Red and purple coloured potatoes as a significant antioxidant source in human nutrition – a review

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ABSTRACT

Potatoes regarding their consumption are a significant antioxidant source in human nutrition. The main potato antioxidants are polyphenols, ascorbic acid, carotenoids, tocopherols, α-lipoic acid, and selenium. The most contained polyphenolic antioxidants in potatoes are *L*-tyrosine, caffeic acid, scopolin, chlorogenic and cryptochlorogenic acid and ferulic acid. In red and purple potatoes are in addition contained acylated anthocyanins and pigmented potatoes display two to three times higher antioxidant potential in comparison with white-flesh potato. Red potato tubers contain glycosides of pelargonidin and peonidin, purple potatoes glycosides of malvidin and petunidin. New red and purple flesh potato varieties are breeded for their use in food and in the non-food industry. Anthocyanins of potatoes are also useful in the protection against potato blight.

Keywords: red and purple potatoes; antioxidants; polyphenols; anthocyanins; breeding; food and non-food industry use; fungicidal properties

Potato as a significant antioxidant source in human nutrition

One of the richest sources of antioxidants in the human diet is potato tubers (*Solanum tuberosum* L.) (Lachman et al. 2000). Their antioxidant content decreases a great deal from atherosclerotic processes, and is inhibited from cholesterol accumulation in blood serum and enhances the resistance of the vascular walls. Many antioxidants decrease risk of coronary heart disease and have free radical scavenging effect. The main potato antioxidants are polyphenols, ascorbic acid, carotenoids, tocopherols, α-lipoic acid, and selenium. Polyphenolic compounds, esp. flavonoids are effective antioxidants (Bors and Saran 1987) due their capability to scavenge free radicals of fatty acids and oxygen (Good 1994). Vegetables and crops are significant sources of antioxidants in human nutrition either in direct consumption or in the form of vegetable juices. Justesen et al. (1997) estimated the daily flavonoid intake at 26 mg/day. Potato tubers present a very significant source of antioxidants (Al-Saikhan et al. 1995) in human nutrition, e.g. among fruits and vegetables they insure an average daily intake of about 64 mg polyphenols per capita in the U.S.A. and occupy the second place after tomatoes. From antioxidants they are richest in polyphenols (1.226–4.405 mg/kg) and ascorbic acid (170–990 mg/kg). From other antioxidant compounds carotenoids (as high as 4 mg/kg), α-tocopherol (0.5–2.8 mg/kg) and in lesser contents selenium (0.01 mg/kg) or α-lipoic acid are occurring. Potato tubers contain secondary metabolites – polyphenolic compounds – presenting substrates for enzymatic browning of potatoes that is occurring during peeling, cutting or grating of raw potato tubers, which is caused by polyphenol oxidase (Jang and Song 2004). *L*-Tyrosine (L–2 × 10^{-3}M) and chlorogenic acid (2–6 × 10^{-4}M) (Dao and Friedman 1992) are major polyphenolic potato constituents (Leja 1989, Matheis 1989). The most presented polyphenolic compound in potato tubers is amino acid tyrosine (770–3.900 mg/kg), followed by caffeic acid (280 mg/kg), scopolin (98 mg/kg), chlorogenic acid (22–71 mg/kg), ferulic acid (28 mg/kg) and cryptochlorogenic acid (11 mg/kg). Caffeic acid may be a product of hydrolysis of chlorogenic acid and possess strong antioxidant activity as well as its related hydroxycinnamic acid compounds (Chen and Ho 1997). Yamamoto et al. (1997) have found caffeic acid level in the edible parts of potato as high as 0.2–3.2 mg/kg, the total polyphenols were 422–834 mg/kg. The skin parts contained double in each case. Some polyphenols are presented only in lesser levels such as neochlorogenic acid (7 mg/kg), *p*-coumaric acid (4 mg/kg), sinapic acid (3 mg/kg), and 3,4-dicaffeoyl-quinic acid (3 mg/kg).

