Acta Univ. Sapientiae, Alimentaria, **2,** 2 (2009) 166–173

The effect of thermic treatment conditions on the amino acid composition of soybean and maize

É. Varga-Visi[1]
email: vargane.eva@ke.hu

Cs. Albert[2]
email:
albertcsilla@sapientia.siculorum.ro

Zs. Mándoki[1]
email: mandoki.zsolt@ke.hu

J. Csapó[1,2]
email: csapo.janos@ke.hu

[1]University of Kaposvár,
Faculty of Animal Science,
Guba S. u. 40, 7400 Kaposvár, Hungary

[2]Sapientia–Hungarian University of Transylvania,
Csíkszereda Campus, RO-530104, Libertatii 1., Miercurea-Ciuc

Abstract. Protein is one of the most valuable components of the fodder, therefore there is a concern preserving of these components in an available form during the different treatments wherein heating is applied. The aim of the research was to investigate the influence of toasting of fullfat soybean and air-drying of corn on the amino acid profile of the products. Dried corn was sampled at two Hungarian drying plants. The corn was dried with an industrial Bábolna B1-15 type gravitational drying tower.

The influence of toasting on two sorts of fullfat soybean products (hydrothermic soy coarse and "natural" hydrothermic soy) was investigated. Soybeans were heat processed with an industrial KAHL HR-1600

Key words and phrases: thermic treatment, soybean, corn, toasting, air-drying, amino acids

type hydrothermic reactor after cracking. The amino acid analysis of samples was carried out with amino acid analyzer, moreover amino acid enantiomers were quantified with a LaChrom type MERCK-Hitachi high performance liquid chromatograph.

The D-amino acid content of the samples before and after drying did not differ significantly, not even at the applied highest temperatures (100 °C drying air temperature and 40–45 °C kernel temperature).

Pressurized steam cooking of fullfat soy did not result in significant increase of the amount of D-enantiomers or the decrease of the concentration of the L-amino acids ($P>0.05$), while the trypsin inhibitor activity (TIA) was reduced to the required level (TIA<1.5 mg/g) and the results of the urease test (ΔpH<0.2) also verified the adequate intensity of the heat treatment.

1 Introduction

Processing steps can increase considerably the amount of D-amino acids, when they include heat treatment, alkaline treatment or fermentation [5, 6, 7]. Processes with heat treatment accelerate racemization, since higher temperatures result in increasing reaction rate of the racemization according to the Arrhenius equation. In case of a given production process a concrete experiment is required in order to decide whether the degree of the conversion into D-amino acids is considerable.

When feeding a crude soybean bean without heat treatment the fodder utilization can be reduced even by 20 to 30% in the case of the monogastric species and young ruminants, as the soya contains considerable amount of antinutritive substances (eg. protease inhibitors, lectins). Some of these loss their activity when high temperature is applied, so there is a chance to lessen the unfavourable effect. There are several thermal procedures to heat treat the soybean: extrusion, puffing-up, as well as toasting, when the soybean is cooked in the presence of water steam at 115–120 °C for 15–40 min [1]. Any of these treatments are used, the working parameters (temperature, moisture content, particle size, other physical effects) should be chosen so that the level of antinutritive substances is appropriately reduced without deterioration of the nutritive value of the protein [9].

In Hungary, among cereals maize is used in the highest amount for fodder-ing purpose. Maize needs to be dried in order to be stored safely. Drying of corn fodders is carried out by blowing-through of high temperature air, and in most of the agricultural plants so-called drying towers are used [4]. Inappropriate drying (overdrying) decreases the digestibility of the feeding stuff

proteins. Deterioration of the corn fodder during the drying can be avoided if the temperature of the drying air does not exceed 80–130 °C, and so the temperature of the seeds does not rise above 60–80 °C. If still overdrying occurs, digestibility of the proteins decreases, utilizability of amino acids reduces. To the highest degree the utilizability of lysine reduces which is especially harmful as to the nutritive value of maize, as in the zein the lysine is the primary limiting amino acid.

