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RELATION BETWEEN CHEMICAL STRUCTURE OF AMINO ACIDS AND THEIR THERMAL DECOMPOSITION
Analysis of the data by principal component analysis

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The influence of substituents on the thermal decomposition of monomeric organic compounds was studied. For this purpose the thermal destruction of dozen or so α-amino acids of the diversified chemical constitution, among others compounds containing the second amine group, additional carboxyl group, amino acids containing hydroxyl or sulfhydryl groups and amino acids connected with five-member heterocyclic ring or existing in the form of hydrates or hydrochlorides were investigated. The analyses were performed using a derivatograph in an air atmosphere, sample sizes were from 50 to 200 mg and heating rate from 3 to 15 K min^{-1}. It has been established that the thermal decomposition of studied compounds occurs in three stages. The temperature ranges, in which the analyzed compounds undergo thermal transformations were established. For evaluation of the thermoanalytical results an advanced multivariate data processing method, principal component analysis (PCA), was used. By this method the influence of the specific functional groups on the thermal decomposition of α-amino acids was determined. The stage of decomposition, in which the thermoanalytic data are the best correlated to the chemical constitution of the compound, is the second stage. It has also been recognized, that better discrimination among the analyzed compounds was obtained for the data set of the DTA.

Keywords: *α-amino acids, DTA, influence of chemical structure on thermal decomposition, principal component analysis, TG and DTG analyses, thermal decomposition*

Introduction

Thermal methods of analysis are widely used in the studies on the stability and thermal decomposition of drugs and substances of pharmaceutical interest [1–5]. The studies of monomeric organic compounds revealed that the differences in chemical structure of compounds are reflected in the shape of the DTA/DSC and TG curves of their thermal decomposition. The DTA analysis of β-lactam antibiotics, which points to the essential influence of the substituents at the β-lactam-thiazol arrangement on the thermal decomposition of I, II and III cephalosporine generation can be treated as an example [6]. Similar relations were observed in the case of sulfonamides [7, 8]. It was found that the stability of the sulfonamides containing heterocyclic substituents at the nitrogen atom of the basic structure of *p*-aminobenzenesulfonamides is different than for sulfonamides with the isothiocyanate group. Also behavior of the derivatives of benzoic acid is different during decomposition [9]. Principal component analysis used for interpretation of the thermal decomposition results for these compounds has revealed that destruction of the derivatives of benzoic acid depends on the kind of substituent and place of its localization in the benzene ring.

Taking all the above points into consideration, the aim of the present work is to testing the influence of the chemical structure of α-amino acids on their thermal decomposition. α-Amino acids, in which amine group is connected with carbon nearest to the carboxyl group considered as the main group, were chosen for the studies [10]. α-Amino acids of diverse chemical constitutions, among others containing the second amine group, which is at the end of the aliphatic chain, additional carboxyl group in the side chain and amino acids containing hydroxyl or sulfhydryl groups, were analyzed. Moreover, amino acids connected to a five-membered heterocyclic ring or which exist as hydrates or hydrochlorides were also used. The aim of the studies was achieved through determining of the thermal decomposition of the tested amino acids and definition with the use of an advanced multivariate data processing method, principal component analysis (PCA), the influence of chemical constitution of the tested compounds on their thermal decomposition course.

Experimental

Materials and methods

α-Amino acids used in the studies were as follows (manufacturers are given in the parentheses): *L*-glycine

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(**1**) (POCh, Gliwice, Poland); *L*-alanine (**2**), *L*-threonine (**4**), *L*-glutaminic acid (**5**), *L*-glutamine (**6**) and hydrate of *L*-histidine hydrochloride (**14**) (Reese and Beintema-Interpharm N. V., Rotterdam-Meppel, Holland); *L*-valine (**3**), hydrochloride of *L*-ornithine (**7**), hydrochloride of *L*-lysine (**9**), hydrate of *L*-cysteine hydrochloride (**11**), *L*-proline (**12**) and *L*-histidine (**13**) (Reanal, Budapest, Hungary); hydrate of *DL*-lysine (**8**) and *L*-cysteine (**10**) (Carl Roth KG, Karlsruhe, Germany).

