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EXPLORATION OF THE BIOACTIVE COMPOUNDS OF *MALUS DOMESTICA* AND POSSIBILITIES OF USING BY-PRODUCTS OF FRUIT PROCESSING IN THE JUICE INDUSTRY – REVIEW

Mandache Maria-Bianca[1], Cosmulescu Sina-Niculina[2]
[1]Doctoral School of Plant and Animal Resources Engineering, Faculty of Horticulture, University of Craiova, A.I. Cuza Street, no. 13, 200585 Craiova, Romania
[2]Department of Horticulture and Food Science, Faculty of Horticulture, University of Craiova, A.I. Cuza Street, no.13, 200585 Craiova, Romania
**Correspondence author. E-mail*: mandachemaria@yahoo.com

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ABSTRACT

The by-products of the apple processing industry are abundant in nutrients and bioactive compounds that can improve the nutritional properties of food products and have the potential to prevent or treat a number of diseases, representing an opportunity for the food industry. In the current world context, where the focus is on sustainability and the efficient use of natural resources, apple by-products are becoming more and more relevant. The purpose of this paper was to analyze the specialized literature regarding the chemical composition of by-products from apples as well as their integration potential in the food industry. Current research is focused on the development of new methods of valorizing these by-products, which allow to obtain ingredients with improved functional properties, and as consumers become more and more aware of the benefits of healthy foods, apple by-products should represent an increasingly attractive raw material for the food industry. As the food industry generates effective alternatives for the integration of by-products, they will become an important segment on the consumer market.

INTRODUCTION

The progressive trend of by-products generated from fruit processing has a negative impact in different spheres of activity, which determines an integrated approach, which can consist in their valorization and reduction. Secondary products can be considered valuable reusable sources of raw materials, the variety of functions performed by them being an important promoter in the field of the food industry due to the biologically active substances provided, known for their major contributions in the prevention of some ailments but also for the optimal functioning of the human body, and economically, it could reduce production costs, generating new income for producers and processors. The attention of contemporary society is directed towards a healthier diet, preferring foods that contain mainly natural substances. This change in preferences has a number of implications for the food industry, with producers having the obligation to adapt to meet the needs and expectations of consumers by developing new food products or improving existing ones. By-products from fruits can constitute a major premise in the functionality of various fields of processing, including dairy products, meat, confectionery, bakery. Due to the positive characteristics regarding the nutritional potential, different methods of transformation and valorization can be addressed, establishing a sustainable food system. The apple is a fruit that holds major importance in the food industry, its processing generating significant amounts of resources composed of skin, pulp and seeds. A large part of the production of cultivated apples is intended for the juice industry, with the resulting by-product being the pomace (Cargnin & Gnoatto 2017). This residual product, which occupies a weight of approximately 30% of the mass of the fruit, often remains underutilized, despite the large amounts of constituent bioactive compounds. It is mentioned that only a percentage of approximately 0.6%-18% of the total phenolic substances remains in the juice, the rest being concentrated in the secondary product (Awasthi et al. 2021).

Apple pomace is a complex product, whose chemical composition is influenced by a number of factors, such as types, cultivation area, manufacturing process and extraction parameters (Iqbal et al. 2021). Although these parameters can influence the amount and concentration of nutrients, they are present in significant percentages (Bhushan et al. 2008). Apples include high proportions of insoluble and soluble fibers, most of which are concentrated in by-products (Waldbauer et al. 2017). Proteins are found mainly in the skin and seeds, in relatively low amounts, with 2.3% being attributed to amino acids, including essential ones (Sato et al. 2010, Juśkiewicz et al. 2012). They are a valuable source of minerals, including calcium, magnesium, iron (Dhillon et al. 2013) and vitamins, such as vitamin C, E and beta-carotene (Waldbauer et al. 2017). They are also major suppliers of phenolic compounds, including flavanols, hydroxycinnamates, flavonols, dihydrochalcones and anthocyanins.

The individual compounds of apple by-products show a rich phenolic profile with high concentrations of chlorogenic acid, caffeic acid, catechins, epicatechins, rutin and quercetin glycosides (Ćetković et al. 2008). Flavanols are the most abundant phenolic compounds present, being mainly represented by catechins and proanthocyanidins (Barreira et al. 2019). Triterpenoids are another class of organic compounds found in apples. They are mainly located in the wax layer of the cuticle (Cargnin & Gnoatto 2017) and include ursolic acid (Belding et al. 1998) and oleanolic acid (Frighetto et al. 2008).

