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Stability of quercetin derivatives in vacuum impregnated apple slices after drying (microwave vacuum drying, air drying, freeze drying) and storage

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ABSTRACT

Microwave vacuum drying (MVD) was investigated for apple slices enriched with quercetin derivatives by vacuum impregnation (VI). Additional freeze drying (FD) and air drying (AD) were conducted. Compared to native apples, the impregnated tissue resulted in higher moisture content, elevation of weight and significant browning, due to the incorporated VI solution. The total quercetin content and quercetin glycoside composition were not affected by MVD and FD. The vacuum conditions protect the polyphenols from oxygen dependent degradation and browning reactions. AD resulted in an average quercetin glycoside loss of 44% and undesirable changes, particularly discoloration. The degradation is caused by both non-enzymatic and enzymatic reactions. The pulsed microwave energy intake improved the drying result in structure and led to a faster drying process of 130 min. The bulk density of MVD apple chips (0.69 g/ml) ranged between 0.33 g/ml for FD and 0.75 g/ml for AD. The final moisture content was the lowest after FD (6.8 g/100 g), followed by 9.0 g/100 g after MVD and 12.7 g/100 g after AD. The shelf life was significantly influenced by storage temperature and time. After 12 month at 20 °C, the total quercetin content decreased by 21%.

1. Introduction

Apples (*Malus domestica*) are one of the most widely grown and economically important fruit crops all over the world, which are rich in quercetin glycosides. These naturally occurring antioxidative secondary plant products belong to flavonoids, a group of polyphenols with cardio and cancer protective effects (Ekström et al., 2011; Hertog, Feskens, Hollman, Katan, & Kromhout, 1993; Knekt et al., 2002). In apples, quercetin glycosides are located in the apple peel and provide protection against stress induced by UV-B and visible light (Hagen et al., 2007; Solovchenko & Schmitz-Eiberger, 2003). However, during industrial processing apples are often used in their peeled form, thus secondary plant compounds, especially the quercetin glycosides, are removed. Food industry and the food scientists are therefore searching for ingredients rich in quercetin glycosides and innovative methods to incorporate the lost flavonoids. Apple peel extract and apple pomace could potentially be functional food ingredients that are high in quercetin and beneficial for consumer's health (Schieber et al., 2003; Wolfe & Liu, 2003).

Vacuum impregnation (VI) is a food preparation technique that changes food composition. In recent studies, VI was used to change the properties of food with regards to nutritional, sensory, shelf life and physicochemical characteristics (Chiralt et al., 2001; Guamis et al., 1997; Lin, Leonard, Lederer, Traber, & Zhao, 2006). VI is characterized by replacing the initially occluded air in pores of the fruit or vegetables with a liquid, which is the impregnation solution. With pressure gradients, air of the porous fraction is released until atmospheric pressure conditions are restored and the external liquid phase penetrates the plant tissue.

Preserving polyphenols and their bioavailability in spite of drying depends on the preparation technique and the control of food processes such as time and temperature conditions. 3-glycosidic bonded sugars with quercetin are especially temperature-sensitive compounds (Rohn, Buchner, Driemel, Rauser, & Kroh, 2007). Sensory characteristics (color, texture, taste) can also be influenced by drying. Apple processing is combined with enzymatic and non-enzymatic browning of fruit tissues. The enzymatic browning reaction in plants is based on polyphenoloxidase (PPO). This copper containing metallo-enzyme

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catalyzes degradation reactions of natural phenols to *o*-diphenols and *o*-quinones in the presence of oxygen (Jimenez & Garcia-Carmona, 1999).

Drying vacuum impregnated fruits may cause undesirable changes. In particularly, fruits containing sugar required special drying methods to decrease the water content. For high-quality products, it is essential to avoid drying methods with high temperatures and long drying times. Freeze drying (FD) is considered as a process that preserves quality characteristics; however it is a time-consuming process that requires high energy. In contrast air drying (AD) is a low cost procedure; however quality parameters such as flavor, color, nutrients, bulk density and rehydration capacity may be negatively affected (Drouzas, Tsami, & Saravacos, 1999; Lin, Durance, & Scaman, 1998; Yongsawatdigul & Gunasekaran, 1996). Microwave vacuum drying (MVD) offers an alternative method to preserve temperature-sensitive compounds (Böhm, Kühnert, Rohm, & Scholze, 2006) and to economize energy and time (Gunasekaran, 1999). In recent years, MVD has been investigated as a potential method for obtaining several high-quality dried agricultural products, such as fruits (Böhm et al., 2006; Mousa & Farid, 2002; Yongsawatdigul & Gunasekaran, 1996), herbs (Soysal, 2004; Yousif, Durance, Scaman, & Girard, 2000) and vegetables (Cui, Xu, & Sun, 2004b; Lin et al., 1998).

MVD is a technique which combines the microwave heating technique with vacuum drying. The microwave radiation is transformed, directly in the product, to kinetic energy. The vacuum conditions lower the liquid vapor pressure, so that drying of thermo-sensitive products can be performed in the absence of oxygen. Efficient water evaporation can also be used for structural changes and the prevention of shrinkage due to food puffing and induced porous tissues.