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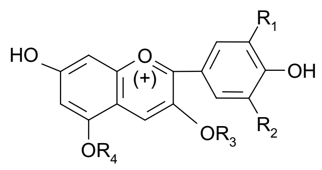
Only in small levels were found 3,5-dicaffeoylquinic acid, scopoletin, *trans*-feruloylputrescine. Negrel et al. (1996) have found the occurrence of ether-linked ferulic acid amides (feruloyltyramine and/or feruloyloctopamine) in suberin-enriched samples of natural and wound periderms of potato tubers. The major part of the ether bonds involved the ferulic moiety of the amides. In the plant total were identified glycosides of delphinidin (3-*O*-rutinoside), quercetin (3-*O*-glucoside or rutinoside), kaempferol (3-*O*-diglucoside-7-*O*-rhamnoside, 3-*O*-triglucoside-7-*O*-rhamnoside), and petunidin (3-*O*-rutinoside). Among free phenolics in potatoes is also included (+)-catechin (Mendez et al. 2004). As Lærke et al. (2001) found, the changes in blackspot susceptibility and in the colour of the blackspots during growth and storage of the potato cvs. Dali and Oleva tubers could not be ascribed to changes in the discolouration potential, PPO activity and concentrations of phenols in the tuber cortices.

Anthocyanin colorants in potato tubers with red and purple coloured flesh

Anthocyanins both in fresh and also processed fruit and vegetables serve two functions – they improve the overall appearance, but also contribute to consumers' health and well being (Stintzing and Carle 2004). An important attribute of these pigments is that they are potent antioxidants in the diet (Brown et al. 2003, Brown 2004). They are widely ingested by humans and their daily intake has been estimated around 180 mg (Galvano et al. 2004). They are mainly contained in red and purple coloured potato varieties in skins and flesh of tubers and protect the human organism against oxidants, free radicals and LDL cholesterol (Hung et al. 1997). The natural variation of cultivated potato germplasm includes types that are red and purple pigmented due to the presence of anthocyanins (structure of aglycons is given in Figure 1) in the skin and/or flesh (Brown et al. 2003). Red coloured potato tubers (skins and flesh) contain pelargonidin glycosides – 3-*O*-*p*-coumaroylrutinoside-5-*O*-glucoside (200–2000 mg/kg FW), in lesser amounts glycoside of peonidin – 3-*O*-*p*-coumaroylrutinoside-5-*O*-glucoside (20–200 mg/kg FW) (Lewis et al. 1998). Purple tubers contain similar levels of glycoside of petunidin – 3-*O*-*p*-coumaroylrutinoside-5-*O*-glucoside and much higher amounts of malvidin glycoside of 3-*O*-*p*-coumaroylrutinoside-5-*O*-glucoside (2000–5000 mg/kg FW). Total anthocyanins ranged from 69 to 350 mg per kg FW in the red-fleshed and 55 to 171 in the purple-fleshed clones (Brown et al. 2003). Acylated pigments form more than 98% of the total anthocyanin content of potatoes. Individual glycosides differ in acylation pattern by acid type, e.g. caffeic acid is contained in peonidin 3-*O*-[6-*O*-(4-*O*-*E*-caffeoyl-*O*-α-rhamnopyranosyl)-β-glucopyranoside]-5-*O*-β-glucopyranoside (10% anthocyanin content) and petunidin (6%). Naito et al. (1998) found that acylated glycosides of pelargonidin are characteristic for red potato. The major pigment was identified as pelargonidin 3-*O*-[4′′-*O*-(*trans*-*p*-coumaroyl)-α-*L*-6′′-rhamnopyranosyl-β-*D*-glucopyranoside]-5-*O*-β-*D*-glucopyranoside by chemical and spectral measurements and as minor pigment pelargonidin 3-*O*-[4′′-*O*-(*trans*-feruloyl)-α-*L*-6′′-rhamnopyranosyl-β-*D*-glucopyranoside]-*O*-β-*D*-glucopyranoside was determined. In other glycosides *p*-coumaric acid is bound, e.g. in peonarin (25%) and petanin (37%). The same anthocyanins, but in other ratios, are contained in the purple potato flesh (4, 54 and 32%). The other acylating acid is ferulic acid, e.g. in the purple variety Congo 3-*O*-[6-(4′′-feruloyl-*O*-α-rhamnopyranosyl)-β-*O*-glucopyranoside]-5-*O*-glucopyranosides of petunidin and malvidin are present. The content of anthocyanins is stated as high as 20–400 mg/kg of fresh weight of tuber (Rodriguez-Saona et al. 1998). In red varieties pelargonidin 3-*O*-rutinoside-5-*O*-glucoside acylated by *p*-coumaric acid represents about 70% from the total anthocyanin content. Red pigmented potatoes contained predominantly acylated pelargonidin glycosides comprising about 80% of the total, while blue-fleshed potatoes contained these compounds, and, in addition, acylated petunidin glycosides in a 2 to 1 ratio of the former to the latter (Brown 2004). Structures of major anthocyanidin glycosides are given in Table 1. Glycosides of peonidin, petunidin and malvidin are major anthocyanidin glycosides that contribute to antioxidant properties of coloured potato tubers.

