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Evolution of sulforaphane content in sulforaphane-enriched broccoli during tray drying

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ABSTRACT

Sulforaphane is a natural anticancer compound found in broccoli that comes from hydrolysis of glucoraphanin. Conversion of glucoraphanin to sulforaphane has been optimized, however, its use as functional ingredient is limited because sulforaphane is thermo-labile. We investigated the effect of drying air temperature (60, 70, 80 °C) in tray drying of sulforaphane-enriched broccoli on the evolution of sulforaphane content. Broccoli temperature and sulforaphane content were registered in time. Sulforaphane content profiles were adjusted to a first-order kinetic model, showing acceptable agreement ($r > 0.90$). Sulforaphane formation occurred below 40 °C; formation and degradation occurred at broccoli temperature above 40 °C, until the low content of glucoraphanin and moisture, prevents reaction. After that, only sulforaphane degradation was detected. The highest sulforaphane content at $X/X_0 = 0.1$ was 67.6 mg/100 g DW, obtained with drying air temperature of 70 °C, being 4-fold higher than that found in fresh broccoli, and the highest reported so far in any dehydrated food.

1. Introduction

Sulforaphane is an isothiocyanate that comes from *brassicaceae* vegetables, and it is considered to be a powerful natural anticancer compound (Matusheski et al., 2004; Elbarbry and Elrody, 2011). Its precursor is glucoraphanin, which is the most abundant glucosinolate in some broccoli cultivars. Among *brassicaceae*, broccoli has by far the highest content of glucoraphanin. The hydrolysis of glucoraphanin to yield sulforaphane (Fig. 1A) proceeds through the action of myrosinase (EC 3.2.1.147) to give an unstable intermediate, which can be subsequently converted spontaneously into nitriles, thiones, thiocyanates or isothiocyanates, depending on the chemical conditions i.e. pH, temperature, presence of Fe^{+2}, presence and activity of epithiospecifier protein (ESP) (Gu et al., 2012). Sulforaphane is the main product of the reaction when it proceeds at neutral pH and when ESP is inactive (Shen et al., 2010). Although glucoraphanin can be hydrolyzed by myrosinase, which is released from the myrosin cells of the vegetable during mastication and digestion in the intestine, the bioavailability of sulforaphane in this case is rather low, since the chemical conditions in intestine disfavor sulforaphane formation. As an option to deliver sulforaphane instead of its precursor in the vegetable, Pérez et al. (2014) proposed an optimized process that consists of blanching at 57 °C for 3 min, followed by an incubation step at 40 °C. This resulted in 94% conversion of glucoraphanin to sulforaphane, reaching a concentration of 142 mg sulforaphane per 100 g dry weight, the highest sulforaphane content reported so far (Pérez et al., 2016). In order to exploit these results in the field of functional foods, the pre-processed broccoli, rich in sulforaphane, could be dehydrated so that it can be incorporated as a functional ingredient in further elaborated foods. The main hindrance of this approach relies on the thermal instability of sulforaphane, which can result in considerable loss of the compound during hot air drying.

Research about the behavior of bioactive compounds and sulforaphane content in *brassicaseae* during drying is scarce. Jin et al. (2014) reported a dynamic optimization strategy to determine the best moisture-temperature trajectories that maximize retention of glucosinolates and vitamin C in broccoli stalks with minimum energy consumption in convective drying. They developed a model that considers degradation kinetics of glucosinolates and vitamin C, both following first order reaction models. The authors showed that this strategy allowed keeping 55% vitamin C and improved energy efficiency in 65%. However, this is a theoretical study that lacks experimental verification. Tanongkankit et al.