The effect of the above thermic treatments on the amino acid content has already been reported in a number of publications, however, according to our knowledge it has not been measured yet in what ratio the amino acids bound in proteins convert into D-amino acids during toasting of the soybean and drying of maize.

2 Material and methods

2.1 Conditions of the drying of maize and toasting of soybeans

The dried maize samples were taken partly at the drying plant of Agria Mezőgazdasági és Szolgáltató Szövetkezet (Agria Agricultural and Servicing Co-operative) in Szentgáloskér, partly at the drying plant of Kapostáj Mezőgazdasági Termelőszövetkezet (Kapostáj Agricultural Co-operative) in Zimány. Drying of the crops was performed at both sites with a Bábolna B1-15 dryer that is commonly used in Hungary. This equipment belongs to the group of the gravitational tower dryers, where the drying (and cooling, respectively) air touches indirectly the particles of the crop. On the border of the drying and the cooling zone there are sensors installed measuring the moisture content of the seeds, the corn temperature and the temperature of the drying air on both sides of the hot air channel (T_1, T_2) at a certaine height. Parameters read off from the displays during the drying and data measured in the collected samples at the Analytical Laboratory are shown in *Table 1.*

During the sampling, sample was taken from a given lot before drying, then from the dried maize continuously until the given lot exited the drier.

The hydrothermal treatment was carried out at the feeding stuff plant of Bóly Rt. (Bóly-Állomáspuszta) in Törökdomb. The whole soybeans stored in silos were carried through two rolling mills after cleaning, where the seeds were cracked into 9 to 12 pieces, then the material entered the toaster (KAHL HR-1600 hydrotermic reactor).

Table 1: Data of plant drying of maize

Conditions of drying		Place of sampling		
		Szentgáloskér	**Zimány (1)**	**Zimány (2)**
Values measured at drying				
Average temperature of the drying air (°C)				
	T_1	100	78	45
	T_2	100	83	39
Moisture content above the cooling zone (%)		20–21	13–14	12–13
Corn temperature (°C)		40–45	39–40	32–33
Values measured in the laboratory				
Moisture content before drying (%)		16.6	17.1	16.6
Moisture content after drying (%)		13.1	12.5	13.1

This autoclave with a mixing part cooks the soya in pressurized steam with an average residence time of 30 min at 120 °C. Due to the wet heat treatment most of the anti-digestive trypsin inhibitors present in the soybean becomes inactivated. During production in the first case the heat treatment is followed by milling with a hammer mill, and the product obtained is sold as "hydrothermal soya grits". In the case of the second product this last milling is omitted, and the soybean remains in cracked form, this is called "natural hydrothermic soya".

2.2 Chemical examinations

The chemical analysis of the samples were carried out at the Department of Chemistry and Biochemistry, University of Kaposvár, Faculty of Animal Science. Moisture content of the samples was determined according to the standard MSZ ISO 1442, and trypsin inhibitor activity of the soya products was determined according to the standard EN ISO 14902. In order to determine the amino acid enantiomers, after hydrolysis of the protein (6 M hydrochloric acid, 24 h, 105±1 °C) diastereomer pairs were formed from the D- and L-amino acids with o-phthaldialdehyde (OPA) and 1-thio-β-D-glucose tetraacetate (TATG) according to the method of Einarsson et al. [3], as well as Csapó et al. [2]. The analyses were performed using a MERCK-Hitachi LaChrom high-performance liquid chromatograph. The derivatives were separated on a Superspher 60 RP-8e column (125 mm×4 mm i.d.). Fluorescent signals of the diastereomers were measured (λ_{ex}: 325 nm, λ_{em}: 420 nm). The statistical evaluation was performed with SPSS for Windows 10.0 (1999) software.

