

ANTIOXIDANT AND CHROMATIC CHARACTERIZATION OF PHENOLIC CONTENT IN RED CABBAGE

CARACTERIZAREA ANTIOXIDANTĂ ȘI CROMATICĂ A CONȚINUTULUI FENOLIC DIN VARZA ROȘIE

PATRAȘ Antoanela^{1*}

*Corresponding author e-mail: apatras@uaiasi.ro

Abstract. Red cabbage is a widely consumed vegetable, with a high content of health-promoting compounds: minerals, vitamins, phenols and glucosinolates. The phenols group is very well represented and includes, among others, the anthocyanin pigments, which are responsible for the specific colour of red cabbage. The present research analyses the total and individual phenolic content (measured spectrophotometrically and, respective, by HPLC), the total and monomeric anthocyanins content, the chromatic parameters (colour density, polymeric colour, percent of polymeric colour, browning index, the CIELab colour parameters: lightness, green/red colour component, blue/yellow colour component, colour intensity, tone), the antioxidant activity, as well as the pH of an ethanolic red cabbage extract. The results revealed a high content of phenolic compounds and an important antioxidant activity. The main phenols identified are: gallic acid, ellagic acid, procyanidin B1, m-hydroxybenzoic acid, ferulic acid and protocatechuic acid. The results proved an important quantity of anthocyanins, of which 82.59% are monomeric. The values of polymeric colour, percent of polymeric colour and browning index confirm the preponderance of monomeric phenols in the studied red cabbage extract.

Key words: colour, antioxidant activity, anthocyanins

Rezumat. Varza roșie este o legumă consumată pe scară largă, cu un conținut ridicat de compuși benefici sănătății: minerale, vitamine, fenoli și glucozinoizi. Grupa fenolilor este foarte bine reprezentată și include, printre altele, pigmenții antocianici, care sunt responsabili pentru culoarea specifică a varzei roșii. Prezenta cercetare analizează conținutul fenolic total și individual (măsurat spectrofotometric și, respectiv, prin HPLC), conținutul de antociani totali și monomerici, parametrii cromatici (densitatea culorii, culoarea polimerică, procentul culorii polimerice, indicele de brunificare, parametrii de culoare CIELab: luminozitate, componentă de culoare verde/roșu, componentă de culoare albastru/galben, intensitatea culorii, tonul), activitatea antioxidantă, precum și pH-ul unui extract etanolic de varză roșie. Rezultatele au relevat un conținut ridicat de compuși fenolici și o activitate antioxidantă importantă. Principalii fenoli identificați sunt: acidul galic, acidul elagic, procianidina B1, acidul m-hidroxibenzoic, acidul ferulic și acidul protocatehic. Rezultatele au dovedit o cantitate importantă de antociani, din care 82,59% sunt monomeri. Valorile culorii polimerice, procentul culorii polimerice și indicele de brunificare confirmă preponderanța fenolilor monomerici în extractul de varză roșie studiat.

Cuvinte cheie: culoare, activitate antioxidantă, antociani

¹University of Agricultural Sciences and Veterinary Medicine Iasi, Romania

INTRODUCTION

Red cabbage (*Brassica oleracea* L., convar. *capitata* (L.) Alef, var. *rubra* DC) is a widespread variety of cruciferous vegetable. It is rich in bioactive compounds with antioxidant and health-promoting properties, which reduce the risk of cancer, cardiovascular and degenerative diseases (Cruz *et al.*, 2016; Jahangir *et al.*, 2009; Kristal and Lampe, 2002). The main bioactive compounds are phenolics and glucosinolates. Within phenol group can be mentioned flavonoids and non-flavonoids as phenolic acids, cinnamic acids, stilbenes. The profile of red cabbage's flavonoids is complex and a special importance have the anthocyanin pigments. Anthocyanins are responsible for the colour of fruits, vegetables and flowers, exhibiting different colours from nuances of red, to magenta, violet, or blue, depending on the physiological pH (Mazza and Miniati, 1993). The colours are due to the structure adopted by this heterocyclic compounds at various pHs, e.g. the flavylium cation (pH 1-3) is red, the quinonoidal base (pH 6-7) is violet, the anionic quinonoidal base (pH 7-8) is blue (Castaneda-Ovando *et al.*, 2009; Patras *et al.*, 1995).

