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Enhancement of sulforaphane content in cabbage outer leaves using hybrid drying technique and stepwise change of drying temperature

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ABSTRACT

Sulforaphane is a hydrolysis product of glucosinolates, which are plant secondary metabolites found in various kinds of *Brassica* vegetables including white cabbages (*Brassica oleracea* L. var. capitata). Sulforaphane is of interest as it is claimed to possess chemoprotective effect against an array of cancers. The formation of sulforaphane is via enzymatic reactions and the rates of formation and degradation are strongly dependent on the temperature. Careful regulation of the material temperature during drying to maximize the formation and minimize the degradation of sulforaphane should therefore be possible. In this study, the effect of stepwise change of medium temperature during hot air drying, vacuum drying and hybrid drying, i.e., low-pressure superheated steam drying (LPSSD) followed by vacuum drying, on the evolution of sulforaphane in white cabbage outer leaves was investigated; the results were compared with those in the cases of constant drying medium temperature. Similar evolution patterns of sulforaphane were noted in all cases; sulforaphane first increased before reaching the maximum and then decreased towards the end of drying. Nevertheless, the cabbages undergone LPSSD at 60 °C for 10 min and then vacuum drying at 45 °C until reaching the final moisture content exhibited the highest amount of sulforaphane.

1. Introduction

Glucosinolates, which are plant secondary metabolites, are an important group of phytochemicals found in *Brassica* vegetables including broccoli, Brussels sprouts, cabbage, white mustard, kale, and cauliflower (Keck and Finley, 2004). Disrupting of the plant tissues via cutting, grinding and even chewing can result in the hydrolysis of glucosinolates by an endogenous enzyme myrosinase into an array of hydrolysis products. The activity and stability of myrosinase and its isoenzymes vary widely depending on *Brassica* species as well as plant parts (Rungapamestry et al., 2007). In addition to the species and parts of the vegetables temperature also plays an important role on the myrosinase activity. Yen and Wei (1993), for example, reported that the optimum temperature for maximizing the myrosinase activity in both white and red cabbage varieties was approximately 60 °C and that myrosinase was destroyed after heating at 70 °C for 30 min. Ludikhuyza et al. (1999) reported that the activity of myrosinase from broccoli remained rather constant at 30 °C and heat treatment at 60 °C for 3 min resulted in the reduction of the enzyme activity by 90%.

Among the hydrolysis products of glucosinolates, isothiocyanates are claimed to exhibit high anticarcinogenic activities (Halkier and Gershenzon, 2006). Sulforaphane (4-methylsulfinybutyl isothiocyanate) is, in particular, an isothiocyanate that has been identified as one of the most naturally potent anticarcinogens (Matusheski et al., 2004; Elbarbry and Elrody, 2011). During hydrolysis glucoraphanin, one of glucosinolates, is hydrolyzed by myrosinase and an intermediate is formed before being rearranged into sulforaphane. Simultaneously, epithiospecifier protein (ESP), which is a myrosinase cofactor, can bind the sulfur of the intermediate, resulting in the formation of sulforaphane nitrile, which possesses no anticarcinogenic properties (Matusheski et al., 2004). Unfortunately, in many cases, more glucoraphanin is converted into sulforaphane nitrile than into sulforaphane. Mithen et al. (2003), for example, noted that approximately 80% of glucoraphanin from broccoli was hydrolyzed into sulforaphane nitrile, while only 20% was converted into sulforaphane.

Heating at certain temperatures and time has been reported to increase the rate of sulforaphane formation. This might be because of the inactivation of ESP at temperatures higher than 40 °C. Matusheski et al. (2004), for example, studied the effect of heating on sulforaphane formation in broccoli florets. Their results showed that heating at 60 °C for either 5 or 10 min led to significantly increased sulforaphane content. Rungapamestry et al. (2006) also reported that heating at temperatures in the range of 50–60 °C helped accelerate the rate of sulforaphane formation in cabbages. Note that myrosinase is active at temperatures up to 60 °C. Sulforaphane is nevertheless susceptible to heat (Jin et al., 1999; Van Eylen et al., 2007), so care must be exercised to minimize the deg-

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radation of newly formed sulforaphane. Tanongkankit et al. (2011), who studied the effect of hot air drying at various temperatures (40–70 °C) on the evolution of sulforaphane in cabbage outer leaves during drying, indeed reported that the formation of sulforaphane occurred when the cabbage temperature during drying was in the range of 25–53.5 °C; thermal degradation of the formed compound took place once the cabbage temperature exceeded this range. Most sulforaphane formed during an early period of drying degraded at prolonged drying time, resulting in very low retention of sulforaphane in the final dried samples.

To achieve higher retention of sulforaphane in dietary fiber powder from cabbage outer leaves, stepwise change of drying medium temperature is proposed here. As mentioned earlier, ESP is active within the temperature range of 20–40 °C and is damaged at temperatures above 40 °C, while myrosinase is stable up to 60 °C. Therefore, the heating (and hence drying) rate during an early period of drying should be high to rapidly increase the material temperature to a value higher than 40 °C. After this period the material temperature should be controlled to be not higher than 50 °C to retain the activity of myrosinase and to preserve the sulforaphane that is formed during an earlier period of drying. Hot air drying as well as vacuum drying and low-pressure superheated steam drying (LPSSD) were tested in this study. Vacuum drying and, in particular, LPSSD were attempted as these two drying methods could yield much higher rates of increase of material temperature during an initial period of drying (Devahastin et al., 2004). Lowering the operating pressure of the dryer should also help preserve the sulforaphane as the overall drying time would be shorter (Methakhup et al., 2005).