DTA, TG and DTG curves of the thermal decomposition of each α-amino acid was carried out using an OD-103 derivatograph (MOM, Hungary). 100 mg samples were heated in an air, in a platinum crucible at a heating rate of 3, 5, 10 and 15 K min^{-1}. Additionally, 50 and 200 mg samples were heated at a heating rate of 5 K min^{-1}. As the reference material α-Al_2O_3 was employed. Each curve was recorded at least three times.

Each DTA curve consists of measuring the temperatures of the onset (T_i), completion (T_f) and peak maximum (T_p), and the temperature ranges of endo- and exothermic peaks (ΔT) in three consecutive stages of the thermal decomposition of tested compounds. In the case of the TG and DTG curves, the temperatures of onset (T_i) and completion (T_f) of the mass losses, the temperature ranges of reaction intervals (ΔT) and mass losses (Δm) for the second and third stage of decomposition were determined. Moreover, the temperatures of the DTG peaks (T_p) were also determined.

Calculations

Principal component analysis (PCA) was applied for interpretation of the results [11–14]. Starting point for calculations was matrix of the data X with dimensions n×p, where n – is a number of objects (rows) and p – is a number of variables (columns). In each matrix α-amino acids were used as the rows. Columns were the thermal parameters read from the DTA (T_i, T_f, T_p and ΔT), and the TG/DTG (T_i, T_f, ΔT, Δm and T_p) curves of thermal decompositions of the analyzed compounds.

Matrix X is at first standardized, then matrix R is calculated according to it. After further calculations, columns in matrices P and W were obtained, which were called principal components (PC). New matrix P reflects main relations among objects and makes possible classification of the tested compounds according to their chemical structure, whereas matrix W illustrates main relations among variables and enables selection of key thermal parameters, which make the best classification of the analyzed compounds.

For PCA calculations six matrices X were constructed – two for the DTA curves, two for the TG/DTG curves, and two for the connected results from the DTA, TG and DTG traces. The matrices for the first stage of decomposition have not been constructed, because this stage was not distinctly marked on the thermoanalytical curves. For the remaining stages, matrices consisted of 14 rows for the second stage of decomposition (all amino acids under analysis), and of 13 rows for the third stage (because III stage was not found during thermal analysis of *L*-valine). In contrary to the results obtained from the TG/DTG curves, matrices of which included 30 columns (6 weighed samples at four heating rates and for each weighed sample 5 parameters determined from the TG/DTG curves – T_i, T_f, ΔT, Δm and T_p), the matrices elaborated basing on data obtained from the DTA curves consisted of 24 columns (6 weighed samples at four heating rates and for each weighed sample 4 parameters from the DTA curves – T_i, T_f, T_p and ΔT). The matrices for the connected data sets obtained from the DTA, TG and DTG curves consisted of 54 columns.

Results and discussion

The structural formulas of the α-amino acids investigated are shown in the Fig. 1, and the data which characterize these compounds are listed in the Table 1. The analysis of melting points as well as the temperatures of sublimation and decomposition [15–17] has revealed that hydrochloride of *L*-ornithine (**7**) melts at the lowest temperature and then *L*-glutamine (**6**). They are characterized by melting points below 480 K. But remaining amino acids melt with simultaneous decomposition at above 480 K. In the accessible literature, no information about melting point of hydrate of *L*-cysteine hydrochloride (**11**) was found.

Results of the thermal decomposition of α-amino acids are compiled in the Table 2. Arabic digits in the first column denote numbers, by which the same α-amino acids compiled in the Table 1 were described. It was found that thermal decomposition of all tested compounds, excluding *L*-valine (**3**) occurs in three stages, as shown in the Fig. 2.

