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ACRYLAMIDE CONTENT AND ANTIOXIDANT CAPACITY IN THERMALLY PROCESSED FRUIT PRODUCTS

Kristína Kukurová, Oana Emilia Constantin, Zuzana Dubová, Blanka Tobolková, Milan Suhaj, Zografia Nystazou, Gabriela Rapeanu, Zuzana Ciesarová

ABSTRACT

Acrylamide as a known processing contaminant was determined in various heat-treated plum products purchased from a local market using LC/ESI-MS-MS. The highest level of acrylamide in the range up to 60 µg/kg was detected in a plum stew known as a "povidla", and in prunes, respectively. These products typically undergo intensive heat treatment that may take from several hours to days. Using a fruit dehydrator in home production of prunes, a low level of acrylamide under LOQ (15 µg/kg) was detected in comparison to most commercial products. Only in one of the prune samples from the market was the acrylamide content near to LOQ. The highest content of acrylamide (46 µg/kg) was detected in the Slovak sample of prune originated in Nitra region. High acrylamide content, in the range from 23 to 45 µg/kg, was observed in prunes from South America. In the rest of analysed heat-treated plum products such as plum juice, plum compote or baby food with plum puree, acrylamide was not detected due to moderate conditions during thermal processing: temperature below 120 °C and a shorter time of thermal exposure. The total phenolic content and antioxidant capacity of prunes were analysed using a UV-VIS-NIR spectrophotometer and an electron paramagnetic resonance (EPR) spectroscopy. Home-prepared prunes were characterized by the highest content of phenolics (4780 mg GAE/kg) and antioxidant capacity (14.6 mmol TEAC/kg). Commercial samples of prunes reached phenolics in the range from 1619 to 3461 mg GAE /kg, and antioxidant capacity was observed between 6.1 and 12.1 mmol TEAC/kg. Antioxidant capacity of prunes strongly correlated with total phenolic content and yellow and red colours measured in a CIELab system. However, no significant correlation between the acrylamide and antioxidative or organoleptic properties of prunes was observed. Moreover, it was noticed that bio production of plums did not demonstrate any positive impact on final acrylamide content or antioxidant capacity in comparison to conventional technology.

Keywords: acrylamide; fruit; thermal processing; antioxidant capacity

INTRODUCTION

Thermal processing is frequently used in food manufacturing to obtain safe products with prolonged shelf-life and has a strong impact on the final quality of products. One of the purposes of thermal input is to improve the sensory properties, palatability and to extend the intensity of colour, tastes, aromas and textures of food. However, undesired effects due to various chemical reactions being Maillard reaction, caramelization and lipid oxidation are the most prominent **(Capuano and Fogliano, 2011)**. On the other hand, it is well known that some substances arising from the heating processes can play a positive role on human health. Many neo-formed compounds showing antioxidative, antimicrobial, antiallergenic effects or modulation activity in vitro have been observed **(van Boekel et. al., 2010)**. In addition to these positive effects, some detrimental consequences of thermal processes must be carefully evaluated, such as the loss of thermolabile compounds (vitamins, essential amino acids - lysine, tryptophan) or the formation of undesired tastes and off-flavours. Moreover, a major concern arising from heating processes comes from the formation of compounds that are not naturally present in foods, but which may develop during heating or preservation processes and which reveal harmful effects such as mutagenic, carcinogenic and cytotoxic effects known as neo-formed contaminants. Well-known examples of these compounds are heterocyclic amines, nitrosamines, polycyclic aromatic hydrocarbons **(Knize et al., 1999)** and recently discovered acrylamide with a high toxicological potential.

Acrylamide is formed during thermal processing of many types of foods. The highest acrylamide levels have been found in fried potato products, bakery wares and coffee **(Ciesarová, 2013)**. Acrylamide levels in food monitored between 2007 and 2010 have been compiled by the European Food Safety Authority (EFSA) in the Scientific Report **(EFSA, 2010 and 2012)**. On the basis of investigation results obtained during 2011 and 2012, and on the basis of the monitoring results obtained pursuant to Recommendations 2007/331/EC and 2010/307/EU, it was appropriate to modify certain indicative values provided for in the Annex to the Commission Recommendation 2013/647/EU. However, acrylamide has been found in food products other than those listed in the report of EFSA such as hazelnuts, almonds, olives or dried fruits **(Amrein et al., 2007)**. Due to a lack of relevant information in literature and databases, the presented study focused on acrylamide analysis in thermally processed plum products available on the local market and consequently in correlation with beneficial properties of thermally processed fruit such as total phenolic content and antioxidant capacity.

