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Review article

SYNHESIS, SPECTROSCOPIC AND THERMAL CHARACTERIZATION OF *γ-L*-GLUTAMYLCYCLOHEXYLAMIDE

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Abstract

L-Glutamic acid is one of the most important amino acids, presents as a key intermediate in the biosynthesis of other amino acids by a transamination process, as a flavor-enhancing component for food and as an excitatory neurotransmitter in the vertebrate nervous system. *L*-Glutamylamide derivatives were also tested as a low-molecular weight organogelator and showed thixotropic property. Considering the important biochemical application of *L*-Glutamic acid and its derivatives, this paper presents a new route to obtain *γ-L*-glutamylcyclohexylamide. This derivative was synthesized by regioselective acylation of cyclohexyl amine using *N*-phthaloyl-*L*-glutamic anhydride, followed by hydrolysis of phthaloyl group with hydrazine hydrate. All of the obtained compounds were characterized via their spectral and thermogravimetric analysis. The identity of the ligand was confirmed by spectral analysis such as ^{1}H-NMR, ^{13}C-NMR and HRMS. The thermal stability of the *γ-L*-glutamylamide was discussed in the 20-800 °C temperature range. *γ-L*-glutamylamide decomposed in multistage, where some of the stages were weakly separated one from another. The *γ-L*-glutamylamide was completely pyrolyzed at 586 °C and the final product of the pyrolysis was ash.

Keywords: synthesis, *L*-glutamic acid, glutamylamides, structure, thermal behavior, spectra.

1. Introduction

L- Glutamic acid is one of the most important amino acids, and presents as a key intermediate in the biosynthesis of other amino acids as a transamination process, as a flavor-enhancing component for food, and as an excitatory neurotransmitter in the vertebrate nervous system. Diagnosis of some pancreatic and liver diseases [1] is based on the determination of enzymatic activity of γ-glutamyl transpeptidase (GGT).

Starting from these results, other glutamyl amides were tested for this purpose with satisfactory results [2,3]. Other glutamyl derivatives were tested [4,5] as a substrate for γ-Glutamylamine cyclotransferase (gGACT) or glutamate carboxypeptidase II (GCPII).

The amino acid derivatives have both amino and carboxyl functional groups, which exhibit excellent coordination capabilities [6,7]. *L*-Glutamyl amide derivatives were also tested as a low-molecular weight organogelator and showed thixotropic properties [8].

A theoretical study provides the amino acids including L-Glutamic acid or L-Glutamine and its derivatives as a chelating agent to remove metals cations such as Cd2+, Cu2+, Fe3+, Hg2+, Mn2+, Ni2+, and Zn2+. The removal can reduce the heavy metal pollution in water and soil environments [9].

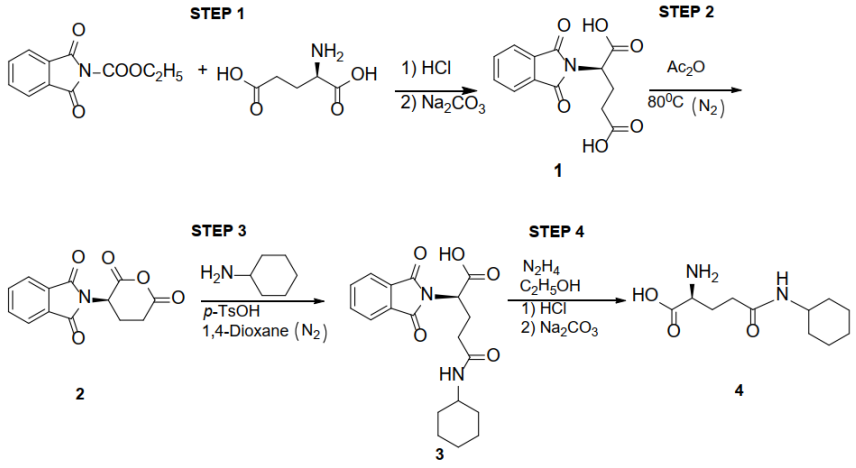
Considering the important biochemical application of L-Glutamic acid and its derivatives, this paper presents a new route for the synthesis of the γ-L-Cyclohexyl glutamyl amide, analog to the synthesis of other γ-L-Glutamyl amides that were reported [10]. The literature mentioned synthesis of this ligand from N-(Benzyloxycarbonyl)-L-Glutamic acid, Benzyl bromide, Dicyclohexylamine and Cyclohexylamine to another route with a 50% yield in the last step. After recrystallization from a 50% hot ethanol/water mixture overall yield was 27% [4,11]. We obtained the ligand with a 62% yield in the last step via a mild phthaloylation. The

new synthetic method of the ligand (**4**) is more advantageous, because after purifications, the overall yield increased to 41%.