The objective of this study is to investigate the effect of different drying techniques on various parameters of vacuum impregnated apple slices. To our knowledge, this is the first investigation of flavonoid enriched food dried by MVD.

2. Materials and methods

2.1. Materials

For determination and quantification, the quercetin derivatives quercetin dihydrate, quercetin-3-*O*-glucoside, quercetin-3-*O*-galactoside, quercetin-3-*O*-arabinopyranoside, and quercetin-3-*O*-rhamnoside were used as standards and obtained from Roth (Karlsruhe, Germany). Apples (*Malus domestica* Borkh. cultivar 'Braeburn') were purchased from a local producer and stored at ambient temperature (20 °C) until experimental use. The bulk density of whole apple fruits measured by water displacement was 0.913 ± 0.013 g/cm^3 (n = 24). The native Braeburn slices contained 87.6 ± 0.5 g/100 g moisture, which equals a water activity of 0.97. The used Braeburn apples had a fruit firmness of 8.2 ± 1.1 kg/cm^2 and the soluble solids (11.9 ± 1.0 °Brix).

2.2. Sample pre-treatments

For physicochemical analysis, the apples were washed with distilled water and peeled. The firmness of the fruit flesh was measured with an Effegi penetrometer (Alfonsine, Italy) fitted with an 11.1 mm tip. The soluble solid concentration (SCC) was determined using a hand-held refractometer (Model HRT 32, Krüss Optronic, Hamburg, Germany) at 20 °C. Afterward, the apple core was removed with a core borer and the apples were parted in 6 mm slices. The used Braeburn apple slices had an average initial surface area of 39.9 cm^2.

2.3. Vacuum impregnation (VI)

The impregnation solution consisted of apple juice with 0.3 g/100 mL apple peel extract high in flavonoids (hfv) (Val de Vire Bioactives, Condé sur Vire, France) with an SCC of 11.1 ± 0.1 °Brix. The total quercetin derivative content of the impregnation solution averaged 96.4 ± 2.5 mg/g dry mass (DM); the pH was 3.38. Apple slices were immersed in the VI solution, high in apple peel flavonoids, and fixed with watch-glasses to avoid floating. The vacuum phase of impregnation was carried out using the vacuum chamber of the microwave vacuum dryer (μWaveVac0150 1c, Püschner, Schwanewede, Germany) at a pressure of 100 hPa for 5 min at room temperature. Afterward, the apple parenchyma remained in the impregnation solution for 10 min at atmospheric pressure. The concentration of quercetin glycosides in apple slices increased with the VI process (Schulze, Peth, Hubbermann, & Schwarz, 2012).

2.4. Drying techniques

After vacuum impregnation, three drying techniques were performed; freeze drying (FD), convective hot air drying (AD) and microwave vacuum drying (MVD). For all drying procedures, 6 apple slices of each apple (n = 8) were pre-treated by VI and dried.

2.4.1. Microwave vacuum drying equipment

The drying method for convective drying or MVD of non-impregnated apple slices was not transferable to impregnated apple parenchyma, capable drying conditions and drying parameters for MVD of enriched Braeburn apples were investigated. The MVD were performed with a lab scale MVD dryer (μWaveVac0150 1c, Püschner, Schwanewede, Germany). The system consisted of a vacuum vessel with an integrated wall heater to avoid condensing vapor in the system. The vessel wall was adjusted to 50 °C during the drying process. The dryer had a maximal microwave power of 1000 W produced by 1.2 kW/2450 MHz magnetron and a magnetron protection system. During the drying process, the pressure was decreased by a vacuum pump. To avoid overheating and product hot spots, a rotary plate for product movement was used. To measure the drying procedure the drying temperature was checked with a fiber-optical thermometer. In addition, the reflected microwave energy, the drying rate, the product weight and the actual vacuum conditions were controlled via a real-time computer system.

2.4.2. Microwave vacuum drying method

The cell load weighed approximately 125 g and the process started at a product temperature of 20 °C. Throughout the drying period, the vacuum was set to 20 hPa. The drying started after starting the magnetrons at a vacuum level of 100 hPa. The microwave power entry was set to 500 W for 25 min (period 1). In addition, a microwave stop time of 5 min and a short power-on time of 60 s with an energy entry of 1000 W were programmed (period 2). To reduce high temperature peaks the energy intake was set to 80 W until the end of drying (period 3 and 4). The drying conditions were normally held constant during each experiment (n = 8).

2.4.3. Freeze drying (FD)

For FD after VI, the fruit material was immediately shock frozen in liquid nitrogen and freeze dried for 72 h (Christ Gamma 1-20, Osterode am Harz, Germany).

2.4.4. Air drying (AD)

The AD of impregnated apple slices was performed continuously using a convection oven under hot air at 50 °C for 14 h (Zanussi FCV/E10L6, Pordenone, Italy) until constant weight was achieved.