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PHENOLICS COMPOUNDS IN FRUITS OF DIFFERENT TYPES OF BERRIES AND THEIR BENEFICENT FOR HUMAN HEALTH

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Abstract

The cultivated berry species are considered to be economically important freshly consumed fruits, and the production volumes are rapidly increasing worldwide during recent years. Among the colorful fruits, berries such as blueberry (Vaccinium corymbosum), red raspberry (Rubus idaeus), red and black currants (Ribes spp) and strawberry (Fragaria ananassa) are popularly used in the human diet either fresh or in processed forms. The berry fruits have gained significant attention by consumers due to a high content of health promoting compounds based on considerable quantities of different phytochemicals. Polyphenols comprise a wide variety of compounds, divided into several classes like hydroxybenzoic acids, hydroxycinnamic acids, anthocyanins, proanthocyanidins, flavonols, flavones, flavanols, flavanones, isoflavones, stilbenes, and lignans that occur in berry fruits. The anthocyanins have a wide range of bioactivities including antioxidant, anti-microbial and anti-inflammatory properties. The antimicrobial effects of berry extracts against gram-negative bacteria decreased in the following order: raspberry> strawberry> blueberry> currant.

Among fruits, strawberries are one of the richest sources of natural folate, also, manganese, iodine, magnesium, copper, iron, and phosphorus. Raspberry and its isolated compounds like lutein, vecetin, quercetin, and rutin play an important role for development of normal vision in human beings. Blueberry is especially rich in phenolic compounds, such as anthocyanins, hydroxycinnamic acid derivatives, tannins and flavonols. Health benefits of currants berry are associated with chronical noncommunicable diseases, neuroprotective and anticonvulsant, anti-inflammatory, chemoprotective, antimicrobial, antifungal activity as well as the properties improve cognitive behavior reduced risks of cancer, heart disease and stroke. The phenolic compounds found in berries are natural gifts for human health.

***Key words*: anthocyanins, antioxidant capacity, flavanoids, organic acids**

INTRODUCTION

In the past two decades, interest in study to determine health compounds in fruits has increased. The different types of berries are rich in biochemical content and supply lots of health benefits for humans, due to they are rich in bioactive compounds such as phenolic acids, flavonoids, sugars, organic acids, vitamins and anthocyanins. The cultivated berry species are considered to be economically important freshly consumed fruits, and the production volumes are rapidly increasing worldwide during recent years (Fotirić Akšić et al., 2019; Urun et al., 2021). In a current context of increasing demand for healthy foodstuffs, a growing of berry fruits is gaining interest within consumers and producers. Besides their exquisite flavor, berry fruits have gained significant attention by consumers due to a high content of health promoting compounds based on considerable quantities of different phytochemicals (Nile and Park, 2014). Berries belong to several genus, although the three key families examples are the Rosaceae, including strawberry (Fragaria ananassa), red raspberry (Rubus ideaus), black raspberry (Rubus occidentalis), blackberry (Rubus fruticosus), follow the Ericaceae, which including cranberry (Vaccinium macrocarpon), bilberry (Vaccinium myritillus), lowbush blueberry (Vaccinium angustifolium), highbush blueberry (Vaccinium corymbosum) and family Grossulariaceae which including black (Ribes nigrum) and red (Ribes rubrum) currants (Olas, 2018). The highest annual production among berry fruits have strawberries, raspberries, currants and blueberries (FAO, 2023).

Berry fruits are popularly consumed not only in fresh and frozen forms but also as processed and derived products, including dried and canned fruits, yogurts, beverages, jams, and jellies (Nile and Park, 2014). Among the colorful fruits, berries such as blueberry (*Vaccinium corymbosum*), red raspberry (*Rubus idaeus*), red and black currants (*Ribes* spp) and strawberry (*Fragaria ananassa*) are popularly used in the human diet either fresh or in processed forms. The chemical composition of berry fruits can be highly variable depending on the cultivar, growing location, ripeness stage, harvest and storage conditions. Studies have shown that the bioavailability of phenolic compounds differs from berry to berry, and this can also be affected by the method of processing (Kuntz et al., 2014). The among commonly consumed berries, blueberries and currants contain predominantly proanthocyanidins, red raspberries and strawberries contain predominantly ellagitannins. Nevertheless, a genotype has a profound influence on concentrations of bioactive compounds in berries. It has already been demonstrated that a wide diversity of phytochemical levels and antioxidant capacities exist within and across genera of small fruits. (Anttonen and Karjalainen, 2005; Joseph et al., 2014). Phenolic compounds, mainly located in the cell wall tissue of berries, are major secondary metabolites in berry fruits with important implications for human health (Cesa et al., 2017). It is well known that phenolic compound family biosynthesis follow the phenylpropanoid and flavonoid pathways in the endoplasmic reticulum of the plant cell. Berries provide significant health benefits because of their high levels of polyphenols, vitamins, minerals, antioxidants and fibers. Polyphenols include a wide range of compounds, divided into several classes like hydroxybenzoic acids, hydroxycinnamic acids, anthocyanins, proanthocyanidins, flavonols, flavones, flavanols, flavanones, isoflavones, stilbenes, and lignans that occur in berry fruits. They also contain high contents and wide diversity of nonessential biologically active components, such as organic acids or polyphenols, with their subclasses, tannins and flavonoids (Giampieri et al., 2015). Also, a lot of studies show, that leaves and seeds of berries species are a valuable source of antioxidant substances, especially polyphenols (Teleszko and Wojdyło, 2015).