The first stage comprises the temperature ranges, in which the process connected with the alternation of chemical composition of the tested compounds does not occur. It is reflected by the lack of mass loss on the TG and DTG curves and by the high, narrow and sharp ended DTA peaks connected with first order phase transitions, most often melting, occurring at this stage for some compounds. The melting is connected with violent decomposition, starting the second stage of the thermal decomposition. The II stage is dependent on the chemical constitution of analyzed compounds. The intermediate products of the thermal decomposition, the chemical structure of which due to the multidirectional thermal destruction reaction of

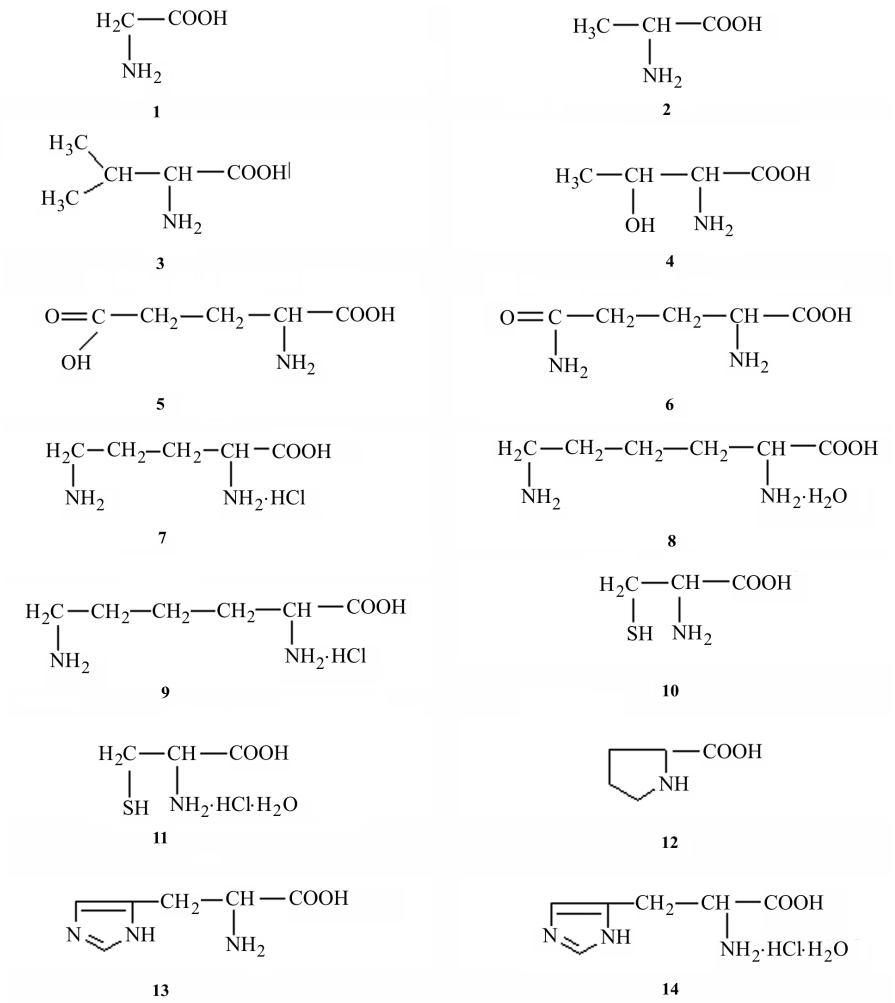

Fig. 1 Chemical structure of α-amino acids: *L*-glycine (**1**), *L*-alanine (**2**), *L*-valine (**3**), *L*-threonine (**4**), *L*-glutaminic acid (**5**), *L*-glutamine (**6**), hydrochloride of *L*-ornithine (**7**), hydrate of *DL*-lysine (**8**), hydrochloride of *L*-lysine (**9**), *L*-cysteine (**10**), hydrate of *L*-cysteine hydrochloride (**11**), *L*-proline (**12**), *L*-histidine (**13**), and hydrate of *L*-histidine hydrochloride (**14**)

the tested amino acids, are produced in this stage, is very difficult to be fixed.

In order to facilitate the thermograms interpretation, the second stage is divided into two substages – IIa and IIb. From analysis of data presented in the Table 2 and on the Fig. 2 it appears that the IIa substage reflects dozen or so per cent loss of mass, running slowly and in relatively wide range of temperatures. It precedes the IIb substage, which runs considerably faster, in the more narrow scope of temperatures and with several dozen per cent of the mass loss. The IIa substage reflects more often, the dehydration or hydrogen chloride release process, but in the IIb substage run the most important processes connected with decomposition of the tested compounds. In each of the substages, the endothermic effect on DTA curve commences the decomposition. The amino acids, in which decomposition of the IIa substage was not found, comprise the following – *L*-glycine (**1**), *L*-alanine (**2**), *L*-valine (**3**), *L*-threonine (**4**), *L*-cysteine (**10**), *L*-proline (**12**) and *L*-histidine (**13**) as well as hydrochlorides of *L*-ornithine (**7**) and of *L*-lysine (**9**).