2. Results and Discussion

2.1. The ligand synthesis: The ligand (**4**) *γ-L*-Cyclohexylglutamylamide, namely *(S)*-2-amino-5-(Cyclohexylamino)-5-oxopentanoic acid, was obtained in four steps, analog to the peptide synthesis, under mild conditions. A convenient method for the preparation of the *γ-L*-Glutamylamides consists of the use of the phthaloyl rest as an amino protective group in the first synthetic step (Scheme 1). In our previous research, we identified *N*-ethoxycarbonylphthalimide as an easy-to-use reagent, with good yields, in the protection stage. Our investigation has shown that, when *N*-protected amino acid (**1**) was treated with acetic anhydride by heating, under a nitrogen atmosphere, the phthaloyl-*L*-glutamic anhydride (**2**) was obtained as an activation form for the carboxylic group, in the second synthetic step. The third step consists of a condensation of the *N*-protected anhydride (**2**) with Cyclohexylamine, under nitrogen atmosphere, in 1,4-dioxane and *p*-toluenesulfonic acid as catalyst, to obtain the *N*-protected *L*-Glutamicamide. The first three steps were monitored by TLC in ethanol:acetone = 3:1 (*v*/*v*) (visualization under UV at λ = 245 nm).
After this, in the last step, we easily removed the phthaloyl group with hydrazine hydrate 100% in ethanol under reflux. The free amide (**4**) was obtained at pH 6-6.5 as a white solid. The process was monitored by TLC in 1-propanol: acetic acid: water = 8:1:1 and visualization by ninhydrin spray or I_2 vapors.

Scheme 1. Synthesis of *γ-L*-Cyclohexyl glutamyl amide (4) by phthaloylation method



The identity of the obtained product (**1**) was confirmed by analyzes such as: ^{1}H-NMR (figure 1a), ^{13}C-NMR (figure 1b) and HRMS spectrum (figure 1c). The ^{1}H-NMR spectrum for *N*-phthaloyl-*L*-glutamic acid (**1**) was recorded in DMSO-d_6 at 600 MHz. The one in region 12.03 ppm shows a broad signal which is characteristic of the protons of the two COOH groups, while the integration of this signal is usually difficult due to the high acidity of these protons ("proton exchange"). Then, in the region 7.85-7.93 ppm, it shows superimposed signals characteristic of the protons of the aromatic part, namely of the benzene ring with integral 4. In the region 4.80-4.84 ppm, a triplet signal is presented that is characteristic of the proton of the chiral carbon atom related to nitrogen (N) with an integral of 1. Finally, in the region 2.22-2.40 ppm, a multiplet signal from the protons of two methylene groups (CH_2) at positions 3 and 4, with a total integral of 4, is presented, with which the entire spectrum gives all expected signals according to the expected structure of the product **1**. In the ^{13}C-NMR spectrum recorded in normal mode, 9 carbon signals can be counted. Considering that three atoms of the aromatic ring are equivalent and two of the heterocyclic rings (the carbons of the carbonyl groups) are also equivalent, in summery these eight atoms will give only 4 signals, while the amino acid part has five more so

that the total is expected with it actually being nine signals. Afterwards, DEPT-^{13}C-NMR was also recorded, and according to the predicted structure, two pairs of aromatic carbons are connected by one hydrogen each and the chiral carbon as well, so that there should be three positive signals in total. If the DEPT-^{13}C-NMR spectrum (figure 1b) is well analyzed, indeed three positive signals will be observed at 135.23, 123.83 and 51.49 ppm, of which the two signals on the highest field are obviously from the aromatic carbons while the signal at 52.49 ppm is in the region of aliphatic carbons so that there is no doubt that it is derived from the chiral carbon. All other atoms should give 6 negative signals, of which three signals in the upper field from two carboxyl and carbonyl groups, one from two aromatic carbons (at 132.02 ppm) and two from aliphatic carbons (CH_2 groups), so a total of 6 signals. All these facts are completely consistent with the predicted structure of product (**1**). Finally, by recording the HRMS spectrum (ESI+) of *N*-phthaloyl-*L*-glutamic acid (**1**) its structure is confirmed, since it has the peak $[M+Na]^+$, as a molecular point, at the value of 300.0472 *m/z*.