The systemic biological activity of most phenolic compounds is limited by their low bioavailability, which is around 0.2% for hlorogenic acids and ranges from 0.7% to 1.1% for anthocyanins and most hydroxycinnamic acids from blueberry (Rodriguez-Mateos et al., 2016; Zhong et al., 2017). In general, phenolic compounds are absorbed throughout the gastrointestinal tract, especially in the stomach, small intestine and colon (Teng and Chen, 2019). The portion of phenolic compounds that is not absorbed up to the small intestine can be extensively metabolized by the colonic microbiota into a series of simple phenolic acids that can reach the circulation and are likely implicated in many health benefits (Augusti et al., 2021). Anthocyanins are absorbed and metabolized into the colon; only a low number of dietary anthocyanins are absorbed into the stomach and small intestine when they are in their glycosidic forms. Moreover, the absorbed anthocyanins are metabolized to sulfate, glycine, glucuronide and methylate derivatives in the intestine epithelium, liver and kidneys (Ludwig et al., 2015)

The berries are an important part of a healthy diet. Berries and their products are very often recognized as “superfoods.” They possess high concentrations of phenolic compounds, which have been found in in vitro and in vivo studies to possess a range of biological activities (Kristo et al., 2016). Various phytochemicals from berries are thought to be antioxidants, which help to protect the body against various diseases and disorders and the damaging effects of free radicals which results in chronic diseases that are associated with aging. The anthocyanins have a wide range of bioactivities including antioxidant, anti-microbial and anti-inflammatory properties. The antimicrobial effects of berry extracts against gram-negative bacteria decreased in the following order: raspberry> strawberry> blueberry> currant (Fereira et al., 2005). Also, anthocyanins have been found to exert the most significant inhibition effect on the proliferation of colon cancer cells in vitro, followed by flavonols and tannins, being the fraction of phenolic acids the less effective (Massarotto et al., 2016). Berry bioactive components manifest anticancer effects through various complementary and overlapping mechanisms of action, including the induction of metabolizing enzymes, modulation of gene expression and their effects on cell proliferation, apoptosis, and subcellular signaling pathways. Some berries, have been identified as sources of phenolic compounds like gallic and ellagic acid, which have potential cancer chemopreventive activity. Also, chemopreventive agents present in berries include vitamins A, C, and E, and folic acid; calcium and selenium; carotene and lutein; phytosterols such as sitosterol and stigmasterol. berries contain low concentrations of lipids but high concentrations of dietary fiber, which has a nutritional function and reduces the level of low density lipoprotein (LDL).The high dietary fiber content is important because fruit pectin acts as an intestinal regulator, while high tannin content and their antiseptic properties of berries make them good for tightening tissues as well as treating minor bleeding (Ferreira et al., 2005; Manach et al., 2005; Puupponen-Pimia et al., 2005; Nile and Park, 2014; Skrovankova et al., 2015).

Strawberry

The strawberry is a member of the genus Fragaria (family: Rosaceae) and one of the most widely grown type of berries fruit. Today, it is widely cultivated, especially in Europe, and can be consumed not only fresh but also processed into marmalade, jam, fruit juice, and beverages. Yearly production of strawberry is ~ 8.500,000 tones, and the majority of the production originates from China, USA, Mexico and Egypt. In Europe, the top producers are Turkey, Spain, Italy and Greece (FAO, 2023). Strawberry fruits are an important source of health-promoting compounds for mankind. Among the berries, it is the most preferred due to its pleasant aroma, charming color, good taste, flavor, and bioactive compounds (Agehara and Nunes, 2021).