After comparison of the referenced melting temperatures of studied amino acids presented in Table 1 with those in columns IIa and IIb of Table 2, being the results of their thermal decomposition, it has been observed that the decomposition of certain amino acids: hydrochloride of *L*-ornithine (**7**), hydrate of *DL*-lysine (**8**), hydrochloride of *L*-lysine (**9**) and hydrate of *L*-histidine hydrochloride (**14**) starts at temperature range which is a few tens and even over 100 degree lower than those included in the referenced data [15–17]. The reason for such outcome could be the fact that analyzed substances are hydrates or hydrochlorides. Considering the above, the process of decomposition will be preceded by the dehydration or hydrochloride release, and as the next in sequence the melting of the amino acid accompanied by violent decomposition. These two processes distort the crystalline structure of the mentioned amino acids and thus their melting process.

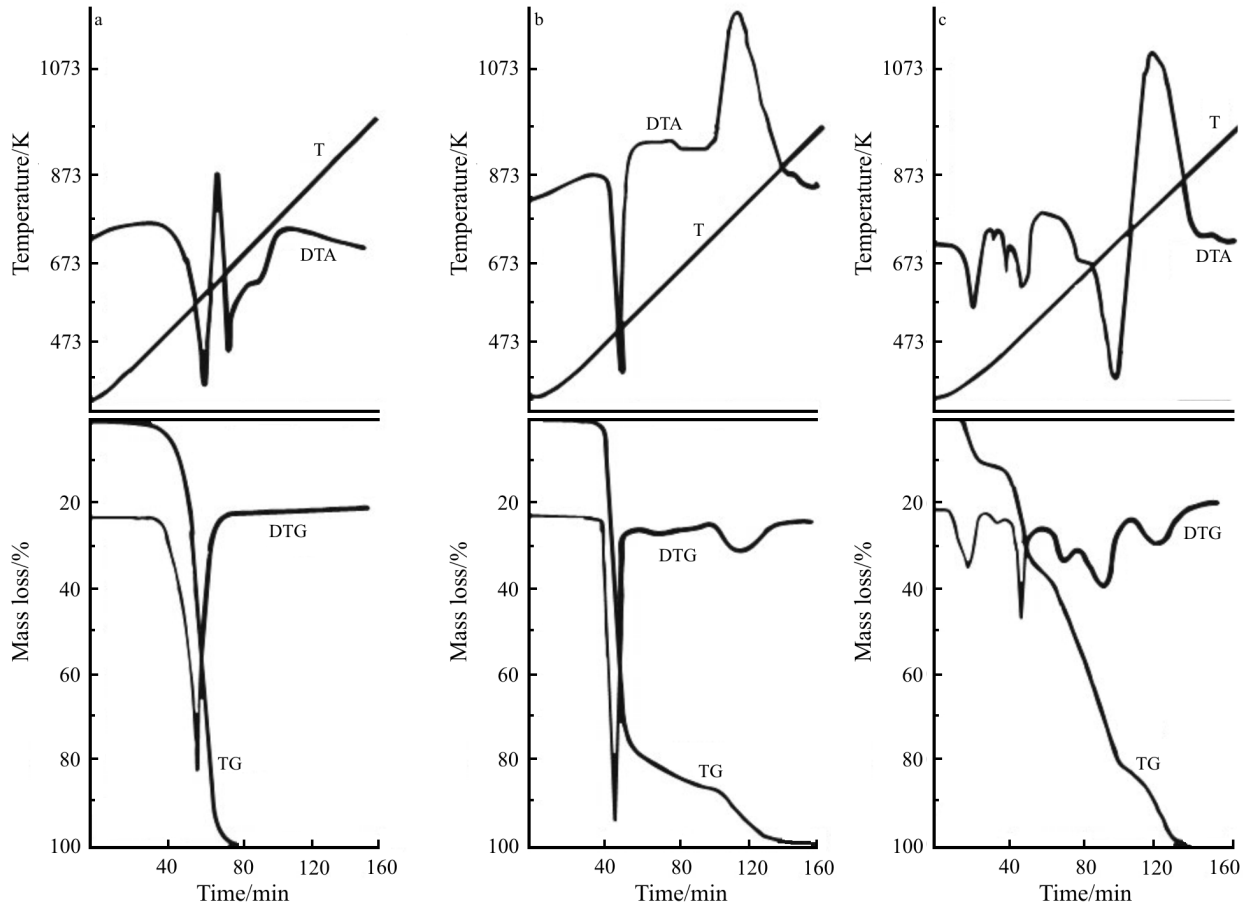

Fig. 2 DTA, TG and DTG curves of the thermal decomposition of: a – *L*-valine (**3**), b – *L*-cysteine (**10**) and c – hydrate of *DL*-lysine (**8**); 100 mg samples were heated at 5 K min^{-1} heating rate

Table 1 Chemical formulas, molecular masses and melting points of tested α-amino acids

