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Broccoli by-products improve the nutraceutical potential of gluten-free mini sponge cakes

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Glucoraphanin (PubChem CID: 6602383)
Gluconasturtiin (PubChem CID: 5464032)
Glucobrassicin (PubChem CID: 5484743)
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ABSTRACT

This study describes the successful development of new gluten-free (GF) mini sponge cakes fortified with broccoli leaves. The aim of this study was to evaluate the effect of broccoli leaf powder (BLP) on the content of biologically active compounds and the antioxidant capacity of GF mini sponge cakes. Broccoli leaf powder was a good source of nutritional components, including proteins and minerals, as well as bioactive compounds such as glucosinolates and phenolics. Glucosinolate content was higher than expected, which points to a synergistic interaction between bioactive compounds and the food matrix. The incorporation of BLP into GF mini sponge cakes significantly ($p < 0.05$) increased their antioxidant capacity. The overall sensory acceptance of GF mini sponge cakes was affected by increasing BLP content. The addition of 2.5% BLP as a starch substitute resulted in an optimal improvement in the nutraceutical potential of GF cakes without compromising their sensory quality.

1. Introduction

The incidence of gluten-sensitivity disorders caused by allergic and immune reactions is on the rise (Sicherer & Sampson, 2014). Celiac disease and other gluten-related disorders are frequently accompanied by nutritional deficiencies that contribute to chronic conditions. Patients with celiac disease are also at a higher risk of lymphoma, in particular enteropathy-associated T-cell lymphoma (ETL) (Malamut et al., 2009). A gluten-free (GF) diet is the only approved method of treating gluten intolerance. However, GF products are characterized by lower palatability and nutritional value than gluten-containing foods, and their nutritional and sensory properties can be improved with supplements containing functional ingredients (Drabińska, Zieliński, & Krupa-Kozak, 2016; Krupa-Kozak, Altamirano-Fortoul, Wronkowska, & Rosell, 2012). Unfortunately, food products enriched with nutrients and biologically active compounds are often more expensive. By-products from fruit and vegetable processing can be used as additional sources of nutrients and functional ingredients (O'Shea, Arendt, & Gallagher, 2014) without increasing production costs.

Epidemiological studies have demonstrated that a diet rich in cruciferous vegetables, including broccoli, can reduce the risk of cancer and cardiovascular diseases (Higdon, Delage, Williams, & Dashwood, 2007; Zhang et al., 2011). Brassica vegetables, including cabbage, cauliflower and broccoli, contain glucosinolates (GLS), a large group of sulphur-containing glucosides with chemopreventive properties. Unhydrolysed GLS are not biologically active. The endogenous enzyme myrosinase (EC 3.2.3.1.) which hydrolyses GLS into several biologically active isothiocyanates and indoles is released when plant tissue is damaged by crushing or chewing. Sulforaphane is the most widely studied isothiocyanate which is a degradation product of glucoraphanin, the main GLS in broccoli. Numerous in vivo and in vitro studies have demonstrated that isothiocyanates and indole derivatives exhibit chemopreventive activity against cancer (Angelino & Jeffery, 2014; Higdon et al., 2007).

Broccoli is also a good source of polyphenolic compounds (Domínguez-Perles, Martínez-Ballesta, Carvajal, García-

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Viguera, & Moreno, 2010) with high antioxidant activity, and it could play a significant role in the prevention of diseases associated with oxidative stress, such as cardiovascular and neurodegenerative diseases as well as cancer (Scalbert, Manach, Morand, Rémésy, & Jiménez, 2005). Polyphenols demonstrate multidirectional antioxidant activity. They remove free radicals and reactive oxygen species, they act as complexing agents for iron and copper (preventing the oxidation of ascorbic acid), they inhibit the activity of enzymes involved in the formation of reactive oxygen species (such as xanthine oxidase), and block enzymatic and nonenzymatic lipid peroxidation (Scalbert et al., 2005).

Most people consume only broccoli florets which account for around 30% of the vegetable's biomass. For this reason, research studies generally focus on florets, whereas information about the nutritional properties of other broccoli parts is generally limited. Only several authors have described the nutritional composition and antioxidant activity of broccoli by-products (Domínguez-Perles et al., 2010; Guo, Lee, Chiang, Lin, & Chang, 2001; Hwang & Lim, 2015; Soengas, Cartea, Francisco, Sotelo, & Velasco, 2012). Broccoli by-products and broccoli florets have similar chemical composition, and they are rich sources of GLS, polyphenols, dietary fibre, proteins and other nutrients (Campas-Baypoli et al., 2009; Domínguez-Perles et al., 2010).

Literature data suggest that broccoli leaves could constitute a functional food additive. The chemical composition and antioxidant potential of bioactive compounds found in broccoli leaves have to be analysed to validate their functional properties. The incorporation of broccoli leaves into functional foods could improve the quality of GF diets and facilitate the management of vegetable processing wastes. Therefore, the aim of this study was to evaluate the effect of broccoli leaf powder on the content of biologically active compounds and the antioxidant capacity of GF mini sponge cakes.