Among fruits, strawberries are one of the richest sources of natural folate, also, manganese, iodine, magnesium, copper, iron, and phosphorus. In addition, strawberries are rich in bioactive compounds, mainly represented by flavonoids, especially anthocyanidins, followed by phenolic acids like hydroxycinnamic, and hydroxybenzoic acids (Nour et al., 2017). Anthocyanins are the most notable and quantitatively the most important type of polyphenol in strawberries. The concentration and composition of anthocyanins are important also for the sensory quality of fruits and products, in addition to their possible health benefits. In strawberry, pel-3-glu is the main anthocyanin (96%). The chlorogenic, ellagic, caffeic and trans-cinnamic acids are identified in strawberry. Also, the major flavan-3- ols are catechin and epicatechin. The main hydrolysable tannin in strawberries is ellagic acid and represents around 80% of total phenolic acids and hydrolysable tannins in strawberry (Ariza et al., 2015; Cervantes et al., 2020).

A many studies have focused on determining the bioactive compound of diverse strawberry cultivars (Aaby et al., 2012; Ganhao et al., 2019). Strawberries as it contains essential phytochemicals, it contributes to human health that because of their astringent and diuretic properties in official pharmacopoeia sources such as skin diseases, LDL-cholesterol oxidation, cardiovascular incidents, inflammation of the nerves and lungs (Skrovankova et al., 2015). Also, strawberry fruits have high oxygen radical absorbance activity against peroxyl radicals. By using an artificial peroxyl radical model system, the extract of fresh strawberries had a greater total antioxidant capacity than extracts of plum, orange, red grape, kiwi fruit, pink grapefruit, white grape, banana, apple, tomato, pear, and honeydew melon. Every days consumption of low dose of strawberry (25 g/day) has effects to anti-inflammatory in subjects with diabetes type II and obese subjects with osteoarthritis and elevated serum lipids (Basu et al., 2014).

Raspberry

Red raspberries (*Rubus idaeus* L.) are native fruits from Europe. The genera *Rubus* contains more than 700 species, which are belonged into 15 subgenera. Raspberries classified to the subgenus Idaeobatus (Hummer, 2010). The red raspberries cultivars are very popular and highly distinguished for their flavor and quality of theirs berries. Yearly production is ~ 850,000 tones, and the majority of the production originates from Europe, where Russia, Poland and Serbia, are the top producers, and followed others countries USA, Mexico and Chile (FAO, 2023).

For healthy nutrition in humans this fruit is known to provide needed contents of vitamins, minerals, fatty acids, proteins, carbohydrates and dietary fibres (Kula and Krauze-Baranowska, 2016). The growth stage and cultivars of raspberry have strong effects to bioactive compound profiles of fruits. Also, plant polyphenols serve a self-protection role in plants, and their concentration can be increased as a response to abiotic and biotic stresses. Additionally, they contain a polyphenolic compound profile associated with the prevention and treatment of some pathologies and chronic degenerative diseases. A phenolic compound family can act as an antioxidant and antimicrobial agent, and to raspberries have been noticed to have a wide antioxidant capacity, approximately 75% is due to their anthocyanin and ellagitannin contents (Rao and Snyder, 2010; Nowak et al., 2018). In raspberries, were recorded at higher concentrations of cyanidin-3-O-sophoroside, cyanidin-3-O- rutinoside and cyanidin-3-O-glucoside, while cyanidin-3-sambubioside-5-rhamnoside is a unique in raspberry fruits. It has long been established that cyanidin-3-glucoside and cyanidin-3-rutinoside are the respective major anthocyanins in raspberry. Amoung ellagitannins compounds, significant contents have sanguiin H-6 and lambertianin C (Kosmala et al., 2015; Mihailovic et al., 2019; Lopez-Korona et al., 2022).