The present research is analysing the red cabbage from the point of view of phenolic content, antioxidant activity and chromatic parameters.

MATERIAL AND METHOD

The studied red cabbage material is represented by the variety Red Dynasty F1, from a private producer. The extraction of phenolic compounds, with 60% ethanol, was performed for 30 min on water bath at 40 °C and was followed by filtration. The ratio mass of plant material/volume of solvent = 1 g/10 mL.

The dry weight was determined gravimetrically and the pH was measured with the WTW portable pH-meter 330i.

Total phenolic content, TPC, was analysed spectrophotometrically using Folin-Ciocalteu method, according to Ribereau-Gayon *et al.* (2006), and the result was expressed as mg gallic acid equivalents/100 g fresh weight (FW).

Total (TAC) and monomeric anthocyanins contents (MAC) were determined by pH-differential method, following the procedure presented by Giusti and Wrolstad (Giusti and Wrolstad, 2001) and expressed as mg cyanidin-3-glucoside/100 g FW.

The contents of individual phenols were measured by HPLC, following the procedure described by Cristea *et al.*, (2019), and expressed as mg/100 g FW.

CIELab colour parameters (lightness, clarity or luminosity, L*; green/red colour component, a*; blue/yellow colour component, b*; chroma or colour intensity, C*; tone or hue angle, H*) were determined according to the method OIV-MA-AS2-11 (2006).

Other measured chromatic parameters are: colour density (CD), polymeric colour (PC), percent of polymeric colour (PPC) and browning index (BI), which were analysed using the metabisulfite-bleaching method (Giusti and Wrolstad, 2001).

The antioxidant activity, AA, was measured by ABTS radical scavenging method (Re *et al.*, 1999) and expressed as μmol trolox equivalents/100 g FW.

All spectrophotometric analyses were performed using the Specord 200 Plus spectrophotometer.

The obtained results are means of 3 measurements of samples resulting from 3 different extractions.

RESULTS AND DISCUSSIONS

The dry weight of red cabbage was 8.19 ± 0.51 % and the pH of fresh extracts had an average value of 6.29 ± 0.03 .

Table 1 presents the total phenolics, total and monomeric anthocyanins contents, antioxidant activity and the main individual phenolics identified by HPLC analysis.

Table 1

Phenolic compounds (groups and individuals) and antioxidant activity of 100 g fresh red cabbage

phenolic compounds/ antioxidant activity	value
total phenolic content	194.30 ± 1.89
total anthocyanins	123.15 ± 3.70
monomeric anthocyanins	101.71 ± 2.55
gallic acid	36.21 ± 1.79
ellagic acid	28.7 ± 1.03
procyanidin B1	12.02 ± 0.93
m-hydroxybenzoic acid	2.09 ± 0.09
ferulic acid	1.99 ± 0.14
protocatechuic acid	1.58 ± 0.07
antioxidant activity	1092.78 ± 48.08

The results proved a high antioxidant activity (more than 1000 μmol trolox equivalents/100 g) of Red Dynasty F1 cabbage, comparable to the value obtained by Podsędek *et al.* in red cabbage cv. Koda, cultivated in the central region of Poland (1418 μmol trolox equivalents/100 g) (Podsędek *et al.*, 2014). The differences, apart from the cultivar and pedo-climatic conditions, may result from the fact that the methods of extraction and the used solvents are not identical.