The purpose of this paper was to analyze the specialized literature regarding the chemical composition of by-products from apples as well as their integration potential in the food industry. Also, the impact on the nutritional and organoleptic properties of the finished product following supplementation was monitored.

RESULTS REGARDING THE CHEMICAL COMPOSITION AND BIOLOGICAL ACTIVITY OF APPLE BY-PRODUCTS

The reserves of bioactive substances in apple by-products have been associated with various health-optimizing mechanisms. Apple by-products provide generous amounts of phenolic compounds, fibers, pigments, vitamins and minerals, having an important role on metabolism due to its positive effects (Szabo et al. 2022). As for minerals, they are essential for the proper functioning of the body and perform multiple functions, including ionic balance and cell function, heart contraction, normal kidney and muscle function, bone and tooth health, nerve transmission signal, oxygen transport and secretion of hormones and enzymes (Mitic et al. 2019). Among the macro and microelements identified in apple by-products are potassium (4.49 g/kg), calcium (1.50 g/kg), phosphorus (1.49 g/kg), magnesium (0.45 g/ kg), iron (91.8 mg/kg), manganese (8.75 mg/kg), zinc (6.90 mg/kg) and copper (1.36 mg/kg) (Pieszka et al. 2017). Essential fatty acids contribute to many biochemical processes, including cardiovascular health, skin health, nervous system health, and reducing inflammation. From the studies carried out, it was found that the seeds from apple by-products integrate most of the **fatty acids** of the fruit, especially linoleic acid and oleic acid (Bhushan et al. 2008). Apple seeds also contain 22.4 mg/100g **vitamin C** and 5.5 mg/100 g vitamin E, being considered a potential source of antioxidant compounds (Pieszka et al. 2015), which protects cells against damage caused by free radicals. Vitamin E is beneficial for the brain and skin (Boccardi et al. 2016) and may have antitumor and photoprotective properties (Keen & Hassan 2016).

And the fiber content is essential for health. Apples are known to be a good source of both soluble and insoluble fiber (Li et al. 2002). Soluble fiber, such as pectin, is associated with a number of health benefits, including lowering cholesterol (Aprikian et al. 2003) and slowing glucose absorption (Schwartz et al. 1988). Since most of the soluble fibers are in the skin, it can be stated that the secondary products have a higher pectin content than industrialized fruits (Skinner et al. 2018). According to Kumar & Chauhan (2010), a pectin intake between 30-50% of the total dietary fiber consumed daily can contribute to the decrease of total cholesterol, LDL-cholesterol and triglycerides. It was also found that pectin can influence the reduction of weight and body mass index (Skinner et al. 2018). By consuming 100 grams of apple pomace you can provide approximately half of the daily recommended amount of fiber (Skinner et al. 2018). Carbohydrates are involved in a number of fundamental biological functions, and among them, in the apple by-products there were identified cellulose (7.2 to 43.6 g/kg dry weight), hemicellulose (4.26 to 24, 40 g/kg dry weight), lignin (15.3 to 23.5 g/kg dry weight), glucose (22.7%), fructose (23.6%) and galactose (6% to 15%) (Dhillon et al. 2013).

Apples also provide large amounts of polyphenols, of which 82-99% are present in the pomace (Antonic et al. 2020). Apple skin is a source of flavonoids, such as procyanidins, catechins, epicatechins, phlorizins and glycosides of quercetin; hydroxybenzoic acids and hydroxycinnamic acids, such as chlorogenic acid (Escarpa & Gonzalez 1998). Among the apple polyphenols, phlorizin, which is predominant in most varieties, has a notable antihyperglycemic effect in the human body (Ehrenkranz et al. 2005, Górnaś 2015). This effect is similar to that of chlorogenic acid, which plays an important role in glucose and lipid metabolism (Meng et al. 2013). Phlorizin acts as a powerful antioxidant, anti-inflammatory, antimicrobial agent, having the ability to neutralize the sodium/glucose cotransporters in the kidneys and intestine (Teshome et al. 2023), which can help control blood sugar levels. These properties have led to multiple investigations for its development as a new antidiabetic drug (Kammerer et al. 2014).