MATERIAL AND METHODOLOGY

Samples of various thermally processed fruit products produced from plum (*Prunus domestica*) were purchased from a local market in the Slovak Republic with focus on dried plums (prunes) and plum stew, moreover in juice, compote and baby food.

A total of 8 samples of prunes with various origin were analysed listed in detail in Tab. 1. Three samples of traditional plum stew known as *'povidla'* produced by different companies from the Czech Republic and the Slovak Republic (represents one sample with declared 5% content of apples), plum compote (halved, pitted, sterilized) produced in Hungary, plum juice with 25% of fruit juice content (from plum puree and plum juice concentrates) originated in Austria, two samples of baby food with various content of plums (80% plums, 20% apples) from the Czech Republic, and baby food originated from Hungary with 50% plum content and with declared bio-production and starch addition.

Samples were collected for acrylamide and colour analysis and further evaluations of total phenolic content and antioxidant capacity.

Acrylamide determination

Acrylamide (ACR) was extracted from samples into water and pre-extracted into ethylacetate with an internal standard D3-acrylamide addition according to **Bednáriková and Ciesarová (2012)** and **Ciesarová et al. (2009)**. Acrylamide was analysed by LC/ESI-MS-MS using an HPLC system 1200 Series (Agilent Technologies, USA) with positive electrospray ionization (ESI+) and mass spectrometer 6460 Triple Quad detection with LOQ of 15 µg/kg. The analytical separation was performed on Atlantis dC18 column (100 mm x 2.1 mm, 1.8 µm particle size; Waters, Milfor, MA, USA) using isocratic mixture of 1 % of methanol and 0.2 % of glacial acetic acid in water at flow rate 0.4 ml/min at ambient temperature.

Total phenolic content and antioxidant capacity

Prune sample was mixed with 50% ethanol (1 h, 200 rpm), centrifuged (10 000 rpm, 10 min, 20 °C) and appropriately diluted.

Total phenolic content in prune samples was determined by Folin-Ciocalteau method (**Singleton et al., 1999**) and expressed as an equivalent of gallic acid (GAE, mg/kg). UV-VIS-NIR spectrophotometer UV-3600 (Shimadzu, Japan) was used.

Antioxidant capacity was measured by an EPR spectroscopy and the results were expressed as Trolox equivalent using a standard solution of ABTS cation radical ($\text{TEAC}_{\text{ABTS}^{\bullet+}}$) according to **(Polovka et al., 2010)**.

Colorimetric Analysis

Measurement of product colour was carried out using a UV-3600 spectrophotometer (Shimadzu, Japan) in reflectance mode with 10° Observer, D65 Illuminant and wavelength range 380 – 780 nm. CIELAB parameters L^*, a^*, b^* were collected and a hue angle as an attribute of a visual sensation was calculated according to the formula

$$\mathbf{Hue} = \mathbf{tan^{-1}}\left(\frac{\mathbf{b}*}{\mathbf{a}*}\right)$$

Statistical Analysis

All results presented are means of three replicates along with standard deviations. Correlation coefficients were determined between colour parameters, antioxidant capacity, phenolic compounds and acrylamide content.

RESULTS AND DISCUSSION

Acrylamide content in thermally processed fruit products are not restricted till now by the law, however the European Commission have proposed an indicative value of acrylamide for baby foods of 50 µg/kg, and for products containing prunes of 80 µg/kg, respectively (**EC Recommendation, 2013**). In our study, acrylamide content below LOQ (<15 µg/kg) was detected in the products of plum juices, canned sterilised plum products and baby food in general. On the other hand, a significant content of acrylamide was detected in plum stew and prunes which were consequently subjected to further deeper study focused on an evaluation of beneficial properties and correlations with visual parameters measured in a CIELab system.