Sample	Compound	Formula	Molar mass	Melting point/K
1	*L*-glycine	$C_2H_5NO_2$	75.07	535 D [15]; 513 D [16]
2	*L*-alanine	$C_3H_7NO_2$	89.10	570 D, S [15]; 587 D [16]
3	*L*-valine	$C_5H_{11}NO_2$	117.15	588 D, S [15]; 568–573 S [16]
4	*L*-threonine	$C_4H_9NO_3$	119.12	526 D [15]; 529 D [16]
5	*L*-glutaminic acid	$C_5H_9NO_4$	147.13	497–498 [15]; 520–522 D [16]; 478 D [10]; 473 D [17]
6	*L*-glutamine	$C_5H_{10}N_2O_3$	146.15	457–458 [15]; 458 D [16]
7	hydrochloride of *L*-ornithine	$C_5H_{12}N_2O_2{\cdot}HCl$	168.62	413 [15]; 518 D [16]
8	hydrate of *DL*-lysine	$C_6H_{14}N_2O_2{\cdot}H_2O$	164.21	498 D [15]
9	hydrochloride of *L*-lysine	$C_6H_{14}N_2O_2{\cdot}HCl$	182.64	99% – 536 D [16]
10	*L*-cysteine	$C_3H_7NO_2S$	121.16	97% – 493 D [16]; 99%>513 D [16]
11	hydrate of *L*-cysteine hydrochloride	$C_3H_7NO_2S{\cdot}HCl{\cdot}H_2O$	175.64	
12	*L*-proline	$C_5H_9NO_2$	115.13	493–495 [15]; 501 D [16]
13	*L*-histidine	$C_6H_9N_3O_2$	155.16	550 [15]; 555 D [16]
14	hydrate of *L*-histidine hydrochloride	$C_6H_9N_3O_2{\cdot}HCl{\cdot}H_2O$	209.63	527 D [16]

D – melting with decomposition; S – sublimation

Table 2 Results of the thermal decomposition of tested α-amino acids; 100 mg samples were heated at 5 K min^{-1} heating rate