Antioxidant activity of potato anthocyanins

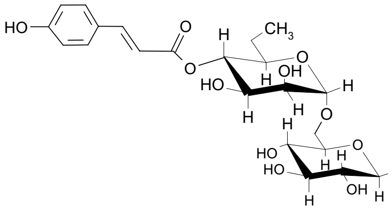
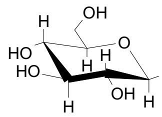
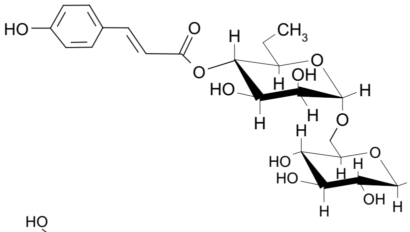
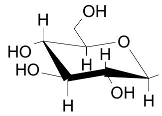
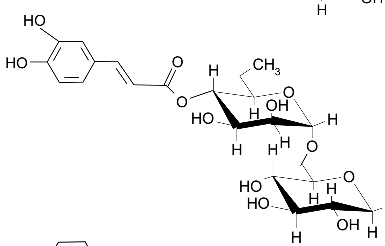
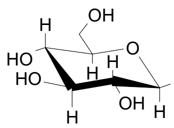
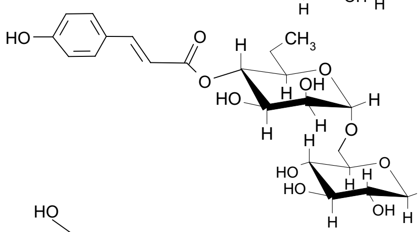
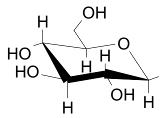
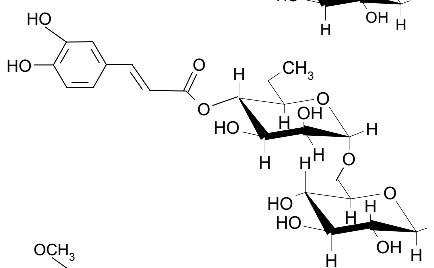
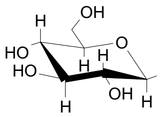
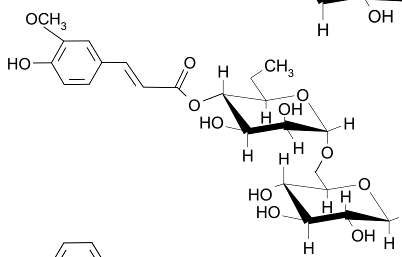
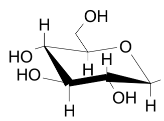
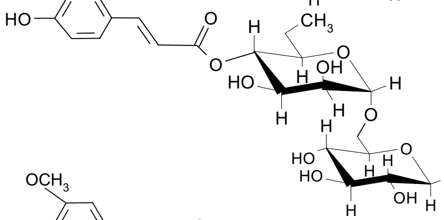
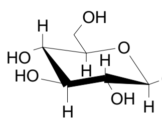
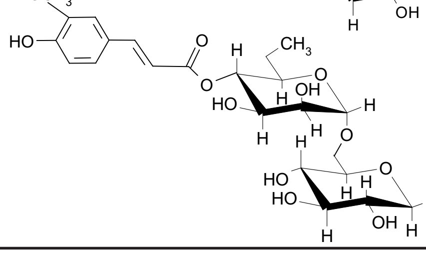
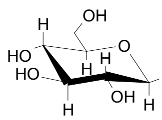
Antioxidant activity of anthocyanins is among other properties determined by the number of free hydroxy groups in their molecule, so petunidin