Acrylamide content in plum stew

The highest content of acrylamide was detected in traditional stew prepared from plums known in Czech, Slovak or Polish market as a *'povidla'*. This type of product produced by traditional technology is characterized with dark colour and a very thick consistency that is most suitable as a filling of dumplings. Traditional *'povidla'* is prepared by long term boiling without any addition of sugar or other additives from ripe fruits, harvested as late as possible, ideally after the first frosts, in order to ensure they contain enough sugar. For this moderate thermal treatment the authentic samples of plum stew were characterized by presence of acrylamide in concentration of 60 µg/kg ±5 µg/kg (data not shown). On the other hand, acrylamide content in the commercial sample of plum stew with declared 5% addition of apples was not detected.

Acrylamide content in prunes

Similarly to plum stew also prunes are typically processed by heat treatment, therefore in this type of plum products a significant acrylamide content was determined in concentrations comparable to plum stew. The drying process of prunes is intensive and slow, taking a long time to complete, up to 35 hours, depending on the drying conditions **(Sabarez, 2012)**.

Table 1 Acrylamide, total phenolic compounds, antioxidant capacity and colour evaluation of prune samples.

Origin	Production	Acrylamide content (μg/kg)	Antioxidant activity (mmol TEAC/kg)	Total phenolic content (mg GAE/kg)	L^*	a^*	b^*	Hue
Slovak Republic	Home	<LOQ	14.6 ±0.2	4780 ±76	-	-	-	-
Slovak Republic	Conv.	46 ±4	6.1 ±0.1	2599 ±34	69	3.6	3.2	41.5
France	Conv.	<LOQ	6.3 ±0.1	1997 ±12	72	3.0	2.4	39.1
Turkey	Conv.	19 ±3	11.5 ±0.3	3385 ±75	74	1.9	1.3	33.6
USA	Conv.	45 ±2	9.2 ±0.1	3461 ±14	71	4.2	4.7	48.2
Argentina	BIO	36 ±2	12.1 ±0.1	3426 ±21	68	4.6	4.8	46.4
USA	BIO	33 ±3	7.0 ±0.1	2503 ±34	64	2.8	1.2	23.4
Chile	Conv.	23 ±2	6.4 ±0.3	1619 ±45	73	3.4	3.0	40.9

Table 2 Correlation analysis.

Acrylamide content (μg/kg)	Antioxidant activity (mmol TEAC/kg)	Total phenolic content (mg GAE/kg)	*L**	*a**	*b**	*Hue*
1						
0.1431	1					
0.4816	**0.8388**	1				
0.5163	-0.2392	-0.2123	1			
-0.3471	**-0.7267**	-0.4777	-0.2667	1		
-0.2299	**-0.7458**	-0.5061	0.0253	**0.9442**	1	
0.0148	**-0.7686**	-0.5378	0.4037	**0.7533**	**0.9131**	1

Results of acrylamide analysis of a sample of prunes obtained from the local market and a sample of home-prepared prunes using a kitchen dehydrator are summarized in Table 1. The lowest acrylamide content was determined in domestically prepared prunes as well as in the product of European origin (France) in concentration near to LOQ (<15 μg/kg). The rest of prune products obtained from market contained acrylamide in the range from 19 μg/kg (Turkey) to 46 μg/kg (Slovakia, obtained from marketplace in Bratislava, produced in Nitra region). Samples from South America were characterized by an acrylamide content in the range from 23 to 45 μg/kg. Higher acrylamide content led to an assumption of more intensive heat treatment of raw material or other specific technological procedure. Moreover, in prunes declared with bio origin, the acrylamide content was 33 and 36 μg/kg, respectively. It can be concluded that bioproduction declared on the packaging did not result in lower acrylamide content.

Total phenolic content and antioxidant capacity of prunes and their correlations

Prunes contain naturally high levels of fibre and have been shown to have one of the highest antioxidant levels of the common fruits and vegetables **(Stacewicz-Sapuntzakis et al., 2001; Cantu-Jungles et al., 2014; Jarvis et al., 2015)**. Aforementioned beneficial properties of prunes expressed as antioxidant capacity and total phenolic content are summarized in Table 1. Home-prepared prunes were distinguished from commercial samples by the highest content of phenolics (4780 mg GAE/kg) as well as antioxidant capacity (14.6 mmol TEAC/kg). Commercial samples of prunes were low in both phenolics (from 1619 to 3461 mg GAE/kg) and antioxidant capacity (from 6.1 to 12.1 mmol TEAC/kg). Phenolics, commonly found in fruits, have been reported to exhibit antioxidant activity due to the reactivity of the phenol moiety, and have the ability to scavenge free radicals **(Donovan et al., 1998)**. A correlation analysis presented in Table 2 pointed out that antioxidant capacity of prunes strongly correlated with total phenolic content (a correlation coefficient 0.8388). However, acrylamide content as a potentially harmful compound was not correlated with health beneficial properties such as the total phenolic content or antioxidant capacity of products (correlation coefficient 0.4816 and 0.5163, respectively).