Sample	Decomposition stages				
	Temperature range of DTA peak, ΔT/K; temperature of DTA peak, T_p/K Temperature range of decomposition stage, ΔT/K; temperature of DTG peak, T_p/K; mass loss in TG, Δm/%				
	substage IIa	substage IIb			stage III
1		478–533; 498 478–573; 503 (47.0)	533–638; 608 573–693; 623 (15.5)		638–888; 818 693–868; 808 (37.5)
2		488–588; 543 468–653; 543 (97.0)	588–733; 613		733–858; 763 653–828; 763 (3.0)
3		463–598; 563 413–628; 568 (100.0)			
4		498–543; 523 478–568; 518 (86.0)	543–663; 648 568–683; 613 (4.0)		663–893; 733 683–863; 793 (10.0)
5	438–498; 448 438–468; 453 (12.0)	498–703; 543 468–693; 553 (52.0)			703–923; 828 693–898; 843 (36.0)
6	398–478; 423; 438 403–468; 438 (13.0)	478–573; 513; 543 468–648; 548 (44.0)	573–668; 638		668–853; 788 648–838; 793 (43.0)
7		453–508; 483 423–738; 528 (76.0)	508–558; 538	558–738; 598	738–888; 818 738–873; 823 (24.0)
8	328–403; 348; 358 328–393; 358 (12.0)	403–533; 403; 428 393–518; 463 (24.0)	533–738; 673 518–613; 578 (18.0)	613–733; 673 (31.0)	738–873; 808 733–863; 798 (15.0)
9		498–553; 508 498–618; 533 (62.0)	508–598; 513 618–783; 708 (22.0)	598–703; 663	703–873; 828 783–853; 813 (16.0)
10		453–518; 473 438–533; 473 (78.0)	518–713; 653 533–698; 598 (8.0)		713–873; 758 698–858; 773 (14.0)
11	308–358; 318 298–408; 388 (10.0)	358–513; 428 408–518; 443 (55.5)	513–593; 578 518–613; 583 (15.5)		593–803; 658 613–828; 778 (19.0)
12		448–513; 458; 468 433–498; 463 (33.0)	513–698; 583; 683 498–663; 553 (61.0)		698–883; 738 663–843; 753 (6.0)
13		518–558; 523 493–558; 528 (25.0)	558–713; 633 558–663; 583 (13.0)		713–903; 833 663–888; 823 (62.0)
14	383–463; 413 388-463; 413 (10.0)	463–648; 498; 553 463–538; (13.0)	538–658; 563 (24.0)		648–903; 838 658–888; 828 (53.0)

In the third stage, the decomposition products are subjected to the final destruction connected with the total combustion of the coked organic residue. The total thermal effect of this stage is exothermic and is confirmed by the extensive peak on the DTA curve. The III stage was not found in case of the thermal decomposition of *L*-valine (**3**). This compound sublimes simultaneously with the decomposition. The substance and the decomposition products evaporate from the crucible in the narrow range of temperatures, in connection to this, the coked residue does not form, which would submit to combustion in the III stage of decomposition.

The thermal parameters determined on the basis of DTA, TG and DTG curves of decomposition of tested compounds were used for the PCA calculations. An analysis of the data compiled in Table 3, separately for the DTA curves and for the TG/DTG curves have revealed, that the first two main components PC1 and PC2 explain totally more than 70% variances, and eigenvalues of PC1 and PC2 are greater than unity. This creates sufficient condition for investigation on the relation between tested compounds in two-dimensional space, PC1 *vs*. PC2.

Dependence between the chemical structure of amino acids and results of the thermal decomposition of these substances in the second stage was presented graphically on the Figs 3a (results of the DTA analysis) and b (results of the TG/DTG analysis). After analysis of amino acids arrangement in two-dimensional space, it was found that in the similar range of PC1 and PC2 values, the compounds of the numbers **1** (*L*-glycine), **2** (*L*-alanine), **3** (*L*-valine) and **4** (*L*-threonine) are located. The common element connecting these substances is a fact that they are aliphatic α-amino acids containing the single group –COOH and the single group $–NH_2$ and they have not the heteroatoms. Also the compounds marked by the numbers **5** (*L*-glutaminic acid) and **6** (*L*-glutamine) lay in the similar range of the PC1 values, from –1.0 to –2.0 on the PCA diagram (data from the DTA curves) and from –0.5 to –1.0 on the PCA diagram (data from the TG/DTG