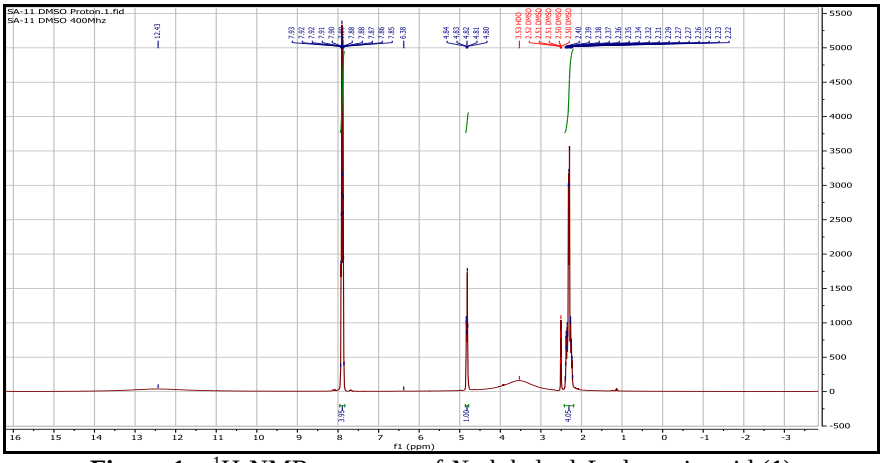


Figure 1a. ^{1}H-NMR spectrum of *N*-phthaloyl-*L*-glutamic acid (**1**)

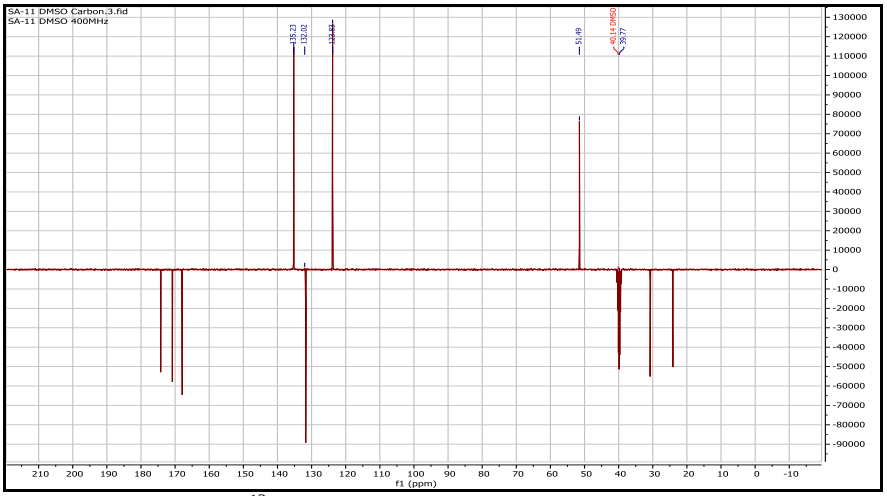


Figure 1b. DEPT-^{13}C-NMR spectrum of *N*-phthaloyl-*L*-glutamic acid (**1**)