2. Materials and methods

2.1. Chemicals

2,2′-Azinobis(3-ethylbenzothiazoline-6-sulphonic acid) diammonium salt (ABTS), 6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid (Trolox), potassium persulphate, 2,4,6-tri(2-pirydyl)-s-tiazine (TPTZ), methanol, were purchased from Sigma Aldrich (Steinheim, Switzerland). Sinigrin, *n*-hexane and acetonitrile were purchased from Merck (Darmstadt, Germany). Ferric (III) chloride was provided by Fluka (Germany). ACW (hydrophilic condition) and ACL (lipophilic condition) kits for the photochemiluminescence (PCL) assay were received from Analytik Jena AG (Jena, Germany). All other reagents were from POCh, (Gliwice, Poland). Water was purified with a mili-Q-system (Milipore, Bedford, USA).

2.2. Preparation of broccoli leaf powder (BLP)

Mature leaves of broccoli (*Brassica oleracea* L. var. *italica* cv. Sebastian) were generously donated by GEMIX (Olsztyn, Poland). Leaves without signs of mechanical damage were selected, washed and blanched in hot water for 1 min to inactivate enzymes hydrolysing biologically active compounds (such as myrosinase and polyphenol oxidase). The petioles and the main midribs were removed. Leaf blades were freeze-dried and ground to produce broccoli leaf powder (BLP) with particle size ≤0.60 mm. The powder was stored in a refrigerator in a tightly closed container for further use.

2.3. Preparation of gluten-free mini sponge cakes

Broccoli leaf powder was incorporated into mini sponge cakes in the following proportions: control – 0%, B1 – 2.5%, B2 – 5%, B3 – 7.5% (w/w) by replacing an equivalent amount of potato and corn starch in the standard formulation of GF mini sponge cakes (Table 1). The ingredients were combined in a 5-speed KitchenAid Professional K45SS mixer (KitchenAid Europa, Inc, Brussels, Belgium) in a stainless steel bowl. Dough portions of 30 g were placed in paper cups and baked at 180 °C for 25 min (SVEBA DAHLEN, AB model DC-21, Sweden). Baked GF mini sponge cakes were cooled (2 h at room temperature), freeze-dried, ground into a fine powder (particle size ≤0.60 mm), and stored in the refrigerator in a tightly closed container until analysis.

Table 1
Percentage composition of control and fortified gluten-free sponge cakes.

	Control	B1	B2	B3
Potato starch	30.6	30	29.7	29.6
Corn starch	7.8	7.5	6.9	6.1
BLP*	–	0.9	1.8	2.7
Eggs	43	43	43	43
Sugar	14	14	14	14
Oil	3.7	3.7	3.7	3.7
Salt	0.2	0.2	0.2	0.2
GF baking powder	0.7	0.7	0.7	0.7

* Incorporated into GF mini sponge cakes by replacing an equivalent amount of potato and corn starch in the standard formulation (control – 0%, B1 – 2.5%, B2 – 5%, B3 – 7.5% (w/w).

2.4. Proximate chemical composition

The dry matter content and proximate chemical composition of GF mini sponge cakes, including protein (N × 6.25) and ash content, were determined with the use of standard methods (AOAC, 2011, chap. 32). The dry matter content of GF mini sponge cakes was determined at 66.27 in control, 66.37 in B1, 66.40 in B2, and 66.77 in B3. The protein content of GF mini sponge cakes was determined at 8.46 in control, 8.48 in B1, 8.59 in B2, and 9.75 in B3. The ash content of GF mini sponge cakes was determined at 0.52 in control, 1.30 in B1, 1.41 in B2, and 1.91 in B3.

2.5. Determination of glucosinolate content

The GLS content of GF mini sponge cakes was determined after degreasing. Samples of 2 g of freeze-dried GF mini sponge cakes were vortexed with 5 mL of *n*-hexane for 30 s. They were centrifuged for 15 min at 3500 rpm, and the supernatants were removed. Lipids were extracted in triplicate. Degreased powder was dried under a stream of nitrogen until *n*-hexane was completely removed.

The content of GLS in GF mini sponge cakes and BLP was analysed according to the method described in the Official Journal of the European Communities (1990). Briefly, 500 mg of degreased sponge cakes lyophilisates or 200 mg of BLP were extracted with 70% boiling methanol. The isolation, desulphation and HPLC separation of GLS were carried with the use of the methods described by Ciska, Honke, and Kozłowska (2008). Separation was performed in an HPLC system with an autosampler (LC-20) and the SPD-M20A DAD detector (Shimadzu, Japan). The compounds were separated in the LiChrospher® 100 RP-18 (5 μm, 250 × 4 mm) column (Merck, Darmstadt, Germany) with a flow rate of 1.2 mL/min. Desulpho-GLS was separated in a gradient of water and 20% acetonitrile as previously described (Ciska et al., 2008). Glucosinolates were identified following their UV spectra in comparison to the available literature. The presence of glucoiberin and glucoraphanin was additionally confirmed with the analysis of respective degradation products using 7890A gas chromatograph (Agilent Technologies, Santa Clara, CA, USA) coupled with 5975C mass selective detector, 7683B auto-injector and data station containing the NIST/EPA/NIH Mass Spectral Library (Version 2). UV spectra of compounds eluted as a third and fourth GLS in both BLP and GF mini sponge cakes (Fig. 1A–B) were not found in the available literature, therefore these compounds were not identified and they are presented