$R_1=R_2=R_3=R_4=H$ pelargonidin
$R_1=OCH_3$, $R_2=R_3=R_4=H$ peonidin
$R_1=OCH_3$, $R_2=OH$, $R_3=R_4=H$ petunidin
$R_1=R_2=OCH_3$, $R_3=R_4=H$ malvidin

Figure 1. Main anthocyanin aglycones of potatoes

Table 1. Structure of anthocyanin glycosides in purple and coloured potato tubers

R_1	R_2	R_3	R_4	Anthocyanin glycoside
H	H			pelargonidin 3-[6-*O*-(4-*O*-*E*-*p*-coumaroyl-*O*-α-rhamnopyranosyl)-β-*D*-glucopyranoside]-5-*O*-β-*D*-glucopyranoside
OCH_3	H			peonarin, i.e. peonidin 3-[6-*O*-(4-*O*-*E*-*p*-coumaroyl-*O*-α-rhamnopyranosyl)-β-*D*-glucopyranoside]-5-*O*-β-*D*-glucopyranoside
OCH_3	H			peonidin 3-[6-*O*-(4-*O*-*E*-caffeoyl-*O*-α-rhamnopyranosyl)-β-*D*-glucopyranoside]-5-*O*-β-*D*-glucopyranoside
OCH_3	OH			petanin, i.e. petunidin 3-[6-*O*-(4-*O*-*E*-*p*-coumaroyl-*O*-α-rhamnopyranosyl)-β-*D*-glucopyranoside]-5-*O*-β-*D*-glucopyranoside
OCH_3	OH			petunidin 3-[6-*O*-(4-*O*-*E*-caffeoyl-*O*-α-rhamnopyranosyl)-β-*D*-glucopyranoside]-5-*O*-β-*D*-glucopyranoside
OCH_3	OH			petunidin 3-[6-*O*-(4-*O*-*E*-feruloyl-*O*-α-rhamnopyranosyl)-β-*D*-glucopyranoside]-5-*O*-β-*D*-glucopyranoside
OCH_3	OCH_3			malvidine 3-[6-*O*-(4-*O*-*E*-*p*-coumaroyl-*O*-α-rhamnopyranosyl)-β-*D*-glucopyranoside]-5-*O*-β-*D*-glucopyranoside
OCH_3	OCH_3			malvidin 3-[6-*O*-(4-*O*-*E*-feruloyl-*O*-α-rhamnopyranosyl)-β-*D*-glucopyranoside]-5-*O*-β-*D*-glucopyranoside