Colour of prunes and correlations with beneficial and health hazardous compounds

Colour of prune samples obtained from market varied in visual colour sensation expressed as a hue angle in the range from 23.4 to 48.2. The hue value parameter was in a good correlation with the antioxidant capacity of samples (a correlation coefficient -0.7686). On the basis of individual colour parameters measured in the CIElab system it was observed that antioxidant capacity correlated with redness (a^*) and yellowness (b^*) (correlation coefficients of -0.7267 and -0.7458, respectively), although not with colour saturation (L^*) (a correlation coefficient -0.2392).

On the other hand, statistical analysis presented in Table 2 did not show any significant correlations with neither acrylamide content nor colour of the product (a correlation of 0.0148 for hue angle), that excludes the possibility of a visual estimation of the risk of acrylamide formation in this type of product, which would be useful in practice.

CONCLUSION

The significant content of acrylamide was analysed in dried fruits from plums and plum stews in concentrations up to 60 µg/kg. Acrylamide content was not detected in thermally processed fruit products from plums, in sterilised canned plums, plum juice or baby food. Acrylamide, as a potentially harmful compound, was not correlated with health beneficial properties such as total phenolic content or antioxidant capacity of products.

REFERENCES

Amrein, T. M., Andres, L., Escher, F., Amadó, R. 2007. Occurrence of acrylamide in selected foods and mitigation options. *Food Additives and Contaminants*, vol. 24, suppl. 1, p. 13-25. http://dx.doi.org/10.1080/02652030701242558 PMid:17687696

Bednáriková, A., Ciesarová, Z. 2012. Validation of HPLC-ESI-MS-MS method for acrylamide determination in bakery products (Comparison of simple and improved electrospray ionization). *Chemické Listy*, vol. 106, p. 252-256.

Cantu-Jungles, T. M., Maria-Ferreira, D., da Silva, L. M., Baggio, C. H., de Paula Werner, M. F., Iacomini, M., Cipriani, T. R., Cordeiro, L. M. C. 2014. Polysaccharides from prunes: Gastroprotective activity and structural elucidation of bioactive pectins. *Food Chemistry*, vol. 146, p. 492-499.

Capuano, E., Fogliano, V. 2011. Acrylamide and 5-hydroxymethylfurfural (HMF): A review on metabolism, toxicity, occurrence in food and mitigation strategies. *LWT-Food Science and Technology*, vol. 44, p. 793-810. http://dx.doi.org/10.1016/j.lwt.2010.11.002

Ciesarová, Z., Kukurová, K., Bednáriková, A., Morales, F. J. 2009. Effect of heat treatment and dough formulation on the formation of Maillard reaction products in fine bakery products - benefits and weak points. *Journal of Food and Nutrition Research*, vol. 48, p. 20-30.

Ciesarová, Z. 2013. *The relevance of acrylamide in the food industry: Occurrence, exposure and impact of mitigation tools*. Pedreschi, F. P., Ciesarová, Z. Chemical Food Safety and Health. Nova Publishers, New York. 218 p. ISBN 978-1-62948-339-9

Commission Recommendation 2013/647/EU of 8 November 2013 on investigations into the levels of acrylamide in food. Official Journal of the European Union, L 301/15, 12.11.2013, 3 pp. 3.

Donovan, J. L., Mayer, A. S., Waterhouse, A. L. 1998. Phenolic composition and antioxidant activity of prunes and prune juice (*Prunus domestica*). *Journal of Agricultural and Food Chemistry*, vol. 46, no. 4, p. 1247-1252. [cit. 2015-01-15] Available at: http://pubs.acs.org/doi/abs/10.1021/jf970831x

European Food Safety Authority 2010. Results on acrylamide levels in food from monitoring years 2007-2008. *EFSA Journal* 98 (45) 1599, 2133, 31 p. 48.