The anthocyanins present in raspberries are important for the beneficial health effects associated with their antioxidant, anti-inflammatory, and chemopreventative the biological activity of raspberry against esophageal, colon, and oral cancers has been demonstrated. The antioxidant capacity of phenolic compounds, found in raspberries, is greatly due to their radical scavenging activity, since they can easily donate electrons and hydrogen atoms due to their highly conjugated systems and aromatic structures. Bioactive compounds from raspberry berries could also possibly block the entry of microorganism by preventing them from adhering to the human cells that line the walls of the liver, kidneys or urinary tract. Raspberry and its isolated compounds like lutein, vecetin, quercetin, and rutin play an important role for development of normal vision in human beings. The phenolics and their metabolites from raspberry fruits play a prebiotic and probiotic role. Anthocyanin derived metabolites reduced the concentration of Bacteroides and Clostridium histolyticum (Tungmunnithum et al., 2018). The raspberry extracts have the strongest inhibitors of gram-negative bacteria, especially Typhimurium. Ellagic acid inhibits a range of pathogenic organisms including *Vibrio cholerae*, *Shigella dysenteriae*, and *Campylobacter spp*. Also, prevails a hypothesized that ellagitannins could be one of the components in cloudberries, raspberries causing the inhibition against *Salmonella*. Raspberries contain quercetin glucuronide, which has a rich history in folk medicine as a cold and flu remedy or as a diuretic and antirheumatic, and as its glycoside, by inhibiting protein tyrosine kinase (Seeram et al., 2003). Quercetin, catechin, caffeic acid, sinapic acid, ferulic acid and chlorogenic acid, which are found in raspberries, and also like anthocyanins, can inhibit the peroxidation of lipids, reduce the expression levels of inducible nitric oxide synthase, cyclooxygenase-2, IL-1 and IL-6, reducing inflammation. The anti-inflammatory activity of phenolic compounds may be due to their ability to interfere with oxidative stress signaling and suppress proinflammatory signaling transduction. These compounds have been reported to block the secretion of proinflammatory cytokines (Li et al., 2014; Mah et al., 2017). Further, phenolics compounds of raspberry berries increases metabolic rate, burns fats, improve eye health and strength of body, etc (Szajdek and Borowska, 2008).

Blueberry

Blueberry (Vaccinium spp) is a widely consumed fruit worldwide owing in part to its richness in bioactive compounds and excellent antioxidant activity. New blueberry cultivars had been bred and selected based on their bioactive compounds and antioxidant activity. Blueberries have been recognised as healthy fruits for their high levels of phenolic compounds and the highest antioxidant activity among traditionally-consumed fruits (Pertuzatti et al., 2021). Yearly production is ~ 750,000 tones, and the majority of the production originates from USA, Canada and Mexico. In Europe, the top producers are Poland, Spain and Germany (FAO, 2023)

Blueberry is especially rich in phenolic compounds, such as anthocyanins, hydroxycinnamic acid derivatives, tannins and flavonols. Anthocyanins, flavanols and phenolic acids are the main bioactive compounds of blueberry. Anthocyanin synthesis has been accelerated through the increasing maturity of highbush blueberry, with fruit skin color steadily becoming darker and bluer, reaching a peak value at a purple-black stage (Sun et al., 2016). The distinctive anthocyanin profile in ripe blueberry includes 15 major characteristic anthocyanidin glycosides in different sugar moieties (galactose, glucose and arabinoside) bonded to five aglycones (delphinidin, cyanidin, petunidin, peonidin and malvidin). Among all anthocyanidin glycosides, delphinidin 3-arabinoside is the major anthocyanins of blueberry fruits, follow by delphinidin 3-galactoside, cyaniding 3-arabinoside, petunidin 3-glucoside, while others anthocyanidins glycoside have valeus less than 5% of total anthocyanins (Colak et al., 2016). Blueberry showed significantly higher contents of phenolic acids and hydrolysable tannins than others types of berries. Also, an important phenolics compounds included phenol acids such as quinic acid, chlorogenic acid, gallic acid, p-coumaric acid, caffeic acid, ferulic acid, ellagic acid, follow flavanols catechin and epicatechin and flavonols myricetin, quercetin, rutin and kaempferol (Guofang et al., 2019). Blueberry showed significantly higher contents of phenolic acids and hydrolysable tannins than others types of berries (Ariza et al., 2015). For instance many research show that the major phenolic acids from blueberry fruits is p-coumaric, follow ferulic acids, gallic and vanillic acid (Ayaz et al., 2005; Colak et al., 2016).