has greater antioxidant effects in comparison with malvidin, peonidin or pelargonidin, resp. total antioxidant activity is determined both, by the content of anthocyanins and by the content of phenolic acids, mainly by isomers of chlorogenic acids (Hamouz et al. 1999, Lachman et al. 2000). Acylation of potato anthocyanidins with cinnamic acids shifts the colouration to blue shadow and in great deal enhances their total antioxidant effectiveness. In contrary, glycosidic substitution at position 5 reduces antioxidant activity as well as the substitution at position 3. Antioxidant properties of natural extracts are much higher in comparison with pure individual compounds; this fact shows the synergic effect (de Souza and de Giovani 2004, Garcia-Alonso et al. 2004) of the mixture of anthocyanidins and other antioxidants contained in potato tubers. Pigmented potatoes displayed two to three times higher antioxidant potential than white-fleshed potato (Brown 2004). Regarding this fact, high-anthocyanin potato could be ranged to other vegetables of reputed high antioxidant potentials such as kale or broccoli. Oxygen radical absorbance capacity and ferrous reducing ability of plasma revealed that the antioxidant levels in the red or purple-fleshed potatoes were two to three times higher than white-fleshed potato (Brown et al. 2003). Brown (2004) confirmed by measuring of antioxidant activity (ORAC and FRAP) that the red- and/or purple-fleshed potatoes had significantly higher antioxidant values than the white- or yellow/orange-fleshed potatoes. White flesh varieties have no anthocyanin, however, white they have substantial antioxidant activity by themselves ranging from 930 to 1380 mg Trolox equivalents per kg FW (Brown 2004). Potato offers a vehicle to substantially increase consumption of antioxidants, which have been implicated in benefiting cardiovascular health, preventing certain types of cancers, and retarding macular degeneration of the retina (Brown 2004). Diets rich in anthocyanins and other related phenolic compounds have been associated with a reduced incidence and severity of certain kinds of cancer and heart disease (Hertog et al. 1993).

New potato varieties with red and purple coloured skins and flesh and their breeding

Regarding the fact that antioxidant capacity of red or blue coloured potatoes is 2–3× higher in comparison with potatoes with white/yellow flesh, these potatoes could represent the possibility of enhancing the contribution of the potatoes to the portion of antioxidants in human nutrition. This is the reason why the effort of breeders focuses on the breeding of these phenotypes of potatoes, which could involve different variants: purple skin and flesh, purple skin with partially purple (marbled) flesh, red skin with red flesh or red skin with partially coloured (marbled) flesh. Synthesis of anthocyanidin pigments in potatoes is based on the dihydroflavonol-4-reductase activity, which catalyses reduction of dihydrokaempferol to leucopelargonidin. The potato R-locus encodes a basic factor required for the production of red pelargonidin-based anthocyanin pigments, which encodes dihydroflavonol 4-reductase, is present in all red coloured potato tubers (De Jong et al. 2003), whereas in the tubers with white flesh is lack. R-locus was selected during the domestification of potatoes (De Jong 1991, De Jong and Burns 1993). In present time many coloured varieties are known, e.g. Norland, Red Norland, Dark Red Norland, Congo, Blaue Hindelbank, All Blue, Red Pearl, Purple Peruvian, Russet Norkotah, Cranberry Red etc. (Groza et al. 2004). Clones with red or blue coloured flesh had also every time, identically coloured skin and the formation of these pigments is probably controlled with more genes (Brown et al. 2003, De Jong et al. 2003). The percentage of completive red-fleshed progeny is 14.5% in red × red crosses and 4.1% in red × white crosses. Expression of DNA coding dihydroflavonol-4-reductase could enhance the pelargonidin formation as high as 4×. During the development of coloured tubers the content of anthocyanins is more or less constant, only in the less coloured varieties does it enhance to the defined maximum. Changes in these tubers were observed in anthocyanin content and tuber surface colour during tuber development (Hung et al. 1997). Thus, anthocyanins are synthesized throughout tuber development, and cell division and/or enlargement contribute to a decline in coloration and anthocyanin concentration.