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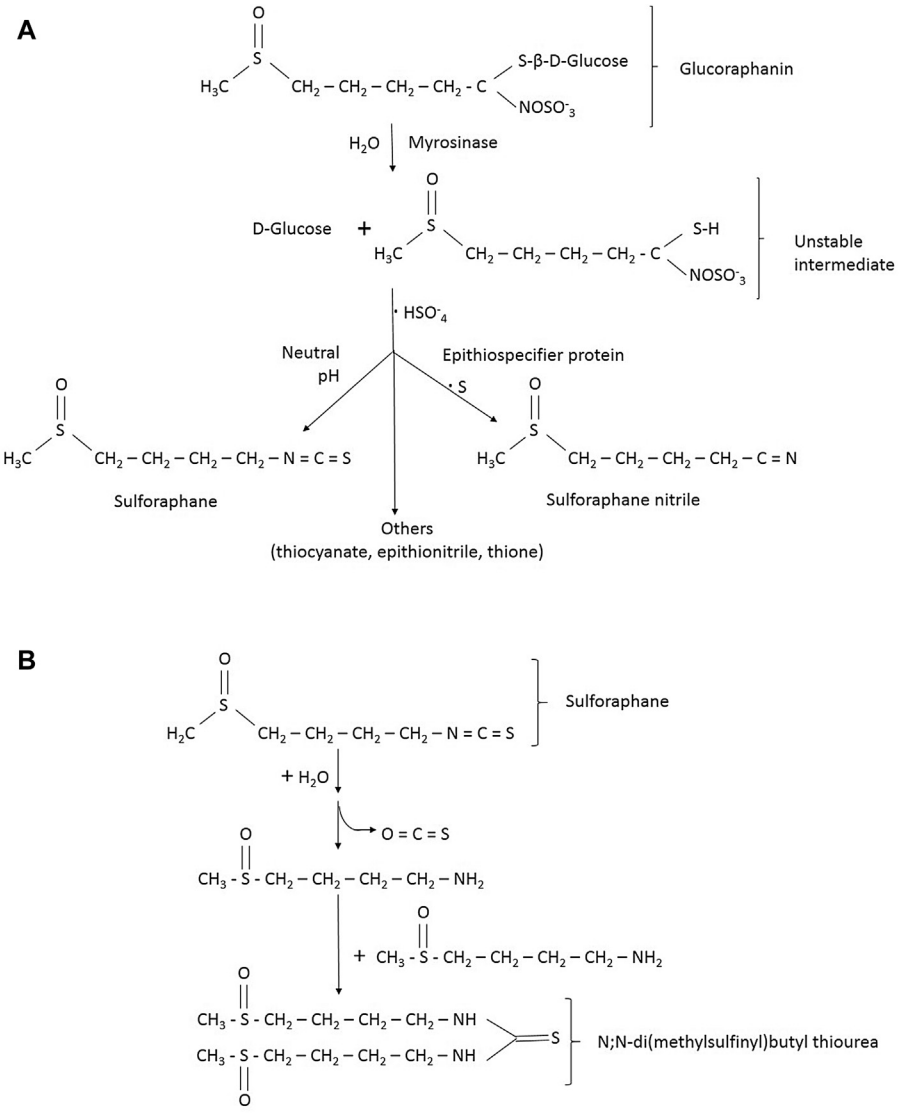

Fig. 1. Representation of (A) the enzymatic hydrolysis of glucoraphanin through the action of myrosinase (adapted from Tanongkankit et al. (2011)), and (B) pathway for degradation of sulforaphane to thiourea proposed by Jin et al. (1999).

(2011) studied the evolution of sulforaphane content in cabbage leaves during hot air drying. They described this behavior through a semi-empirical model that considers heat transfer and synthesis-degradation kinetics. The authors solved the model by adjusting it to experimental data obtained from drying experiences performed in a tunnel dryer at 40, 50, 60 and 70 °C, obtaining good agreement between experimental data and the model ($r > 0.90$). Besides, the authors reported that sulforaphane degradation takes place when the substrate temperature exceeds 40 °C. Based on the results of Tanongkankit et al. (2011), Lekcharoenkul et al. (2014) proposed a hybrid drying technique with temperature stepwise changes to enhance sulforaphane content in cabbage leaves. They found a similar behavior to that reported by Tanongkankit et al. (2011), but with a higher maximum sulforaphane content. Currently, no reports about sulforaphane evolution during drying of broccoli are available.

In this work we investigate the effect of temperature in convective drying of sulforaphane-enriched broccoli on the evolution of sulforaphane content. The results obtained here could be used for designing an industrial process in order to produce a dehydrated functional ingredient naturally enriched in sulforaphane.

2. Materials and methods

2.1. Plant material

Broccoli (*Brassica oleracea* var *italica* cv. Avenger) heads (three days from harvesting) were purchased at the local market (Santiago, Chile) from a single supplier. Broccoli florets were subjected to blanching followed by incubation in previously optimized conditions to maximize the sulforaphane content (Pérez et al., 2014). This optimized process ensures that myrosin cells are broken so that myrosinase can enter in contact with glucoraphanin, the epithiospecifier protein is inactive and myrosinase remains active. Broccoli heads were washed and cut into 5-cm length and 0.7–0.9 cm width (stem). Broccoli pieces were immersed in deionized water in a thermostatic bath (Stuart, United Kingdom, Great Britain) at 57 °C for 13 min. After blanching, broccoli pieces were immediately put in an ice-water bath. After that, broccoli was