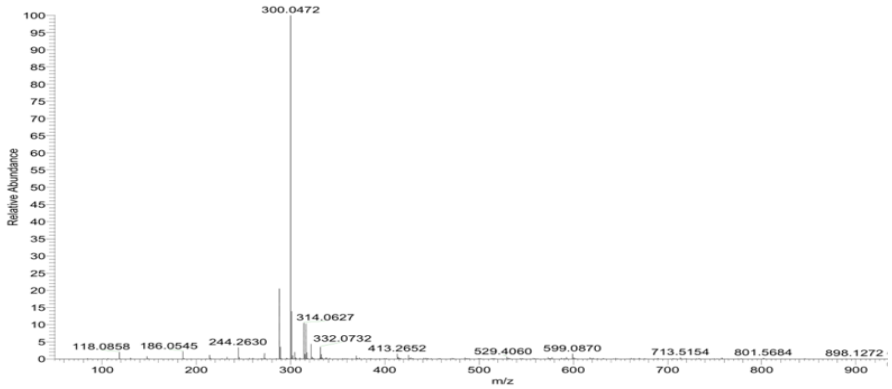


Figure 1c. HRMS spectrum of *N*-phthaloyl-*L*-glutamic acid (**1**)

After the full characterization of product **1**, this compound was used for the next step to protect the carboxylic groups. By treating *N*-phthaloyl-*L*-glutamic acid (**1**) with acetic anhydride at water bath temperature (100 °C), intramolecular anhydride (**2**) was obtained in practically quantitative yields and advanced optical purity. The identity of the obtained product (**2**) was confirmed by the spectroscopic means. The ^{1}H-NMR spectrum for *N*-phthaloyl-*L*-glutamic acid anhydride (**2**) was recorded in DMSO-*d6*, at 600 MHz. The one in the region from 7.90-7.81 ppm shows two doublet signals, characteristic for the protons of the aromatic part, namely of the benzene ring with integral 4. In the region 5.46-5.51 ppm, a signal from the single proton of the group -CH is presented, with an integral of 1. Since the structure is now cyclized, the two neighboring protons from the CH_2 group are not equivalent to give a triplet, but each will influence separately (in terms of spin-spin interaction) so that two doublets with a total integral of 1 and if the spectrum is well analyzed it will be noticed that there are actually two doublets with an integral of 1 in this region. Then, in the region from 1.91 to 3.17 ppm (characteristic region for aliphatic protons) four signals can be observed, each with integral 1, of four different protons of two methylene groups (CH_2). In the ^{13}C-NMR spectrum, 9 signals matching the proposed structure can be clearly identified. Since the ^{13}C-NMR spectrum is coupled with protons (DEPT-^{13}C-NMR), then three signals of doublets and 6 of singlets (or more precisely four singlets and 2 triplets) can be observed, which also fully matches the proposed structure. Finally, in the HRMS spectrum (ESI+) can be observed the main peak at the value of 282.0366 *m/z* which comes from the $[M+Na]^+$ clusters definitely confirming the presence of the *N*-phthaloyl-*L*-glutamic acid anhydride molecule (**2**).

N-phthaloyl-*L*-glutamic acid anhydride (**2**) is an acylating agent with moderate reactivity in the reaction with aromatic and heterocyclic amines. Condensation of *N*-phthaloyl-*L*-glutamic acid anhydride was carried out by cyclohexylamine, which reacted in high yields, without racemization of the chiral carbon atom, in an inert atmosphere (nitrogen), in 1,4-dioxane as solvent and acid *p*-toluenesulfonic acid as a catalyst, at a temperature of 100 °C. During the experimental work, in the third step, it was noticed that the obtained product (**3**) is not stable and quickly decomposed, which made the process of analysis and identification/spectroscopic characterization very difficult. Therefore, it was decided that immediately after isolation the product would be used for the next synthesis.

The last step of the synthesis is the removal of the amino-protecting group. Cleavage of the phthaloyl group was done under the action of hot hydrazine hydrate within 30-60 minutes in ethanolic solution (Scheme 1). When *N*-phthaloyl-*γ*-*L*-glutamylamide was treated with 1-2 equivalents of hydrazine hydrate, an ammonium salt was first formed, from which the amide was released by treatment with an acid or a base and reprecipitation of the compound at pHi.