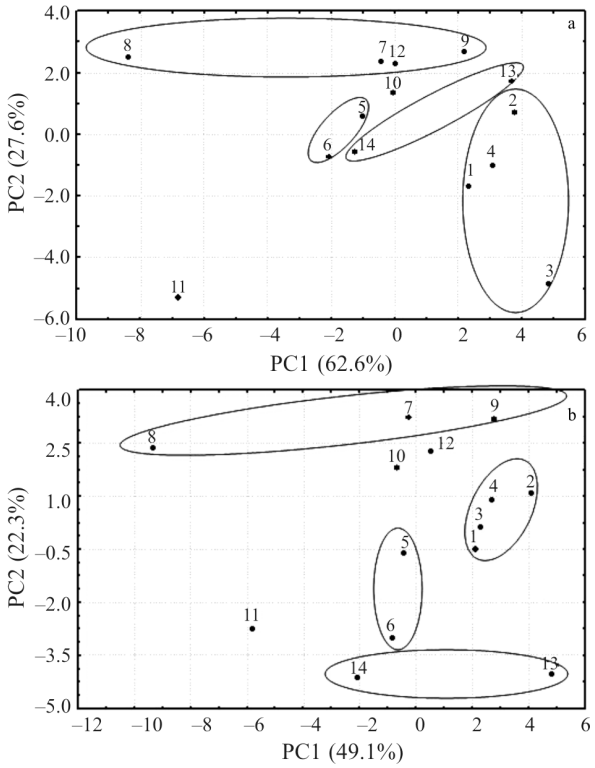

Fig. 3 Two-dimensional plot PC1 *vs.* PC2 for the second stage of the thermal decomposition of analyzed compounds based on the: a – DTA and b – TG/DTG data sets

curves). Their common feature is the presence of two carboxyl groups. The additional carboxyl group appears in *L*-glutamine (**6**) in form of amide.

In the very close values of PC2 also amino acids are located, marked by the numbers **7**, **8** and **9**. They contain additional amino group at the end of aliphatic chain, but *L*-ornithine (**7**) and *L*-lysine (**9**) are hydrochlorides and the compound **8** – is a hydrate of *DL*-lysine. In the case of analysis of the PCA diagram for the data determined from the DTA curves of the second stage of decomposition, in the similar range of PC2 values as for the above given three compounds, there is the compound of the number **12** (*L*-proline). This cannot be explained by the similarity of the chemical constitution, because *L*-proline has the cyclic structure and in position **1** there is a carboxyl group. However amino acids marked by the numbers **7** (hydrochloride of *L*-ornithine), **8** (hydrate of *DL*-lysine) and **9** (hydrochloride of *L*-lysine) are aliphatic compounds. In the similar range of PC2 values, also two compounds, *L*-histidine (**13**) and hydrate of *L*-histidine hydrochloride (**14**), are located.

In the third stage of amino acids decomposition, the single exothermic effect on the DTA curve is observed and also the mass loss occurs from several to several dozen per cent on the TG/DTG curves. Poor condition of the thermal processes occurring in this stage is reflected in the PCA results. From data contained in the Table 3 it appears that PC1 and PC2 for the III stage of decomposition explain totally only 70% variances (in the case of DTA analysis) and 72% (in the case of TG/DTG analysis).

The graphic interpretation of PCA results for the III stage of decomposition of amino acids was shown on the Fig. 4. It should be remembered, that the III stage of decomposition does not occur in the case of *L*-valine (**3**) and for this reason this amino acid was not taken into account in the PCA calculations.

From PCA analysis it appears that in case of data obtained from the DTA curves (Fig. 4a), aliphatic amino acids with single functional groups – amino and carboxyl group (**1**, **2** and **4**) are in the narrow range of PC1 and wide range of PC2. *L*-Glutaminic acid (**5**) and *L*-glutamine (**6**) having two carboxyl groups in the molecule are located in the range of similar PC1 and PC2 values. In the similar range of PC1 values from 1.5 to 3.0 there are amino acids with the numbers **7**, **8** and **9**, which at the end of carbon chain have the second group $–NH_2$. Also in the similar range of PC1 values the compounds of cyclic structure, *L*-histidine (**13**) and hydrochloride of *L*-histidine (**14**), are located.

