ANTIOXIDIZING PROPERTIES OF FRUITS AND VEGETABLES

PROPRIETĂȚI ANTIOXIDANTE LA FRUCTE ŞI LA LEGUME

BECEANU D.
University of Agricultural Sciences and Veterinary Medecine Iaşi

Abstract. *The horticultural products contain numerous principles that have bioactive properties among which a remarkable antioxidizing activity. This property is owed to a series of compounds having a presence and a more or less important level and also a specific evolution during the life of fruits and vegetables (flavones, phenolic acids, tocopherols, ascorbic acid, carotenoids etc). The traditional antioxidants were vitamins (C, E, pro-vitamin A/ β carotene, lycopene etc). More recently they studied the antioxidizing properties of flavones and other phenolic compounds. Gradually there appeared the idea of evolution of these values depending on the stage of maturity. At the moment of maturity of the coloured fruits they made some thorough studies on the contents of anthocianines, flavonols proanthocianidines, hydroxicinamates, β carotene, ascorbic acid and tocopherols. They may speak of an antioxidizing activity specific to Pomaceae fruits, drupaceous fruits, bushes, citric fruits, grapes and for vegetables the crucifers from all the technological groups followed by the radiculaceae and the bulbous ones. Vegetables contain however much lower levels of antioxidizing compounds among which we must mention the green peppers at their physiological maturity, the Brussels sprouts and broccoli besides the species rich in vitamins/provitamins with antioxidants properties.*

Rezumat. *Produsele horticole conțin numeroase principii care au proprietăți bioactive, între care şi o remarcabilă activitate antioxidantă. Această proprietate se datorează unei serii de compuşi care au o prezență şi un nivel mai mult sau mai puțin important, dar şi o evoluție specifică pe parcursul vieții legumelor şi fructelor (flavonoide, acizi fenolici, tocoferoli, acid ascorbic, carotenoizi etc). Antioxidanții tradițional studiați au fost vitaminele (C, E, provitamina A – carotenii). Mai recent au fost studiate şi proprietățile antioxidante ale flavonoizilor şi altor compuşi fenolici. Treptat s-a conturat ideea de evoluție a acestor valori, în funcție de stadiul de maturitate. La maturitatea de consum a fructelor colorate s-au realizat studii amănunțite privind conținutul în antocianine, flavanoli, proantocianidine, hidroxicinamați, β caroten, acid ascorbic şi tocoferoli. Se poate vorbi despre o activitate antioxidantă tipică fructelor pomacee, drupacee, arbuşti, nucifere, citrice, struguri, iar la legume, cruciferele din toate grupele tehnologice, urmate de rădăcinoase, bulboase etc. Legumele conțin totuşi niveluri mult mai scăzute de compuşi antioxidanți, remarcându-se doar ardeii graşi la maturiltatea fiziologică, varza de Bruxelles şi broccoli, alături de speciile bogate în vitaminele specifice.*

The interest for the antioxidizing activity manifesting at the horticultural products is an actual trend that has appeared gradually due to the nutrition studies and food security from the last decades (6, 9).The researchers' attention focused on some groups of specific compounds or some species with significant antioxidizing properties, some species more cultivated respectively, and consequently more available for the daily consumption (2, 8, 13). The main molecules that may have antioxidizing action are vitamin A (retinol), β carotene, vitamins of the B complex, vitamins C and E, coenzyme Q_{10} and the lipoic acid, beside some minerals component of enzymes with antiradical action (manganese, molybdenum, copper selenium, zinc), some vegetal pigments such as flavonols and chlorophyll, some amino acids etc. The more important antioxidizing components from fruits and vegetables are vitamins C and E, phenolic substances, flavonols and anthocyans. (11)

Antioxidants come in a wide range and an unequal capacity to manifest these properties, depending on numerous factors (species, cultivar, technologies of production and keeping, the capitalization channel etc). TAC (total antioxidizing capacity) constitutes a more and more studied characteristic.

Vrhovsek Urska and colab (2004) notice that the occidental diet includes a daily consumption of about 1 g poly-phenols, made from 2/3 flavonols and 1/3 phenolic acids. Poly-phenols from apples constitute the most important antioxidant exceeding vitamin C as importance. They affirm that a regular consumption of apples may ensure a significant part of the necessary poly-phenols especially from the category of flavonols and glycoside flavonols. A recent study estimates that in the American diet, apples are the main source of pro-anthocyanins. Andreotti C. and colab. (2006) notice the impressing diversity of the phenolic compounds associated to a considerable number of representatives (only flavonols are estimated at 6000 molecular forms). The interest caused does not refer only to the colouring properties (related to pigmentation) but also focus on their dietetic and even medicinal features since they reduce the incidence of some specific cancer forms or some cardiovascular diseases. Besides certain vitamins, fibres, phyto-estrogens, they are considered among the most important fruit antioxidants.