3 Results

3.1 The effect of toasting on the D-amino acid content of the fullfat soya

L- and D-amino acid content of the untreated soybean as well as hydrothermally treated fullfat soybean products is shown in *Table 2.*

Table 2: Amino acid content (g/100 g dry matter) (n=5) and trypsin inhibitor activity (TIA) (n=3) of non-heat treated soya and toasted fullfat soya products

Amino acid g/100 g dry matter	Untreated soybean	Hydrothermal soya grits	Natural hydrothermic soya
L-Asp	3.90±0.10	4.20±0.70	4.10±0.20
D-Asp	0.55±0.04	0.62±0.11	0.65±0.04
L-Glu	6.60±0.20	7.00±1.30	7.10±0.50
D-Glu	0.11±0.03	0.12±0.02	0.12±0.01
L-Ser	1.68±0.05	1.76±0.36	1.78±0.13
D-Ser	0.13±0.01	0.13±0.03	0.13±0.01
L-Val	1.70±0.05	1.78±0.31	1.78±0.14
L-Met	0.25±0.04	0.26±0.04	0.28±0.03
L-Phe	1.81±0.07	1.89±0.37	1.92±0.13
D-Phe	0.08±0.02	0.08±0.01	0.09±0.01
L-Leu	2.70±0.06	2.79±0.59	2.79±0.26
D-Leu	0.27±0.01	0.26±0.06	0.26±0.03
L-Lys	1.56±0.14	1.62±0.43	1.60±0.12
D-Lys	0.03±0.01	0.03±0.01	0.04±0.01
TIA (mg/g)	17.2^{b}±0.5	1.1^{a}±0.2	1.2^{a}±0.3

Mean values without marks being in the same row do not differ (P<0.05).
^{ab} There is no difference between mean values marked with the same letters and being in the same row.

Because of the difference in the water content of the samples the analysis results are given on dry matter basis. D-amino acids found in the untreated control sample were formed probably during chemical preparation of the heat treated samples due to acidic hydrolysis of the proteins [8]. For the time being, according to our knowledge there is no chemical method available, using which this phenomenon could be excluded. If the mean values of D-amino acid content of samples taken before and after the heat treatment differ considerably,

this difference can be regarded as the increase of D-amino acids due to the heat treatment [10].

Practically no detectable change occured in the amount of either D- or L-amino acids due to cooking in the pressurized steam, whereas the activity of trypsin inhibitors reduced appropriately in both of the soya products due to the heat treatment *(Table 2).*

3.2 The effect of drying of the maize on the D-amino acid content

The amount of the examined D- and L-amino acids contained in the maize before and after the heat treatment can be found in *Table 3.*

Table 3: Amount of the examined L-and D-amino acids in the maize before and after drying (g/100g dry matter) (n=5)

Amino acid	Place of sampling					
	Szentgáloskér		Zimány (1)		Zimány (2)	
	Drying		Drying		Drying	
	before	after	before	after	before	after
L-Asp	0.66±0.05	0.68±0.03	0.64±0.04	0.65±0.01	0.70±0.04	070±0.03
D-Asp	0.079±0.006	0.081±0.004	0.077±0.005	0.079±0.002	0.095±0.005	0.093±0.006
L-Glu	1.70±0.10	1.74±0.08	1.86±0.11	1.85±0.07	1.81±0.13	1.89±0.10
D-Glu	0.026±0.002	0.027±0.001	0.030±0.003	0.030±0.001	0.031±0.002	0.032±0.002
L-Ser	0.48±0.03	0.49±0.02	0.50±0.03	0.49±0.03	0.49±0.03	0.49±0.02
D-Ser	0.040±0.008	0.043±0.009	0.034±0.01	0.039±0.01	0.068±0.008	0.065±0.007
L-Val	0.49±0.03	0.49±0.02	0.47±0.03	0.046±0.03	0.50±0.03	0.50±0.02
L-Met	0.04±0.005	0.04±0.003	0.04*±0.006	0.03*±0.002	0.04±0.005	0.05±0.01
L-Phe	0.44±0.03	0.45±0.02	0.49±0.03	0.48±0.02	0.47±0.03	0.49±0.02
D-Phe	0.26±0.01	0.23±0.02	0.17±0.02	0.16±0.04	0.21±0.02	0.21±0.02
L-Leu	1.11±0.05	1.11±0.04	1.28±0.08	1.23±0.09	1.14±0.08	1.22±0.06
D-Leu	0.10±0.03	0.11±0.008	0.15±0.01	0.14±0.02	0.16±0.01	0.16±0.008
L-Lys	0.30±0.05	0.32±0.02	0.30±0.03	0.27±0.06	0.29±0.04	0.29±0.02

Remark: Mean values marked with asterisk differ significantly ($P<0.05$).