Identity of the ligand **4** was confirmed by ^{1}H-NMR, ^{13}C-NMR and HRMS spectra (Figure 2a-c). The NMR spectra for the compound (**4**) were recorded in Acetic acid-d_4, at 600 MHz. The multisignals within 1.29-1.51 ppm range are assigned to five (axial) protons of the cyclohexyl rest. The overlapped signals within 1.72-2.01

ppm are assigned to the other five (equatorial) protons belonging also to the cyclohexyl rest. The signals at 2.40 ppm were assigned to protons H_3, at 2.71 ppm to protons H_4, at 3.79 ppm a triplet to proton H_2, at 4.23 ppm to proton H_6. In the ^{13}C-NMR spectra, both the presence of the signals of the compound and of the solvent can be identified. In the proposed structure 9 different carbons can be counted and exactly this is the number of the signals that were measured in the DEPT-^{13}C-NMR spectrum of *γ-L*-Cyclohexylglutamylamide (**4**). HRMS spectrum (ESI+) of *γ-L*-Cyclohexylglutamylamide (**4**) confirms the presence of the $[M+H]^+$ peak, as a molecular peak, at the value of 229.1557 *m/z* (Figure 2c).

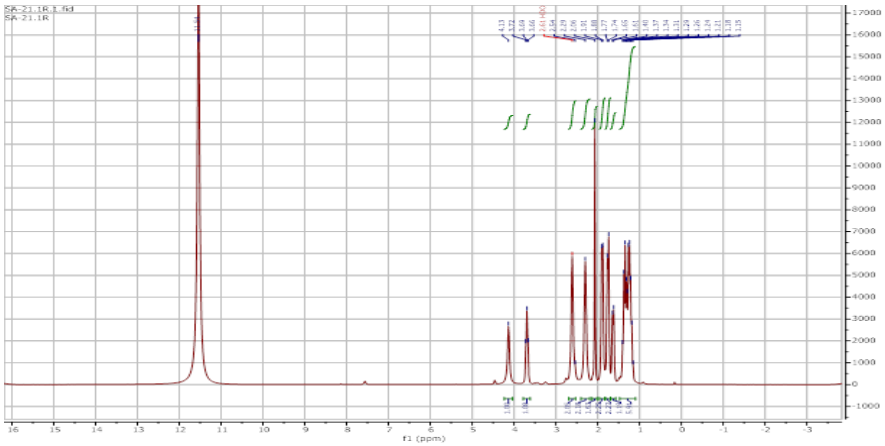


Figure 2a. ^{1}H-NMR spectrum of *γ-L*-Cyclohexylglutamylamide (**4**)

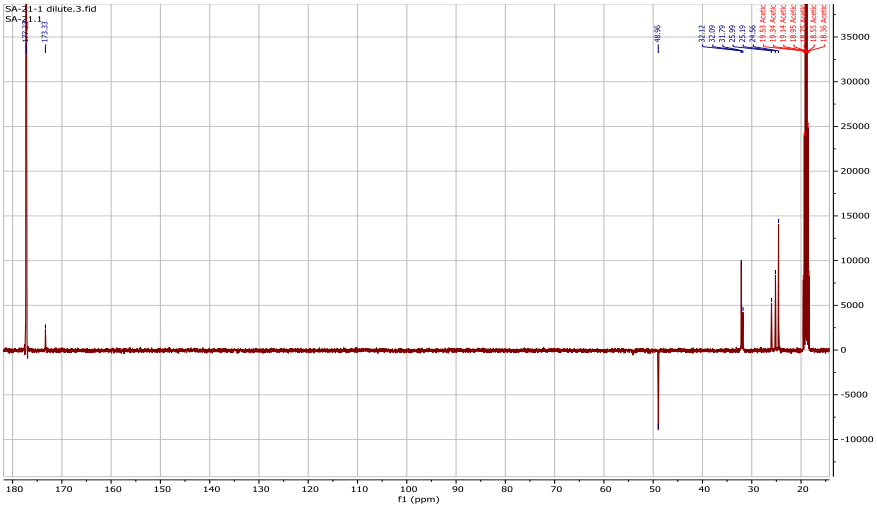


Figure 2b. DEPT-13C-NMR spectrum of *γ-L*-Cyclohexylglutamylamide (**4**)

2.2. Thermal investigation: The thermal decomposition of the ligand (**4**) was investigated using a TGA/DTA in an air atmosphere, in the temperature range of 20-800 °C. Thermal stability domains, decomposition phenomena, and assignments are summarized in Table 1 and Figure 3. For the ligand (**4**) in the temperature range of 20-200 °C two small endothermic peaks at 30 °C and 100 °C with a mass loss of 0.31%, respectively 0.91%, could be assigned to the loss of residual water present in the pores. This phenomenon could be explained by the general synthesis of the ligand from aqueous solution, but the thermogravimetric analysis indicated that the ligand (**4**) is anhydrous. Between 200-400 °C, a strong exothermic peak at 220 °C correspond to the melting, cleavage of the organic rest -$C_2H_4NO_2$, provided from the amino acid accompanied by oxidation

process. This violent burning process of organic rest is generally specific to compounds with a high nitrogen and oxygen content.