MATERIAL, METHOD AND RESULTS OBTAINED

Are published a series of analytical data referring to the chemical composition of the main wood fruits (7 species) harvested from the spontaneous flora of county Neamț (Romania), where one may also find determinations tightly correlated to their antioxidant properties.

The limits of the contents in phenolic compounds range between the maximal values of 0,636 g/100 g analyzed product (bilberries) and 0,071 g/100 g analyzed product (box thorn). Important values are also signaled for blackberries (0,471 g/100 g product) and the wild cherries (0,435 g/100 g product). As for the contents in anthocyans, expressed in g/100 g product, the variation limits range between 0,58 (bilberries) and 0,01 (sea-buckthorns). We generally notice the keeping of the size order from the contents in total phenolic compounds. There is only one exception; the wild cherries exceed the blackberries in terms of the contents in anthocyans situating themselves on the second place.

Table 1

Total contents in phenolic compounds for some species of wood fruits from county Neamț (Romania)

Species	Time of harvest	D 280	Total phenolic compounds (g/100 g fruits)
Bilberries	1-10.08	157.5	0.636
Blackberries	20-30.08	117.4	0.471
Wild cherries	20.06-10.07	107.5	0.435
Rose-hips	1-10.09	50.3	0.205
Raspberry	20.06-10.08	30.1	0.123
Sea-buckthorns	1-10.09	17.5	0.071

Blackberries largely contain a major pigment (cyanide 3 glycoside), in proportion of 90% from the total of anthocyans present in the fruit. In wild cherries, are three major characteristic pigments. Peonidine 3 rutinoside are in the largest proportion followed by cyanide 3 glycoside, and peonidine 3 glycoside is in the lowest quantity.In raspberry the major pigment is cyanide 3 sophorozide, in proportion of about 50%, cyanide 3 glycoside rutinoside and cyanide 3 rutinoside. For bilberries are more than 14 such pigments as different peaks, none of these being major. One of the most important is cyanide - 3 glycoside. (4)

Table 2

Total contents in anthocyans for some species of wood fruits from county Neamț (Romania)

Species	Time of harvest	Total phenolic compounds (g/100 g fruits)
Bilberries	1-10.08	0.58
Wild cherries	20.06-10.07	0.41
Blackberries	20-30.08	0.33
Rose-hips	1-10.09	0.12
Raspberry	20.06-10.08	0.09
Sea-buckthorns	1-10.09	0.01

For most species, the maximal and minimal values of the contents in vitamin C were relatively closed, except the sea-buckthorns samples where a single variant registered double values as compared to the average. The wild cherries and partially the raspberry registered a decrease of the contents within the one month interval. (5)

Table 3

Total contents in anthocyans for some species of wood fruits from county Neamț (Romania)

Species	Time of harvest	Ascorbic acid (vitamin C) (mg/100g fresh product)
Bilberries	I/August	45,10 - 61,12
Raspberry	III/ July	46,84 - 59,40
	I/August	38,92 - 51,75
Sea-buckthorns	I/ July	47,1 - 111,53, media 58,60
Wild strawberry	III/ July	*55,13*
Rose-hips	I/ July	51,07 - 53,69
Wild cherries	III/ June	34,51 - 37,14
	I/ July	21,14 - 29,54
Blackberries	III/ August	10 - 15

Their antioxidizing capacity of some diverse types of peaches and nectarines is influenced in a polyvalent manner by the cultivar, the interaction with the parental plant, the maturation time, the manner and period of keeping. The antioxidizing capacity of peaches expressed in μmol TE/g FW was between at 1for Stark Satume (PG) and 4,1 for Maria Dorata (NG). The total contents in poly-phenols (μg GA /g FW) was between 190 for Stark Satume (PG) and 930 for Maria Dorata (NG). By calculus they determined a correlation with R^2=0,9 between the antioxidizing capacity (FRAP) and the contents in poly-phenols. (11) Apricots are remarcable for their sensitiveness to enzymatic scald due to the oxidization of the phenolic compounds.

The appearance of the unwanted brown color also depreciates the sensorial/nutritive quality of the processed products. Is characterized and identified the main phenolic components of apricots: protocatechic acid (+ catechin), chlorogenic acid (- epi-catechin), naringine 7 glycoside/prunine, quercetin 3 glucoside, quercetin 3 rhamno-glucoside/rutin and campherol 3 rutinoside. The chlorogenic and neo-chlorogenic acids + catechin, - epi-catechin and rutin are major compounds among the apricot ply-phenols. On the other hand, the protocatechic acid, prunine and pro-cyanides B_2, B_3 and C_1 were for the fist time identified in apricots. (10)