In similar way it appears the spatial arrangement of amino acids obtained on the base of thermoanalytic data taken from the TG and DTG curves (Fig. 4b). In the similar way of PC1 and PC2 values are located the compounds with numbers **1**, **2** and **4**. However amino acids **5** and **6** are in the range very similar to PC1 val-

Table 3 Results of PCA calculations for the DTA and for the TG and DTG data sets of the studied compounds

Decomposition stage Thermoanalytical databases	PC1		PC2		PC3	
	Eigenvalues	Variances/%	Eigenvalues	Variances (cumulative variances)/%	Eigenvalues	Variances (cumulative variances)/%
II (DTA)	15.0	62.6	6.6	27.7 (90.3)	1.3	5.6 (95.9)
II (TG, DTG)	14.7	49.1	6.7	22.3 (71.4)	6.5	21.8 (93.2)
III (DTA)	10.9	45.3	6.0	24.9 (70.2)	2.6	10.7 (80.9)
III (TG, DTG)	13.1	43.8	8.5	28.4 (72.2)	3.0	10.1 (82.3)
II (DTA, TG, DTG)	29.3	54.2	12.4	23.0 (77.2)	6.8	12.6 (89.8)
III (DTA, TG, DTG)	20.8	38.5	15.1	28.0 (66.5)	5.4	10.0 (76.5)

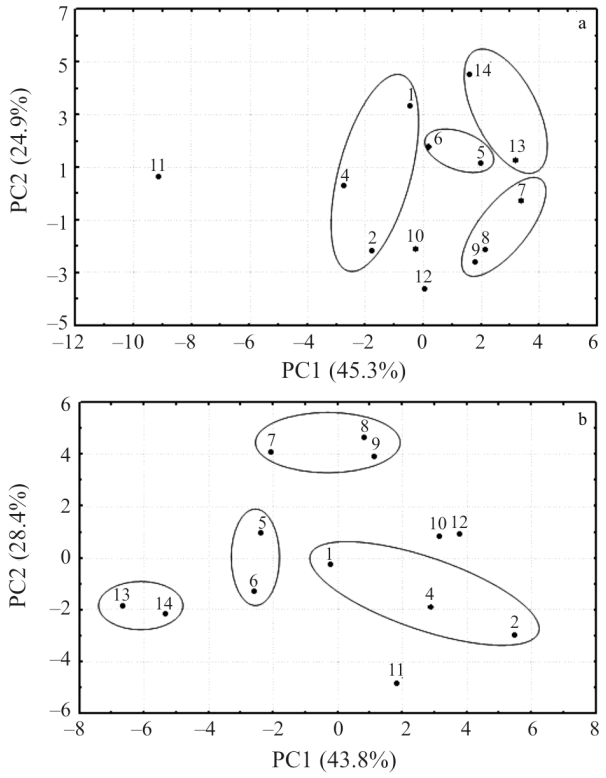

Fig. 4 Two-dimensional plot PC1 *vs*. PC2 for the third stage of the thermal decomposition of analyzed compounds based on the: a – DTA and b – TG/DTG data sets

ues. Then, at the very similar values PC2 from 3.6 to 4.6 lay the compounds marked by the numbers **7**, **8** and **9**. Two amino acids –13 and 14 are located also in the range of the similar PC2 values.

The matrices obtained by connection of the thermoanalytic data determined from the DTA curves with data obtained from the TG/DTG curves, were subjected to the PCA calculations. Also in this case, analysis of the PCA diagrams for the stages II and III of the thermal decomposition of amino acids, allows to find that the tested compounds are located dependently on their chemical constitution in the similar ranges of PC1 and PC2 values. Moreover, it was found that the addition of the two matrices resulted in lowering of the variances per cent explained by two, first main components. It means that PC1 and PC2 describe the relations between the compounds basing on the smaller number of results than in the case of the matrices considered separately.

Conclusions

The results of PCA calculations have revealed that the course of thermal decomposition of the tested amino acids depends on their chemical constitution. It is most profitable to consider this dependence in two-dimensional arrangement of PC1 *vs.* PC2. The two main components explain totally more than 70% of variances, in some cases, even more than 90%. The higher values of the variances are obtained for the matrices created on the basis of the DTA than on TG/DTG analyses, then the smallest values of the variances correspond with the calculations for the matrices including the joined DTA, TG and DTG results. The stage of decomposition, in which the thermoanalytic data are in the best correlation to the chemical constitution of the compound, is the second stage.

The important factor, which is the conclusive for the thermal decomposition of α-amino acids is also the character of the basic chemical structure (aliphatic, heterocyclic) and the presence of the functional groups and other substituents, as well as in the basic unit as in the side chain.

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