European Food Safety Authority EFSA 2012. Scientific report of EFSA: Update on acrylamide levels in food from monitoring years 2007 to 2010. *EFSA Journal* 10 (10) 2938, 38 p. http://dx.doi.org/10.2903/j.efsa.2012.2938

Jarvis, N., O'Bryan, C. A., Ricke, S. C., Crandall, P G. 2015. The functionality of plum ingredients in meat products. A review. *Meat Science*, vol. 102, p. 41-48.

Knize, M. G., Salmon, C. P., Pais, P., Felton, J. S. 1999 *Food heating and the formation of heterocyclic aromatic amines and polycyclic aromatic hydrocarbon mutagens/carcinogens. Impact of processing on food safety*, New York: Springer, vol. 459, p. 179-193. http://dx.doi.org/10.1007/978-1-4615-4853-9_12 PMid:10335376

Polovka, M., Roth, M., Šťavíková, L., Karásek, P., Hohnová, B. 2010. Offline combination of Pressurized Fluid Extraction and Electron Paramagnetic Resonance Spectroscopy for the Antioxidant Activity of Grape Skins Extracts Assessment. *Journal of Chromatography*, vol. 1217, no. 51, p. 7990-8000. http://dx.doi.org/10.1016/j.chroma.2010.08.003 PMid:20810124

Sabarez, H. T. 2012. Computational modeling of the transport phenomena occurring during convective drying of prunes. *Journal of Food Engineering*, vol. 111, p. 279-288.

Singleton, V. L., Orhofer, R., Lamuela-Raventos, R. M. 1999. Analysis of total phenols and other oxidation substrates and antioxidants by means of Folin-Ciocalteu Reagent. *Methods Enzym*, vol. 299, p. 152-178. http://dx.doi.org/10.1016/S0076-6879(99)99017-1

Stacewicz-Sapuntzakis, M., Bowen, P. E., Hussain, E. A., Damayanti-Wood, B. I., Farnsworth, N. R. 2001. Chemical composition and potential health effects of prunes: A functional food? *Critical Reviews in Food Science and Nutrition*, vol. 41, p. 251-286.

Van Boekel, M., Fogliano, V., Pellegrini, N., Stanton, C., Scholz, G., Lalljie, S., Somoza, V., Knorr, D., Jasti, P. R.,Eisenbrand, G. 2010. A review on the beneficial aspects of food processing. *Mol. Nutr. Food Res.*, vol. 54, no. 9, p. 1215-1247. http://dx.doi.org/10.1002/mnfr.200900608 PMid:20725924

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Contact address:

Ing. Kristína Kukurová, PhD., National Agricultural and Food Centre, Food Research Institute, Priemyselná 4, 824 75 Bratislava, Slovakia, E-mail: kukurova@vup.sk

Ing. Zuzana Ciesarová, PhD., National Agricultural and Food Centre, Food Research Institute, Priemyselná 4, 824 75 Bratislava, Slovakia, E-mail: ciesarova@vup.sk

Ing. Zuzana Dubová, PhD., National Agricultural and Food Centre, Food Research Institute, Priemyselná 4, 824 75 Bratislava, Slovakia, E-mail: dubova@vup.sk

Ing. Blanka Tobolková, National Agricultural and Food Centre, Food Research Institute, Priemyselná 4, 824 75 Bratislava, Slovakia, E-mail: tobolkova@vup.sk

Ing. Milan Suhaj, PhD., National Agricultural and Food Centre, Food Research Institute, Priemyselná 4, 824 75 Bratislava, Slovakia, E-mail: suhaj@vup.sk

Oana Emilia Constantin, University Dunărea de Jos of Galaţi, Str. Domneasca 47, 800008 Galati, Romania, econstantin@ugal.ro

Prof. Gabriela Rapeanu, University Dunărea de Jos of Galaţi, Str. Domneasca 47, 800008 Galati, Romania, econstantin@ugal.ro, Gabriela.Rapeanu@ugal.ro

Zografia Nystazou, Aristotle University of Thessaloniki, University Campus, 54124 Thessaloniki, Greece, znystazo@gmail.com