Is studied the exceptional nutritive value of strawberries. Between 9 fruit species cultivated in Italy, the TEAC values (μmol TE/g FW) of the shrubs fruits stand out clearly as plus variants. The bilberries have the highest antioxidizing capacity (39 μmol TE/g FW), due to the high contents in anthocyanins. A remarkable antioxidizing capacity was also noticed for wild strawberries (33 μmol TE/g FW), and raspberry respectively (23 μmol TE/g FW), followed, as an average value, by strawberries (15 μmol TE/g FW). A relatively reduced potential (under 5 μmol TE/g FW) was registered by quinces, kiwi, apples, apricots and peaches. The indicators studied represent a genetic character constituting sometimes an average of parentals for TPH (mg GAE/g), but there are also cases of positive transgression. As for TEAC (mol TE/g FW), most times the values of the descending cultivars are superior to ascendants that served in melioration.

Is studied a number of 16 cultivars of strawberries representative for Europe highlighting the variability manifesting from case to case. The variants were placed in a growing order from Queen Elisa (TPH minimum, about 1,8 mg GAE/g) and up to Sveva (TPH maximum, about 3,1 mg GAE/g). We may not speak of a full concordance between the TPH values and the TEAC values, but the general trend indicates an approximate resemblance, at least for an important part of the variants. Thus, reduced values of TEAC were registered by Queen Elisa, whereas important values were signaled for the last 6 cultivars having high TPH values. We appreciate that the deviation from an ideal up going curve is ± 4 μmol TE/g FW. (3)

Is also investigated the quantity and activity of the poly-phenolic antioxidants from apples. For the immature apples, most of flavonols are made from monomers (epicatechin and catechin), as well as from dimer and trimer pro-antho-cyanides whereas in the next phase they have amore important polymerization degree (depending on the cultivar and tissue, between 5,7 and 7,1). The study focuses on 8 apple cultivars. They dosed 20 of the main monomers and oligomer pro-antho-cyanides, the ascorbic acid as well as the antioxidizing capacity of extracts. The total contents in poly-phenols were on average of about 110 mg/100 g FW (212 for Renette and only 66 for Fuji). Flavonols (catechins, dimer and oligomer pro-anthocyanides) confirm as the main class of apple poly-phenols. The oligomer pro-antho-cyanides varied between about 38,8 mg/100 g for Fuji and 162,2 mg /100 g for Renette. Pro-antho-cyanide B_2 oscillated between 5,6-19,3 mg/100 g, epicatechin between 5,2 and 18,4 mg/100 g and catechin between 0,5 and 4,3 mg/100 g. The study also refer to the hydroxy-cynamic acids (Renette 38,4 mg /100 g, but Granny Smith only 4,5 mg/100 g), flavonols (between 8 mg /100 g for Braeburn and 3,5 mg /100 g for Renette), de-hydro-calcones (between 15 mg /100 g for Renette and about 2 mg /100 g for most variants), anthocyans respectively (alomost 4 mg /100 g for Imperatore, and absent for Renette, Granny Smith and Golden Delicious). The ascorbic acid may be found in higher quantities at Golden Delicious and Braeburn (about 8 mg /100 g), and in very small quantities at Red Delicious and Royal Gala (0,5 ± 0,2 mg /100 g). The antioxidizing activity PRTE (Peroxyl Radical Trapping Efficiency) was determined by groups of cultivars (it is between 1,6 L/g for Renette and 0,5 L/g for Braeburn), and by groups of compounds (high effectiveness for quercetin and cyanide dilutions of 0,2 L/mg, and low for the remainder of compounds, dilutions under 0,05 L/mg). (12)

Others authors study has as subject 4 technological groups of peaches and nectarines represented by cultivars typical to the region (Redhaven yellow pulp peaches, white pulp Fidelia, nectarines yellow pulp Stark Red Gold and white pulp Silver Rome). Qualitatively, the phenolic profile of the variants seems almost homogenous, the chromatograms registered at 280 nm having relatively similar peaks. The cynamic acids are represented by two compounds (chlorogenic acid and neo-chlorogenic acid, with a maximum absorbance at 320 nm). Catechin and epicatechin have a maximum absorbance at 280 nm. Glycoside flavonols (between 2 and 4 peaks) and cyanides (especially cyanide 3 glucoside) specifically complete chromatograms.