Another exo peak at 270 °C, probably corresponds to the split of the > C_3H_4O rest from the amidic bond. Finally, in the domain of 400-800 °C, an exothermic peak at 523 °C indicates the slowly pyrolysis of cyclohexyl rest. As can be noticed in Figure 4, the organic compound is completely pyrolyzed by 586 °C, and finally, some ash remains in the crucible.

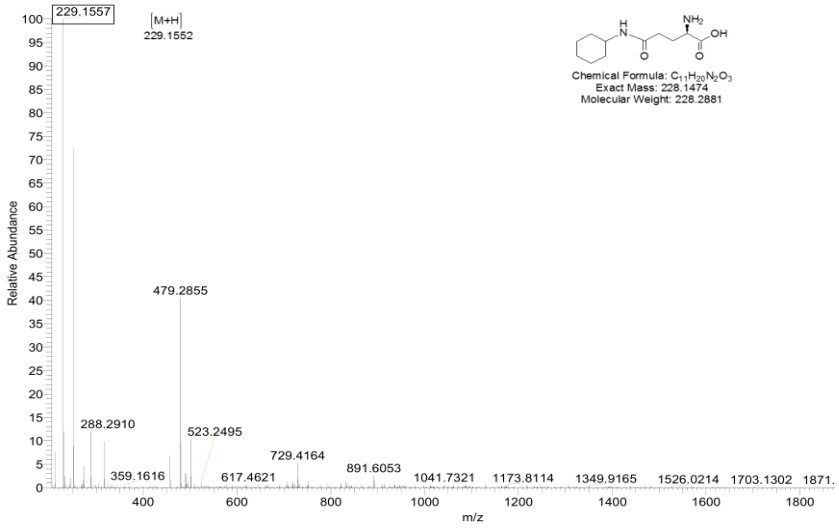


Figura 2c. HRMS spectrum (ESI) of *γ-L*-Cyclohexylglutamylamide (**4**)

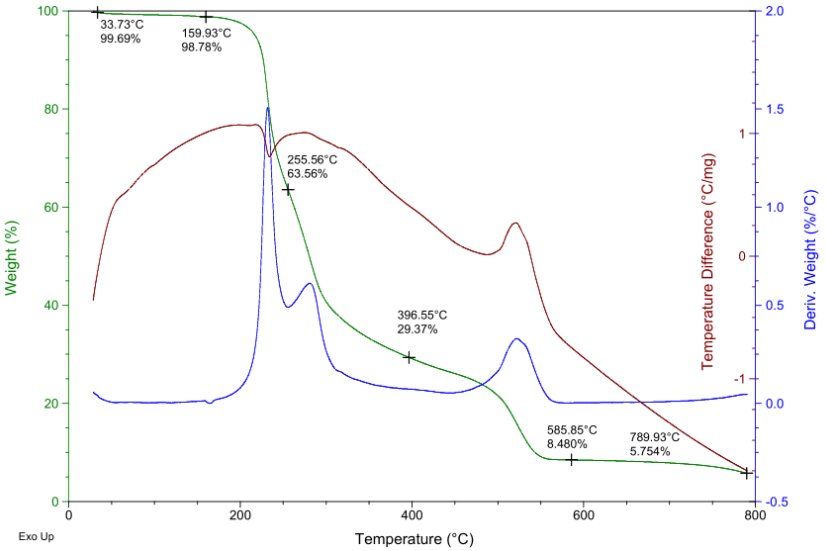


Figure 3. TG-DTG-DTA diagram for the ligand **4**

Table 3. Thermal analysis data of the ligand (**4**)