The obtained content of total phenolics (194.3 mg GAE/100 g FW) is higher than the result of Marinova *et al.*, who obtained 139.3 mg GAE/100 g FW by analysing red cabbage from Bulgarian market (Marinova *et al.*, 2005).

The HPLC analysis showed important quantities of gallic acid, ellagic acid, procyanidin B1, m-hydroxybenzoic acid, ferulic and protocatechuic acids. The procyanidin B2, p-hydroxybenzoic, syringic, p-coumaric, salicylic, caffeic or sinapic acids, as well as cis- and trans-resveratrol, quercetin, morin and rutin were not identified in our samples (data not shown).

An important part of TPC is represented by the anthocyanin pigments, which are responsible for the specific colour of red cabbage. The obtained total anthocyanins content is 123.15 mg cyanidin-3-glucoside/100 g FW, of which 82.59% are monomeric anthocyanins (101.71 mg cyanidin-3-glucoside/100 g FW).

Table 2 presents the main chromatic parameters, including the CIELab colour parameters of the hydroethanolic extract of red cabbage with a pH of 6.29.

Table 2

Chromatic parameters of red cabbage extracts at pH 6.29

chromatic parameter	value
colour density	3.02±0.08
polymeric colour	0.19±0.005
percent of polymeric colour	6.31±0.21
browning index	0.0143±0.0004
lightness (luminosity, L*)	78.66±0.57
green/red colour component (a*)	18.69±0.53
blue/yellow colour component (b*)	-11.85±0.49
tone (hue angle, H*)	-1.36±0.03
chroma (colour intensity, C*)	22.13±0.70

The colour density (CD) is due especially to the concentration of pigments in solution. The obtained value (CD=3.02) is similar to the CD=2.86, obtained in other study (Patras, 2019) dealing with red cabbage waste extracts of same concentration (1 g plant material/10 mL hydroethanolic solvent), even if the concentration of the extraction solution was not 60% ethanol, as in the present study, and the plant material and all extraction procedure were different.

The small value obtained for the polymeric colour (PC=0.19) and the low percent of polymeric colour (PPC=6.31%) confirm that monomeric phenols are predominant in the studied extract, and not the polymerized ones (tannins) or brown compounds. The browning index (BI) is reflecting the content in brown compounds, and the very small value (BI=0.0143) prove the absence of products issued from enzymatic browning.

The analysed CIELab parameters of the red cabbage's hydroethanolic extract at pH 6.29 explain which, exactly, are the chromatic components of the observed magenta colour of the extract. It is known that at pH 6-7, the predominant form of the anthocyanins is the quinonoidal base, which has a violet colour. The lightness, clarity or luminosity of the extract (L*=78.66) is not far from white (which has L*=100, while L*=0 has the meaning of black). The green/red colour component, a*, prove the red nuances of the extract at pH 6.29, as it has a positive value (a*=18.69) and it is known, according to the International Commission on Illumination (Commission Internationale de l'Eclairage), that positive numbers indicate red shades, while negative indicate green shades (OIV-MA-AS2-11: R2006). The blue/yellow colour component, b* has a negative value (b*=-11.85), which indicates blue shades, while positive values of b* indicate yellow shades. The chroma or colour intensity, C*=22.13, shows a rather unsaturated colour, as it is closer to 0 (which reflects completely unsaturated colour) and not to 100 (which reflects pure colour). The hue angle, H*=-1.36, is expressed in radians in present study, and indicates the tone of the colour.

CONCLUSIONS

1. The present research revealed that the red cabbage has a high content of phenolic compounds and an important antioxidant activity.
2. The main phenols identified by the HPLC analysis are: gallic acid, ellagic acid, procyanidin B1, m-hydroxybenzoic acid, ferulic acid and protocatechuic acid.
3. An important quantity of anthocyanins, of which 82.59% are monomeric, was revealed.
4. The values of polymeric colour, percent of polymeric colour and browning index confirm the preponderance of monomeric phenols in the studied red cabbage extract and an insignificant quantity of brown compounds.
5. The CIELab colour parameters are a very useful instrument for the chromatic characterization of the anthocyanin containing extracts, as it is known that the colour of these pigments is highly influenced by the pH.

