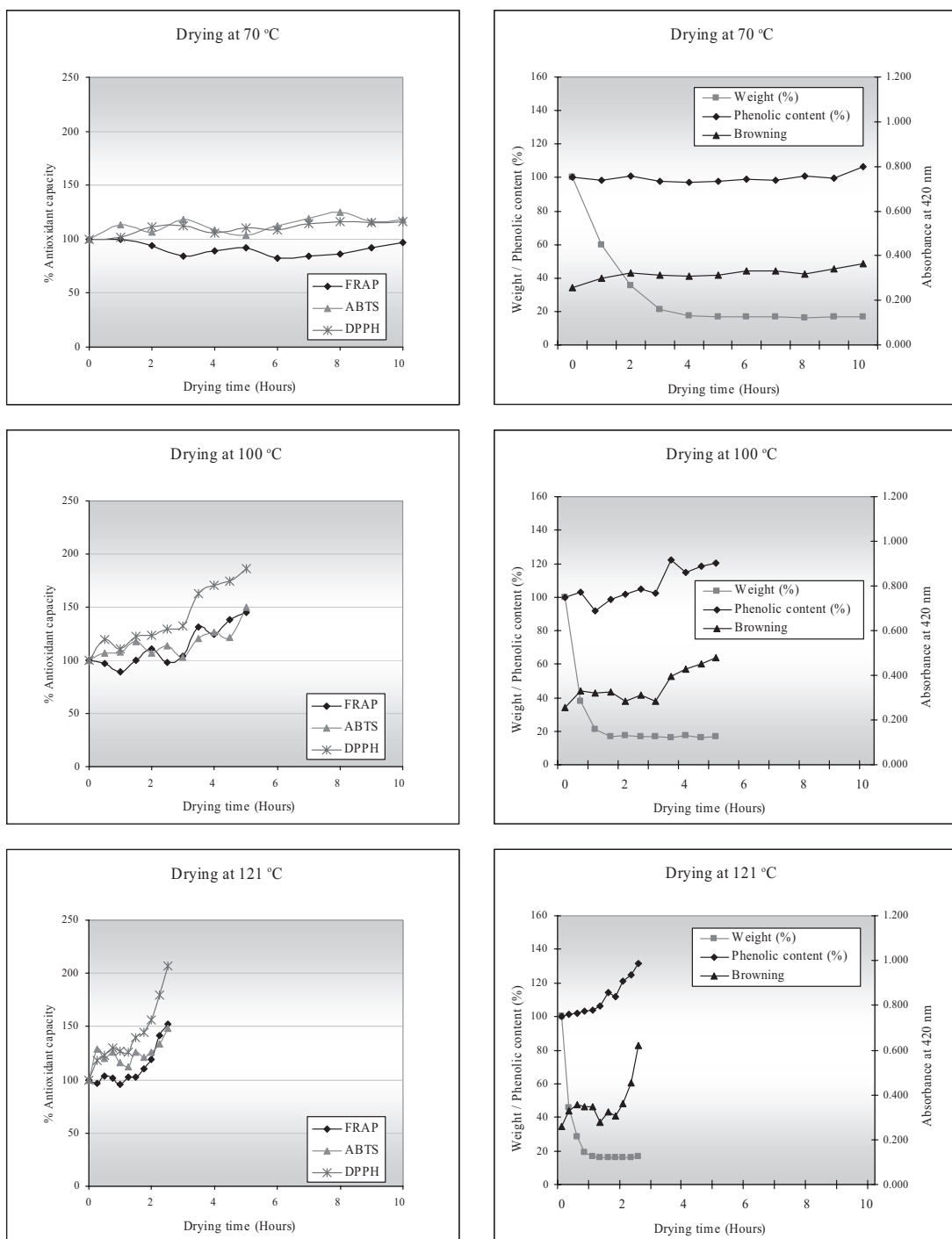
### Green bird chili

The FRAP, ABTS and DPPH values, as well as total phenolic content of fresh, green bird chili were  $7.84 \pm 0.46$ ,  $30.06 \pm 3.09$ , and  $3.06 \pm 0.31$  mg vitamin C equivalent per gram of dried weight, and  $13.15 \pm 1.76$  mg Gallic acid equivalent per gram of dried weight, respectively. Different values of each antioxidant assay from the same sample were also found in previous papers (Wang *et al.*, 1998; Pellegrini *et al.*, 2003; Yang *et al.*, 2006), which could be caused by the unique mechanism of each assay and a different antioxidant capacity and the mechanisms of the compounds in the natural samples.

For the drying process at 70°C, the FRAP value decreased when the drying time was increased, but it seemed to increase up to 6 h, after which the % weight of dried sample was constant (Figure 1). The change within the first 6 h could be explained by the thermal decomposition of some reducing compounds. Commonly,

chlorophylls in green plants would be degraded to pheophytins during thermal processing (Weemaes *et al.*, 1999; Gupte *et al.*, 2006; Gaur *et al.*, 2007). However, the phenolic compounds, a group of reducing compounds, were not significantly changed in this case because of the formation of high-molecular-weight phenolic compounds during heating (Manzocco *et al.*, 2001). The ABTS and DPPH values increased during the drying process and these trends were similar to the change of absorbance at 420 nm and the formation of browning pigments ( $r = 0.593$  and  $0.812$ , respectively). This could be reasoned as due to some compounds with free radical scavenging activities, including melanoidins, being developed from the non-enzymatic browning reactions (Manzocco *et al.*, 2001; Yanagimoto *et al.*, 2002; Benjakul *et al.*, 2005; Yilmaz and Toledo, 2005; Osada and Shibamoto, 2006) and other reactions during drying process.