Apple by-products are important suppliers of phlorizin, containing 15.52 mg/100g dry mass (Gumul et al. 2021). Chlorogenic acid is the most abundant phenolic acid in apple pomace, followed by cryptochlorogenic acid and p-coumaroylquinic acid, according to the study by Gumul et al. (2021). The concentrations of these acids are 20.55 mg/100 g dry weight, 1.03 mg/100 g dry weight and 0.16 mg/100 g dry weight, respectively (Gumul et al. 2021). The ability of apples to provide bioactive compounds with a role in regulating chemical processes occurring at the cellular level is well known. They are major food sources of **flavonoids**, being particularly rich in quercetin and its derivatives (Herranz et al.

2019), subject of several studies confirming their antioxidant (Wang et al. 2020), anti-inflammatory (Tian et al. 2021) and antimicrobial (Yong et al. 2020) properties, as well as antidepressant effects (Dimpfel 2009). Among the quercetin derivatives, quercetin-3-O-galactoside is the most abundant, with a concentration of 22.55 mg/100 g dry matter (Gumul et al. 2021). Quercetin-3-O-rhamnoside and quercetin-3-O-xyloside are also present in significant amounts, with concentrations of 19.21 mg/100 g dry weight and 13.91 mg/100 g dry weight, respectively (Gumul et al. 2021). At the same time, these compounds also protect against arteriosclerosis (Ishizawa et al. 2011) and diabetes (Ebrahimpour et al. 2020).

Quercetin is a powerful antioxidant with 4.7 times the activity of vitamin C, in other words, its antioxidant is equivalent to 1500 mg of vitamin C (Ishartati et al. 2019). Other groups of phenolic compounds present in apple pomace include flavan-3-ols and dihydrochalcones (Gumul et al. 2021). Among flavan-3-ols, catechin, procyanidin B2 and epicatechin are the most important, amounting to 1.44 mg/100 g dry mass, 2.61 mg/100 g dry mass and 0.76 mg/ 100 g dry mass (Gumul et al. 2021). The total content of polyphenols in apple pomace can be between 47 mg gallic acid/100 g dry mass (Adil et al. 2007) and 324.2 mg gallic acid/100 g dry mass (Leyva-Corral et al. 2016). Phenols and triterpenes in apples have positive effects on the cardiovascular system. They improve endothelial function, reduce pro-inflammatory cytokines and oxidative stress by neutralizing free radicals (Caliceti et al. 2022). Ursolic acid and oleanolic acid, two triterpenes present in apple by-products, may help protect against chronic diseases such as cancer, heart and liver disease by neutralizing free radicals, reducing inflammation and boosting immunity (Balanehru & Nagarajan 1992, Ikeda et al. 2008).

The studies show that apple by-products contain significant amounts of biologically active compounds with an important role in human health, which makes them useful in various branches of industry.

RESULTS REGARDING THE INTEGRATION OF APPLE BY-PRODUCTS IN THE FOOD INDUSTRY

The food industry is an important sector of the world economy, which has seen a significant rise in recent years. Fruits are among the main components of this industry, due to their nutritional composition, economic importance and increased consumer interest in healthy foods. Functional food is a continuously developing topic of interest, both among researchers and the food industry (Ishartati et al. 2019). The properties of functional foods are diverse (Muchtadi & Wijaya 1996) and include increasing immunity, preventing disease, restoring the body after illness, maintaining physical and mental health, and slowing down the aging process (Ishartati et al. 2019). Food by-products fulfill these conditions through the high content of bioactive compounds, showing a high commercial interest for this industry, which can use them to produce functional foods (Mateus et al. 2023). The ability to be used as a cost-effective, low-calorie filler, as a partial substitute for sugar, fat or flour, to improve the functionality of foods by improving water and oil retention, represents new points of approach for the food market (Iqbal et al. 2021). Also, fruit pomace can be a promising ingredient for confectionery and bakery products containing high amounts of white flour, as it can increase the nutritional value and improve their texture, flavor and appearance (Tańska et al. 2016).

Among all processed fruits, apple by-products have attracted increased attention in recent years, mainly due to global overproduction, which has led to increased availability of these products. The major presence of nutrients, phytochemical and functional properties in apple pomace have led many researchers to use it as a functional ingredient to replace or fortify conventional food products (Iqbal et al. 2021).