Table 4

Average contents in phenolic substances (monomer forms, mg/g DW) for peaches and nectarines from Bologna – Italy (cf. Andreotti C. and colab. 2006)

Specification	Part of fruit	Stark Red Gold	Silver Rome	Redhaven	Fidelia
Catechin	skin	0,43	0,09	0,61	0,67
	pulp	0,11	0,19	0,18	0,2
Epicatechin	skin	0,15	0,39	0,15	0,1
	pulp	0,06	0,14	0,05	0,06
Pro-cyanide	skin	0,22	2,17	0,38	0,43
	pulp	0,06	1,01	0,15	0,16
Flavan 3-oli (total)	skin	0,8	2,66	1,13	1,19
	pulp	0,23	1,35	0,38	0,42

Table 5

Average contents in the main phenolic compounds (mg/g DW) for peaches and nectarines from Bologna – Italy (cf. Andreotti C. and colab. 2006)

Specification	Part of fruit	Stark Red Gold	Silver Rome	Redhaven	Fidelia
Neo-chlorogenic acid	skin	0,32	1,03	0,31	0,17
	pulp	0,21	0,8	0,25	0,25
Chlorogenic acid	skin	0,95	2,86	1,02	0,84
	pulp	0,3	0,97	0,31	0,12
Total of cynamic acids	skin	1,27	3,88	1,33	1,01
	pulp	0,51	1,82	0,56	0,36
Cyanide 3 glucoside	skin	0,38	0,83	0,36	0,35
Quercetin 3 rutinoside	skin	0,41	0,13	0,18	0,27

Other quercetins	skin	0,19	0,11	0,14	0,06
Total flavonols	skin	0,6	0,24	0,32	0,34

Quantitatively, there is a similitude between the contents in total poly-phenols from pulp (about 1 mg/g DW) and skin (about 3,5 mg/g DW) for 3 breeds (Stark Red Gold, Redhaven and Fidelia), whereas for Silver Rome the values are much higher (about 8 mg/g DW for skin and 3,5 mg/g DW for pulp). They draw the attention on the dietetic and antioxidizing importance of pulp for peaches and nectarines. (1)

Is determined the phenolic composition of 11 cultivars of apples, in epicarp and mesocarp and the phenolic contents. Are identified and measured several groups of phenolic compounds: pro-cyanides, hydroxyl-cinamats, acids, anthocyanins, flavonols and di-hydroxo-chalcones. Pro-cyanides were the most present group in pulp and skin contributing by 52%, and 44%, to the total phenolic index (TPI). The quercetin glucosides were found almost exclusively in skin whereas cyanide –3-galactoside was found only in the skin of the red apples.

The profile of the phenolic compounds for all the 11 genotypes presented differences and was more important in skin than pulp. Reinette russet registered the highest concentration in phenolic substances. The total phenolic contents (TPI/TPC) of extracts from pulp and skin correlated well to the antioxidizing capacity estimated by FRAP. The low contents in chlorogenic acid and the lack of total flavonols in the pulp may be associated to the genotype with the weakest concentration in phenolic substances with the lack of (enzymatic) scald as compared to other cultivars. (7)

REFERENCES

1. **Andreotti C. şi colab., 2006** – *Caraterizzatione del profilo fenolico di alcune pesche e nettarine.* Rev. Frutticoltura nr. 7-8
2. **Barberan, Th., Robins R. J. (edit), 1997**– *Phytochemistry of fruit and vegetables*. Oxford Science Publication
3. **Battino M. şi colab. 2004**– *Fragole e antiossidanti: un primato nutrizionale.* Rev. Frutticoltura nr. 4
4. **Beceanu, D. şi colab., 2003** - *Étude sur les caractéristiques chromatiques de quelques espèces de fruits sauvages provenus du département de Neamț*. Lucrări Ştiințifice U.S.A.M.V. Iasi, Seria Horticultură,vol. 46, Iaşi
5. **Beceanu D. şi colab., 2003** - *Études concernant la composition chimique de quelques fruits de bois récoltés de la flore spontanée du département de Neamț.* Lucrări Ştiințifice U.S.A.M.V. Iasi, Seria Horticultură, vol. 46, Iaşi
6. **Dejica D., 2001**– *Antioxidanți şi terapie antioxidantă*. Edit. Casa cărții de ştiință, Cluj Napoca
7. **Khanizadeh S şi colab., 2007** – *Phenolic composition and antioxidant activity of selected apple genotypes.* Rev. Journal of Food Agriculture et Environment, vol. 5/2007
8. **Mişcalencu D şi colab., 2005** – *Cancerizarea chimică şi substanțe anticancerigene din plante.* Edit. ICAR Bucureşti
9. **Picard Marie- Amelie, 2008**– *Alimentația preventivă împotriva cancerului*. Edit. Polirom, Iaşi
10. **Radi M. şi colab., 2004** -*Characterization and identification of some phenolic compounds in Apricot fruit (Prunus armeniaca L.).* Rev. Sciences des aliments nr. 24
11. **Scalzo Jessica şi colab., 2004**– *La capacita antiossidante di diverse tipologie di pesche e nettarine.* Rev. Frutticoltura nr. 7-8
12. **Vrhovsek Urska şi colab., 2004** – *Gli antiossidanti polifenolici nella mela: quantita ed attivita.* Rev. Frutticoltura nr. 11
13. **Watson R. R. (edit), 2001** – *Vegetables, fruits and herbs in healt promotion.* Edit. CRC Press