Almost all the results of drying at 100 and 121°C were similar to the ones from drying at 70°C. However, the decreasing period of the FRAP value was much shorter and the increase in the ABTS and DPPH values, and absorbance at 420 nm, was faster and higher (Figure 1), because the rate of thermal degradation and the non-enzymatic browning reaction depended on drying temperatures following the Arrhenius relation;  $k_T = k_0 \exp(-E_a/RT)$  (Rapusas and Driscoll, 1995; Ahmed *et al.*, 2000; Ibarz, 2000; Ahmed *et al.*, 2002). In case of the non-enzymatic browning reactions, the rate also varied as a quadratic of the water activity of the samples, for example the maximum browning rate occurred in the 0.6-0.7 range of water activity for drying onion slices (Rapusas and Driscoll, 1995). In addition, the decreasing period of absorbance at 420 nm was found after a short increase at the beginning, when drying at 100 and 121°C, because of the decomposition of some brown pigments such as pheophytins and olive-brown pigments degraded from chlorophylls (Weemaes *et al.*, 1999). For the



**Figure 1** Antioxidant capacity, phenolic content, absorbance at 420 nm and weight of green bird chili during hot air drying at 70, 100 and 121 °C.

phenolic content, the decreasing period was also found at 100°C but it did not significantly change at 121°C for a period of 1.5 h from the beginning. These results might have been due to the fact that there was a decomposition of some phenolic compounds and some pigments, which absorbed 420 nm light, occurring during that decreasing period. The decrease of both absorbance at 420 nm and the phenolic content affected the % antioxidant capacity of the samples at that time as well. All correlations between the % antioxidant capacity, the total phenolic content and absorbance at 420 nm were significant ( $r = 0.734 - 0.962$ ), and it was found that the antioxidant capacity of dried, brown bird chili was higher than for the fresh green one, depending on the degree of browning or the intensity of brown color, as Manzocco *et al.* (2001) indicated that color could be considered an index of the overall antioxidant properties of foods.

The weight of dried, green bird chili was constant at 16.0-16.8% after drying at 70, 100 and 121°C for 6, 2.5, and 1 h, respectively (Figure 1). After that period of drying at 100 and 121°C, a decrease of absorbance at 420 nm was found. This might be explained by the increase of absorbance at 420 nm at the beginning being mainly due to pigment degradation, such as the pheophytinization of chlorophylls. When the weight of dried samples was constant, the decomposition of some brown pigments such as pheophytins would occur. After that, the non-enzymatic browning reaction became dominant, because of appropriate water activity in the samples. In the case of drying at 70°C, the decomposition of some brown pigments and the domination of non-enzymatic browning reaction were not noticeable, because of the lower reaction rate.