Results on the integration of apple by-products into bakery products

Apple by-products are a major source of bioactive compounds that can be used to improve the nutritional properties of bakery products. Gumul et al. (2019) evaluated the impact of different proportions (5%, 10%, 15%) of whole and ground pomace on the chemical, physical and sensory characteristics of wheat bread and found that the protein level was between 13.1% and 14 .4%, the total fat content was reduced by 20-29%, ash content increased by 5-10%, while total sugar content decreased by 8-35%, the fiber level in the bread was significantly increased, and the amount of polyphenols increased by 55-127%, positively influencing the sensory characteristics, represented by volume, taste, texture, both on the day of production and after storage.

It has been noted that apple pomace can improve the nutritional value of bread, even when used at a percentage of 5%, giving the finished product a total content of polyphenols, flavonoids and anthocyanins of 55%, 200% and 160% higher respectively in comparison with control sample (Gumul et al. 2019).

Results regarding the integration of apple by-products in gluten-free products

Adding apple pomace to gluten-free products can also be a solution to improve quality. Gluten-free products are deficient in nutrients, including antioxidants (Gumul et al. 2021). This deficiency can be problematic for celiac patients, who are prone to oxidative stress. Currently, starch and hydrocolloids are often used in gluten-free products to give them texture and consistency similar to regular products (Gumul et al. 2021), but nevertheless, they can increase blood sugar levels with negative effects on health. Supplementation with apple pomace can be an alternative source to eliminate these negative aspects due to the rich content of fiber and antioxidant substances. Specifically, apple pomace increased the content of insoluble dietary fiber by 8-29 times, soluble dietary fiber by 1.5-5 times and total dietary fiber by 3.5-13 times, while a content of fats and minerals by 14% and 58% higher, respectively, the addition of 15% providing a 13-fold increase in chlorogenic acid and 8-fold increase in cryptochlorogenic acid, respectively (Kruczek et al. 2023).

Accordingly, Gumul et al. (2021) analyzed the composition of gluten-free bread, supplemented with different percentages of apple pomace (5%, 10% and 15%), determining the total content of phenolic compounds, flavonoids and total antioxidant activity. This addition provided a 2.5-20-fold increase in total polyphenol content, a higher level of phenolic acids, including chlorogenic, cryptochlorogenic and p-coumaroylquinic acids. This increase can be influenced by later stages of bread production, such as yeast fermentation (Katina et al. 2007) and dough mixing (Boskov Hansen et al. 2002). At the same time, quercetin, especially quercetin-rutinoside can be transformed into phenolic acids during the baking process (Rupasinghe et al. 2008), this explains the high content of phenolic acids (Gumul et al. 2021). Chlorogenic acid, cryptochlorogenic acid, p-coumaroylquinic acid and caffeoyl-dihydroxyphenyl-lactaoyl-tartaric acid experienced a significant intensification (Gumul et al. 2021), in contrast to spermidine p-coumaroyl acid, which showed a lower percentage, this is due to the thermal decarboxylation process occurring during the baking process (Maillard & Berset 1995). During baking, flavanols, procyanidins, and especially catechins in gluten-free pomace bread are significantly degraded (Sivam et al. 2010). This is probably due to processes such as oxidation, isomerization and epimerization, resulting in an insignificant level (Sivam et al. 2010).

The best results of the organoleptic analysis were given to the bread with a level of 5% apple pomace. Bread with this level of addition has 2.5 times more polyphenols, 8 times more flavonoids, 4 times more chlorogenic acid and 21 times more phlorizin than the control sample, resulting in an antioxidant potential of 6.5 times higher. Therefore, the authors suggest that it can be recommended as an innovative product for people with gluten intolerance with the potential to be exploited at an industrial level, agreeing that this type of bread can help reduce oxidative stress that affects inflammation and can protect against DNA-damage (Gumul et al. 2021). In another study, Mir et al. (2017) investigated the effect of incorporating apple pomace at 0%, 3%, 6% and 9% in the formulation of gluten-free brown rice crackers and found that protein levels, fiber content and phenolic compounds increased with increasing the ratio of added pomace. The increase was also directly proportional to the concentration of calcium, copper, iron, potassium and silicon depending on the percentage of pomace used (Mir et al. 2017).