In the samples taken before and after drying the amount of the examined D-amino acids did not differ significantly even in the case of drying at the highest temperature (100 °C air temperature, 40–45 °C corn temperature, sampling in Szentgáloskér), however, it should be kept in mind that what we measured was an average value which has importance for the practice. Layers lying closer to the surface of the seeds were exposed to a heat impact of higher degree than the inner parts, and also inside of the dryer there can be inhomogeneous

temperature distribution, so there can be centers with higher and lower heat burden.

In the amount of the measured L-amino acids there was no difference between the control and the heat-treated groups with one exception, in the second sampling (Zimány (1)) L-methionine content of the dried maize was a little lower than that of the untreated sample.

4 Summary

It can be said that the aim of the examined thermal procedures was accomplished without significant increase in the amount of D-amino acids. During toasting of the soybean the trypsin inhibitors were appropriately inactivated, and at the same time the L-amino acid content did not change. The moisture content decreased to the required level during the drying of maize without a considerable loss of amino acids.

5 Acknowledgements

Authors are grateful to the Sapientia Foundation, Institute of Research Programs for the financial support.

References

[1] L. Bódis, S. Manninger, *Fehérjegazdálkodás Magyarországon,* In: L. Babinszky (eds) Magyarország fehérjegazdálkodásának helyzete és fejlesztési stratégiája. Agroinform Kiadó, Budapest 2002. 45–91.

[2] J. Csapó, Zs. Csapó-Kiss, S. Einarsson, S. Folestad, A. Tivesten, Methods for determination of D-amino acid content of foods and feeds, *Acta Alimentaria,* 24 (1995) 125–126.

[3] S. Einarsson, S. Folestad, B. Josefsson, Separation of amino acid enantiomers using precolumn derivatization with o-phtalaldehyde and 2,3,4,6,-tetra-O-acetil-1-thio-β-glucopyranoside, *Journal of Liquid Chromatography,* 10 (1987) 1589–1598.

[4] P. Francsics, M. Parti, *Energiatakarékos szemestermény-szárítás,* Mezőgazdasági Kiadó, Budapest 1987.

[5] M. Friedman, *Formation, nutritional value, and safety of D-amino acids.* In Nutritional and toxicological consequences of food processing, Plenum Press, New York 1991. 447–481.

[6] K. Imai, T. Fukushima, T. Santa, H. Homma, K. Hamase, K. Sakai, M. Kato, Analytical chemistry and biochemistry of D-amino acids, *Biomedical Chromatography,* 10 (1996) 303–312.

[7] H. Man, J.L. Bada, Dietary D-amino acids, *Annual Review of Nutrition,* 7 (1987) 209–225.

[8] P.M. Masters, M. Friedman, *Amino acid racemization in alkali-treated food proteins - chemistry, toxicology, and nutritional consequences,* In: J.R. Whittaker, M. Fujimaki (eds) Chemical deterioration of proteins. Am. Chem. Soc., Washington DC, 1980. 165–194.

[9] S. Monary, *Fullfat soya handbook,* American Soybean Association, Brüsszel, Belgium. 1996.

[10] M. de Vrese, R. Frik, N. Roos, H. Hagemeister, Protein-bound D-amino acids, and to a lesser extent lysinoalanine, decrease true ileal protein digestibility in minipigs as determined with ^{15}N-labeling, *Journal of Nutrition,* 8 (2000) 2026–2031.

Received: August, 2009