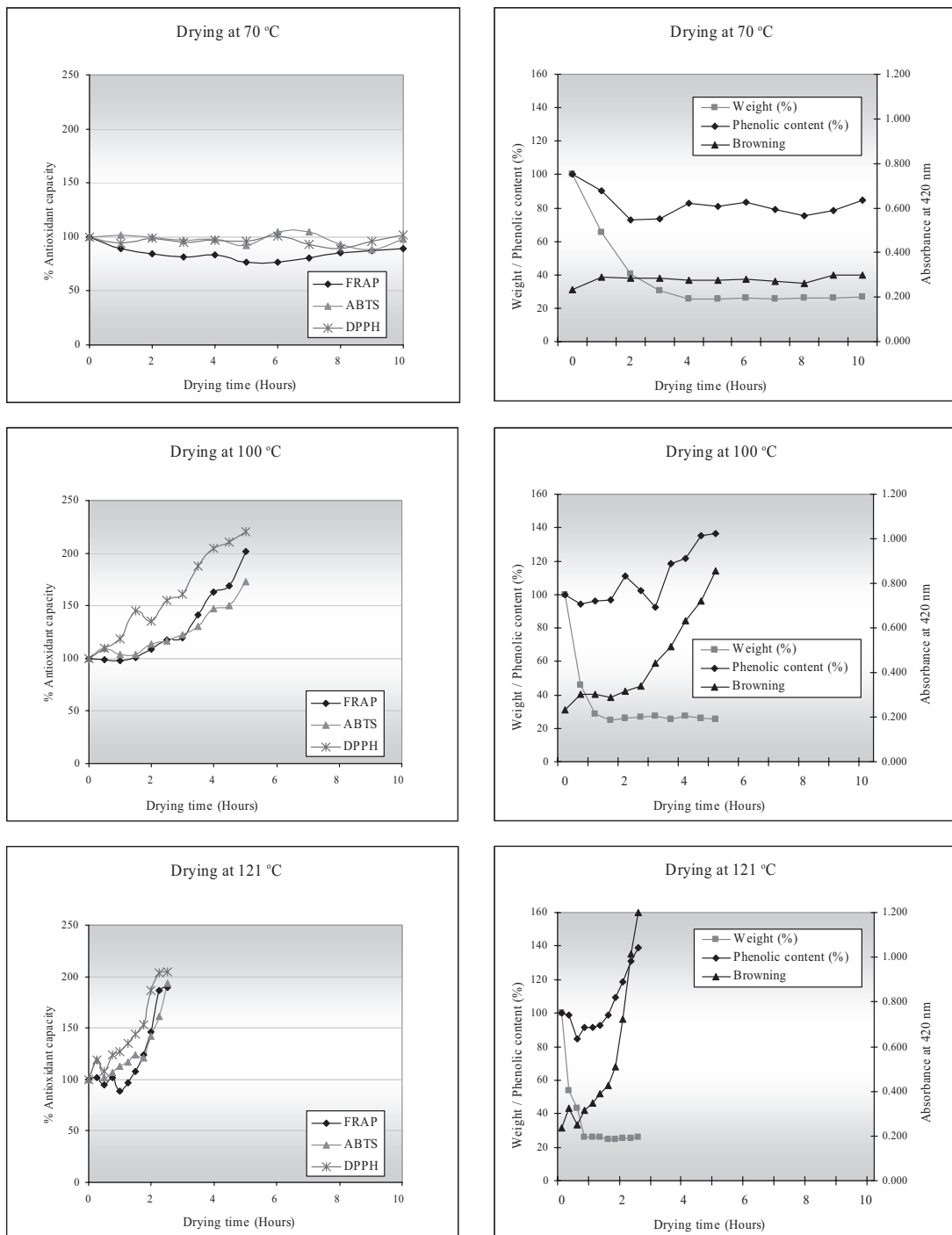
### Red bird chili

The FRAP, ABTS, DPPH values and the total phenolic content of fresh, red bird chili were  $7.11 \pm 0.25$ ,  $19.59 \pm 1.54$  and  $2.39 \pm 0.20$  mg

Vitamin C equivalent per gram of dried weight, and  $10.57 \pm 1.20$  mg Gallic acid equivalent per gram of dried weight, respectively.

Almost all of the red bird chili results were the same as the ones for the green chili, except for a decrease of the phenolic content at 70°C, which also was observed in the beginning period at 100 and 121°C. In addition, the ABTS and DPPH values at 70°C were not significantly changed (Figure 2). The decrease in the phenolic content showed that the phenolic compounds in fresh, red bird chili were less heat stable than the ones of fresh, green bird chili. A correlation between the FRAP value and the phenolic content at 70°C in this case was found ( $r = 0.688$ ). The ABTS and DPPH values at 70°C were not significantly changed, because there were related carotenoid pigments with antioxidant power, including capsanthin, capsorubin, cryptoxanthin, and zeaxanthin as the main pigments in red chili, but they were not heat-stable (Berke and Shieh, 2001). Therefore, they only had an effect on the antioxidant capacity of the samples in the early stages of drying, before they were decomposed by heat. All correlations between the % antioxidant capacity, total phenolic content and absorbance at 420 nm at 100 and 121°C were significant ( $r = 0.846-0.990$ ). The antioxidant capacity of dried, brown bird chili was also higher than that of the fresh red one, depending on the degree of browning.

The weight of dried, red bird chili was constant at 24.9-26.2% after drying at 70, 100 and 121°C for 4, 1.5 and 0.75 h, respectively (Figure 2). The increase of absorbance at 420 nm from the beginning was due to the acceleration of the carotenoid pigment degradation at higher temperatures and water activities (Topuz, 2008). With drying at 100 and 121°C, the decomposition of some browning pigments occurred when the weight of the dried samples was constant, before the rapid increase of non-enzymatic browning, but this change did not appear at 70°C in the same way as in the drying of the green bird chili.



**Figure 2** Antioxidant capacity, phenolic content, absorbance at 420 nm and weight of red bird chili during drying hot air drying at 70, 100 and 121 °C.

Although these results showed a higher antioxidant capacity in dried, brown bird chili, it should be stated that too much thermal processing causes a loss in the antioxidant capacity because of the pyrolysis of antioxidant compounds, including melanoidins and phenols (Manzocco *et al.*, 2001), and some carcinogens could be found at elevated levels in foods heated at high temperatures (Vainio, 2003).

### CONCLUSIONS

The phenolic compounds in fresh bird chili and some browning reaction products developed during hot air drying could be good antioxidant compounds. The antioxidant capacity of dried bird chili was higher than in the fresh chili, depending on the degree of browning and the drying temperature. Drying at 70°C might have decreased the reducing power (FRAP value) of bird chili, but drying at 100 and 121°C did not. Drying at all three temperatures in this study (70, 100 and 121°C) could increase the free radical scavenging activities (ABTS and DPPH values) of green bird chili, but drying at 70°C did not for red bird chili.

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