Acknowledgments: The author would like to thank the Francophone University Agency (AUF).

REFERENCES

1. **Castaneda-Ovando A., de Lourdes Pacheco-Hernandez M., Paez-Hernandez M. E., Rodriguez J. A., Galan-Vidal C. A., 2009** - *Chemical studies of anthocyanins: A review*. Food Chemistry, 113(4), p. 859–871.
2. **Cristea E., Sturza R., Jauragi P., Niculaua M., Ghendov-Moșanu A., Patras A., 2019** - *Influence of pH and ionic strength on the colour parameters and antioxidant properties of an ethanolic red grape marc extract*. Journal of Food Biochemistry, 43 (4):e12788.
3. **Cruz A. B., Pitz H. D. S., Veber B., Bini L. A., Maraschin M., Zeni A. L. B., 2016** - *Assessment of bioactive metabolites and hypolipidemic effect of polyphenolic-rich red cabbage extract*. Pharmaceutical Biology, 54(12), p. 3033-3039.
4. **Giusti M. M., Wrolstad R. E., 2001** - *Characterization and measurement of anthocyanins by UV-visible spectroscopy*. Current Protocols in Food Analytical Chemistry, F1.2.1–F1.2.13
5. **Jahangir M., Kim H. K., Choi Y. H., Verpoorte R., 2009** - *Health-affecting compounds in Brassicaceae*. Comprehensive Reviews in Food Science and Food Safety, 8(2), p. 31-43.
6. **Kristal A. R., Lampe J. W., 2002** - *Brassica vegetables and prostate cancer risk: a review of the epidemiological evidence*. Nutrition and cancer, 42(1), p. 1-9.
7. **Marinova D., Ribarova F., Atanassova M., 2005** - *Total phenolics and total flavonoids in Bulgarian fruits and vegetables*. Journal of the University of Chemical Technology and Metallurgy, 40(3), p. 255-260.
8. **Mazza G., Miniati E., 1993** - *Anthocyanins in fruits, vegetables, and grains*. CRC press, Chapters 10, 11
9. **Patras A., 2019** - *Stability and colour evaluation of red cabbage waste hydroethanolic extract in presence of different food additives or ingredients*. Food Chemistry, 275, p. 539-548.
10. **Patras A., Tibirna C., Cotea V., Odageriu Gh., 1995** - *Aspects concerning equilibrium kinetics of anthocyanins tautomer forms influenced by pH*. Scientific Papers

University of Agricultural Sciences and Veterinary Medicine of Iasi, Series Horticulture, 38, 254–259

11. **Podsedek A., Redzynia M., Klewicka E., Koziolkiewicz M., 2014** - *Matrix effects on the stability and antioxidant activity of red cabbage anthocyanins under simulated gastrointestinal digestion*. BioMed Research International, available on-line at: <https://www.hindawi.com/journals/bmri/2014/365738/>.
12. **Re R., Pellegrini N., Proteggente A., Pannala A., Yang M., Rice-Evans C., 1999** - *Antioxidant activity applying an improved ABTS radical cation decolorization assay*. Free Radical Biology and Medicine, 26(9), p. 1231–1237.
13. **Ribereau-Gayon P., Glories Y., Maujean A., Dubourdieu D., 2006** - *Handbook of enology: The chemistry of wine stabilization and treatments*, 2nd ed.; John Wiley and Sons Ltd.: Chichester, UK, Vol. 2, p. 171–174.
14. *****, 2013** - *Method OIV-MA-AS2-11: R2006, Determination of chromatic characteristics according to CIELab*. Compendium of International Methods of Wine and Must Analysis, International Organisation of Vine and Wine, Paris, Vol. 1