The phenolic compounds of blueberry, including anthocyanins, modulate various cellular processes and have been implicated in the inhibition of cancer cell proliferation and prevention of obesity, type 2 diabetes, inflammation and cardiovascular disease (Fang, 2014; Zhong et al. 2017; Martín-Gómez et al., 2020). One of the most studied flavonols, quercetin, is considered a prominent dietary bioactive compound due to its high bioaccessibility (~80%). Quercetin has been claimed to exert beneficial health effects, including protection against various diseases as osteoporosis, certain forms of cancer, pulmonary and cardiovascular diseases and even against ageing (Boots et al., 2008; Gapski et al., 2019). Further, phenolics compounds of blueberry berries prevent weight loss, macular degeneration, helps in prevent Alzheimer's disease, reverse signs of aging, protects and enhances circulation, reduces cholesterol, good for eyes, mouth and gum health, provides strength, protects blood vessels and strengthens arteries, and improves circulation etc (Yi et al., 2005)

Ribes spp

Black (*Ribes nigrum* L.) and red currant (*Ribes rubrum* L.) belongs to the Ribes genus which consists of nearly 150 diploid species of spiny and non-spiny shrubs. It is a perennial small bush, indigenous to Central and Northern Europe, Caucasus, Central Siberia and Himalaya. It is widely cultivated in Europe, North America, New Zealand, and China, as a garden shrub and as an important commercial crop. Yearly production is ~ 700,000 tones, and the majority of the production originates from Europe, where Russia and Poland are the top producers, followed by Ukraine and the UK.

The currants cultivation is in a continuous expansion, with a huge importance in human nutrition and a high degree of suitability for industrial processing. Due to the high quality of red currant berries, which is based on its phenols content, their importance indicate a need for more intensive exploitation of these species. Also, berries can be very successful in the fresh market because their organoleptic characteristics are usually favored by consumers. Berries of currants are traditionally used for producing juices, jams, purées, jellies, syrups and yoghurt and other dairy products, but can be also eaten raw. Besides berries, the seeds and leaves are a rich source of numerous bioactive ingredients, especially polyphenolic compounds. The size of bushes, ripening time, berry size, yield, and other quantitative and qualitative properties of the fruits differ between the various cultivars, as well as by the plant's age, growing location, environment conditions, cultivation systems, different pre- and post-harvest factors, ripening stage of the berries, and the number of clusters (Brennan, 2008; Vagiri et al., 2012; Lui et al., 2014; Paprstein et al., 2016; Ziobron et al, 2021).

The dark and red color of currant berries is the result of high levels of anthocyanins in the epidermal cells. The anthocyanins and flavonols are the major phenols compounds in currant berries (Pereira et al., 2009). Sugar substitution on anthocyanins and flavonols usually appears as the *O*-glycosides at the 3-position (with follow sugars rutin, glucose and galactose). The major anthocyanins in currants berries are delphinidin and cyanidin glycosides (Djordjević et al., 2013). An important property of anthocyanins is that they are able to cross the blood-brain barrier (Andres-Lacueva et al., 2005). The main components of anthocyanins are delphinidin 3-rutinoside, delphinidin 3-glucoside, cyaniding 3-glucoside and cyanidin 3-rutinoside. The quercetin glycosides were the predominant flavonols, followed by myricetin glycosides. Quercetin 3-rutinoside, myricetin 3-rutinoside, myricetin 3-glucoside and quercetin 3-glucoside were the major flavonols (Borbonaba and Terry, 2008; Milivojević et al., 2012; Mikulic-Petkovsek et al., 2012; Šavikin et al., 2013).

Health benefits of currants berry are associated with chronical noncommunicable diseases, neuroprotective and anticonvulsant, anti-inflammatory, chemoprotective, antioxidative, antimicrobial, antifungal activity as well as the properties improve cognitive behavior reduced risks of cancer, heart disease and stroke (Bishayee et al., 2011; Tabart et al., 2012). Further, phenolics compounds of currants clean and reduces blood cholesterol, stimulates digestion, improves functions of liver, pancreas, spleen and kidneys, etc.

CONCLUSIONS

Berries have chemicals that can cure many diseases, and a drugs obtained from these fruits are being researched against cancer, which is the biggest disease of today. In previusly two decades, a many of studies have researched an effects and influence of phenolic compounds in berries as antioxidants protecting against the most common diseases. The observed phenolics properties of different types of berry fruits point to vast differences in the type of their bioactive compounds. Berries and their products have strongly biological activity. Because of that berries have been shown to play a beneficial role as antioxidants in humans in both *in vitro* and *in vivo* models using dietary supplementation with various berries. The authors proved that most potent antioxidants commonly found in berries may well be the anthocyanins, flavonols and phenolic acids. The most significant health benefits are ascribed to phenolic compounds, which result mostly from antioxidant, anticancer, antimutagenic, antimicrobial, antiinflammatory and neuroprotective properties.

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