Results on the integration of apple by-products into cereal products

Fruit by-products are a rich source of dietary fiber, polyphenols and other bioactive compounds, their use in extruded cereals being a promising way to improve nutritional value and health benefits (Iqbal et al. 2021). In the study by Gumul et al. (2022) it was found that apple pomace can be applied to improve the concentration of polyphenols, flavonoids and chlorogenic acid of corn snacks. Specifically, apple pomace contributed to increasing the concentrations of polyphenols up to 36 times, cryptochlorogenic acid 4 times, catechin 6 times, procyanidin 3 times and epicatechin 8 times, the content of dihydrochalcones, mainly phlorizin, being up to 25 times higher compared to unfortified products, and total, soluble and insoluble dietary fibers increasing up to 3 times. The authors suggest that such an addition can be recommended for the production of innovative snacks at industrial level, in the context where the organoleptic results were promising (Gumul et al. 2022). Also, Reis et al. (2014), developed high-fiber baked and extruded functional snacks by adding 30% apple pomace, and the added amount had a negative impact on the color of the products, but did not affect the sensory properties or storage stability. Incorporation of 30% pomace increased radical scavenging activity by 2.8-fold and 1.6-fold, antioxidant reducing power by 5-fold and β-carotene preservation by 1.5-fold in extruded and baked products, respectively (Reis et al. 2014).

Results regarding the integration of apple by-products in pasta

Apple pomace added in percentages of 10%, 20%, 30% and 50% was integrated in the formulation of pasta by Gumul et al. (2023), following the influence of the addition of different amounts used on the quality. It was found that the addition of pomace led to a decrease in the amount of protein and fat, an increase in the content of reducing sugars by about 27%, an increase in the amount of minerals, polyphenols (by 410%) and flavonoids (by 774%), of the level of quercetin derivatives, flavon-3-ols and dihydrochalcones, total fiber, soluble fiber and insoluble fiber. The authors show that an addition of 10% pomace increased 2-fold the level of polyphenols and flavonoids and ensured suitable pasta processing properties such as adequate hardness and optimal water absorption.

Results on the integration of apple by-products into meat products

Fruit by-products can be used to improve the nutritional properties of meat products by optimizing fiber content and reducing fat content. In this regard, Choi et al. (2016) showed that partial replacement of pork fat with 1% and 2% apple pomace fiber decreased the fat content from 30% to 25% in processed meat products. Analogously, Fu et al. (2022) prepared sausages supplemented with cherry powder, with the aim of reducing the fat content, which is often high in sausages, and found that the addition of cherry powder, at a percentage of 1% powder, improved the flavor of the sausage, without affecting the physico-chemical properties, while the addition of 3% determined a higher antioxidant capacity, inhibiting the oxidation of proteins and lipids, against a decrease in the sensory quality of the finished product.

Results on the integration of apple by-products into dairy products

Fruit pomace is a natural ingredient that can also be used to improve the texture and stability of dairy products. Iqbal et al. (2021) added different concentrations of apple pomace (0.1%, 0.5% and 1%) to skimmed milk and fermented it with Lactobacillus bulgaricus and Streptococcus thermophiles at 42 °C. In the initial phase, yogurt with 1% apple pomace had a higher pH and a shorter gel time than yogurt without pomace. Fortified yogurt also showed improved cohesion and consistency during 28 days of storage (Wang et al. 2019). The addition of 2.5%-10% to whole milk resulted in a yogurt formulation with a lower acidity between 0.15% and 0.09%, a fat content of 1.65%-1.59% and higher fiber concentration (Issar et al. 2017). Also, the addition of 3% pomace to yogurt resulted in a significant decrease in whey separation and an increase in firmness, cohesion, and density of yogurt during storage (Iqbal et al. 2021). At the same time, pomace can also be used as an active source of polyphenols and dietary fiber (Wang et al. 2018).

RECOMMENDATIONS

In order to maximize the benefits of using apple by-products, it is necessary to develop new processing technologies that allow efficient use. The development of these technologies could lead to increased use of by-products in the food industry, especially in the manufacture of gluten-free and low-sugar products, contributing to improving the health and sustainability of the food system.

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