Hot air drying at constant temperatures of 45 °C and 60 °C was compared with hot air drying at 60 °C followed by hot air drying at 45 °C, vacuum drying (5 kPa) at 60 °C, LPSSD (5 kPa) at 60 °C and hybrid drying viz. LPSSD at 60 °C followed by vacuum drying at 45 °C. The upper temperature limit of 60 °C was chosen as it is the maximum allowable temperature to retain the myrosinase activity. In the case of drying with the change of medium temperature, however, the change was made when the sample temperature reached around 50 °C. The lower limit of 45 °C was chosen to avoid the ESP activity and minimize the required drying time.

2. Materials and methods

2.1. Sample preparation

Outer leaves of white cabbages (*Brassica oleracea* L. var. capitata), which were discarded, were obtained from Pakklong Talad market (Bangkok, Thailand). The leaves were kept at 4 °C until the time of experiment. Prior to each experiment, the leaves were washed under running tap water and drained on a screen to get rid of excess water for 30 min. The leaves were then chopped using an electric chopper (Moulinex, DPA141, Ecully, France) at 17,000 rpm for 2 min to obtain the particle size in the range of 1.7–2.5 mm. The preliminary experiments to study the effect of the particle size (or in other words, chopping) of the sample on the sulforaphane formation under ambient temperature (~25 °C) was conducted. The results showed that the particle size in the range of 1.7–2.5 mm was the best condition when the highest content of sulforaphane was concerned. In the present study, cabbages were chopped at room temperature of not higher than 25 °C and immediately dried at the tested temperatures.

2.2. Drying experiments

2.2.1. Hot air drying

Two hundred g of chopped sample was spread on a tray as a single layer; the tray dimensions were 25 × 40 cm and the load per area was 2 kg/m^2. The prepared sample was dried in a hot air oven (Termaks, TS800, Bergan, Norway) either at 45 °C, 60 °C or 60 °C followed by 45 °C at a constant air velocity of 2 m/s and ambient air relative humidity in the range of 55–70%. In the case of hot air drying at 60 °C followed by hot air drying at 45 °C, a preliminary study was conducted to determine the proper time to switch the drying temperature. Cabbages were first subject to drying at 60 °C; once the sample temperature reached around 50 °C, the set drying temperature was switched to 45 °C and the drying was continued until the equilibrium moisture content was reached. The temperature of the sample was measured continuously using type-K thermocouples, which were inserted into the bed of chopped cabbages. During drying 1–2 g of the sample was taken out at various time intervals to determine its moisture content. The moisture content of the sample was determined using a gravimetric method at 105 °C (AOAC Method 984.25; AOAC, 2000). The time to dry a sample to the final moisture content of less than 9% (wet basis) or 10% (dry basis), as suggested by Larrauri (1999), was estimated from the drying curve at each condition.

2.2.2. Vacuum drying and hybrid drying

Approximately 150 g of chopped sample was spread as a single layer on a sample holder with the dimensions of 27 × 27 cm at the load per area of 2 kg/m^2. Vacuum drying experiments were performed at an absolute pressure of 5 kPa and a temperature of 60 °C. In the case of hybrid drying a sample was first dried by LPSSD at an absolute pressure of 5 kPa and a superheated steam temperature of 60 °C until the sample temperature reached around 50 °C; then the process was switched to vacuum drying at 5 kPa and 45 °C simply by closing a steam inlet valve. The mass of the drying sample was monitored continuously using a load cell (Tedea-Huntleigh, 1022, Rancho Cucamonga, CA), while the sample temperature was also monitored via the use of type K thermocouples with an accuracy of ±0.1 °C. A sample was again dried until reaching a final moisture content of less than 10% (dry basis) A schematic diagram of the LPSSD/vacuum drying set-up is shown in Fig. 1 (Devahastin et al., 2004).

2.3. Determination of sulforaphane content

The sulforaphane content of a sample was determined following the method of Liang et al. (2006) with some modifications as suggested by Tanongkankit et al. (2011). Briefly, an either fresh or dried chopped sample (1 g) was extracted 2 times with 50 mL of dichloromethane, which was combined and salted with 2.5 g sodium sulfate anhydrous. The dichloromethane fraction was dried using a rotary evaporator (Buchi, model R-215, Flawil, Switzerland) at 30 °C. The residue was dissolved in 2 mL of acetonitrile and was filtered through a 0.2-μm membrane filter. Ten μL of the filtrate was then injected into a Symmetry® C18 5 μL (3.9 × 150 mm) HPLC column (Waters, Milford, MA) with gradients as follows: 20% acetonitrile and 80% water then changed linearly over 10 min to 60% acetonitrile and 40% water and maintained at 100% acetonitrile for 2 min. The flow rate of the mobile phase was set at 1 mL/min. A UV detector at a wavelength of 254 nm was used for detecting sulforaphane. Quantification of sulforaphane was carried out based on a standard curve of sulforaphane (Sigma–Aldrich, St. Louis, MO) with R^2 of 0.99.

2.4. Statistical analysis

The experiments were designed to be completely random. The data were subjected to analysis of variance (ANOVA) and are presented as mean values with standard deviations. Differences between mean values were established using Duncan's multiple range tests; the differences among the mean values were consid-