Role of anthocyanins in potatoes and their use in food and non-food industry

Anthocyanins contained in red or purple potatoes have antioxidant properties, but they also may block potato blight by their fungicidal properties. Red and purple potato varieties have a high level of durable resistance, which is preventing the blight from reaching the potatoes underground. Also other several abiotic stresses, including wounding, light, temperature, and effects of methyl jasmonate and ethylene were tested for their ability to induce accumulation of phenolic compounds and antioxidant capacity in purple-flesh potatoes. Wounding induced the increase of total phenolics to 60% and a parallel 85% increase in antioxidant capacity (Reyes and Cisneros-Zevallos 2003). As it was been shown in transgenic potato tubers, the flavonoids- and anthocyanin-enriched plants showed improved antioxidant capacity (Lukaszewicz et al. 2004), the same was demonstrated with higher contents of chlorogenic acid (Niggeweg et al. 2004). Changes in the content and yield of anthocyanins and total phenolics during development of purple- and red-flesh potato were studied (Reyes et al. 2004). With tuber growth and maturity content of anthocyanins and phenolics decreased while tuber weight and yield increased. Longer days and cooler temperatures favoured about 2.5–1.5× higher anthocyanin and phenolic content (Reyes et al. 2004). The main aim of breeders and producers in selecting varieties with high anthocyanin content and appropriate growing conditions for the enhancement of natural pigment and antioxidant yields is to obtain high anthocyanin purple- and red-flesh potatoes for the food and nutraceutical industry (Brown et al. 2003). Some among the specialty potatoes were by the evaluators appraised positively (60 to 66% of the evaluators liked), e.g. purple-flesh cultivars All Blue and Mc Intosh Black, pink-flesh cv. Alaska Sweetheart (Sorensen and Mikitzel 1993). In recent times red-flesh and purple-flesh potatoes are used as a source of anthocyanin natural colourants for food or non-food industry intensively studied (Vögel et al. 2004). As Singh and Rajini (2004) showed the multiple antioxidant activity of potato peel powder was evident as it showed superoxide-scavenging ability. Considering the fact that potato peels are discarded as waste and not effectively utilised, these results suggest the possibility that potato peel waste could be effectively used as an ingredient in functional food. Ur-Rehman et al. (2004) recommend potato peel extract in oils, fats and other food products as natural antioxidant to suppress lipid oxidation. The most important factors that are studied, is new variety and cultivars breeding (with high anthocyanin content), effects of fertilisation and region of cultivation, storage and technology of processing, stability of products.

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ABSTRAKT

Červeně a modře zbarvené brambory jako významný zdroj antioxidantů v lidské výživě – studie

Brambory jsou vzhledem k jejich konzumaci významným zdrojem antioxidantů v lidské výživě. Hlavními antioxidanty brambor jsou polyfenoly, askorbová kyselina, karotenoidy, tokoferoly, α-lipoová kyselina a selen. Nejvíce zastoupenými antioxidanty v bramborách jsou *L*-tyrozin, kávová kyselina, skopolin, chlorogenová a kryptochlorogenová kyselina a ferulová kyselina. V červených a modrých bramborách jsou mimo to obsaženy acylované anthokyany a barevné odrůdy brambor vykazují dvakrát až třikrát vyšší antioxidační potenciál ve srovnání s bramborami s bílou dužninou. Hlízy červených brambor obsahují glykosidy pelargonidinu a peonidinu, modrých brambor glykosidy malvidinu a petunidinu. Jsou šlechtěny nové odrůdy červeně a modře zbarvených brambor pro jejich použití v potravinářském i nepotravinářském průmyslu. Anthokyany brambor mají význam v ochraně proti plísni bramborové.

Klíčová slova: červené a modré brambory; antioxidanty; polyfenoly; anthokyany; šlechtění; použití v potravinářském a nepotravinářském průmyslu; fungicidní vlastnosti

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