Compound	Temperature range (°C)	DTA peak (°C) ENDO	DTA peak (°C) EXO	Mass lossTG (%) Calc.	Mass lossTG (%) Exp.	Assignment
$C_{11}H_{20}N_2O_3$ (**4**)	**20-200**					
	20-34	30	-	-	0.31	-residual water present inside pores
	34-160	100	-	-	0.91	
	200-400					
	160-256	-	220	32.44	35.22	-melting, cleavage the -$C_2H_4NO_2$ rest, oxidation process
	256-397	-	270	36.35	34.19	-cleavage the > C_3H_4O rest
	400-800					
	397-790	-	523	31.21	23.62	-pyrolysis of organic rest
		-	-	-	5.75	

3. Experimental part

Materials and instrumentation

All reagents and chemicals were purchased from commercial sources and used as received. TLC monitoring was performed by using aluminum sheets with silica gel 60 F254 (Merck® (visualization in UV at λ = 254 nm; I_2 bath or ninhydrin spray). NMR spectra were recorded on Bruker® AM 600 instruments operating at 600 and 150 MHz for ^1H and ^{13}C nuclei, respectively. All chemical shifts (δ value) are given in ppm without TMS added. The chemical shifts were measured against the solvent residual peak. Elemental analyses were determined on Thermo Scientific Flash EA 1112 Elemental Analyzer. Melting points were measured on an ELECTROTHERMAL® instrument and were not corrected. Mass spectra were carried out on a LTQ ORBITRAP® XL (Thermo Scientific) instrument which was externally calibrated using the manufacturer's APCI or ESI(+) calibration mix. The samples were introduced into the spectrometer by direct infusion.
Thermogravimetry and differential thermal analysis (TG-DTG-DTA) curves were recorded with a Thermal Analyzer TA Instruments SDT Q600 V20.9 Build 20 on an interval of 20-800 °C, at a heating rate of 10 °C/min, in alumina crucibles and a dynamic air atmosphere.

Synthesis of N-phthaloyl-L-glutamic acid (1)

58 g (0.2 mol) of $Na_2CO_3 \cdot 10H_2O$ were measured and placed in a two-necked flask containing a thermometer and a magnetic stirrer. In parallel, 100 mL of H_2O were leveled and added to the flask, after a few minutes of mixing with a magnetic stirrer, the substance dissolved. After the solution had reached room temperature, 12 g (0.08 mol) of *L*-glutamic acid were added in portions under constant stirring. The mixture was cooled externally with ice to -5-0 °C and 25 g (0.11 mol) of *N*-carbethoxyphthalimide was added with stirring over 30 minutes. The reaction was continued for 30 min stirring at 24-28 °C, cooled again and the ethylurethane was removed by filtration. The remaining solution was acidified with 6N HCl to pH = 1.5-2, when an oily product was formed, which crystallized within a few hours in the cold, in the refrigerator. The formed product was filtered, washed with water until free of chlorine, dried for several days in air, then in a desiccator. The

purification was done by dissolving in Na_2CO_3 solution and reprecipitating with HCl. $C_{13}H_{11}NO_6$ (**1**), White solid; MW = 277.2295; Yield 89%, mp = 158-160 ℃ (Lit. [14]160 ℃); TLC analysis yielded a single spot (R_f = 0.49) (ethanol:acetone = 3 :1 (*v*/*v*) (visualization in UV at λ = 245 nm); Elemental Analysis (%) Calcd. (Found) C: 56.32 (56.18), H: 4.00 (4.19), N: 5.05 (5.38); ^{1}H-NMR (DMSO-d_6, 600MHz, δ /ppm: 12.03 (1H, from COOH group); 7.25- 7.92 (overlapped signals, 4H from aromatic rest); 5.31 (1H, s, NH); 2.71 (2H, m); 2.32 (2H, t); ^{13}C-NMR (DMSO, 150MHz, δ/ppm): 180.5; 177,1; 158.9; 137.2; 129.5; 117.8; 56.5; 41.4; 32.3. HRMS (*m/z*): 300.0643 $[M+Na]^+$.

Synthesis of N-phthaloyl-L-glutamic acid anhydride (2)

In a two-necked flask containing a reflux condenser in one mouth, a tube with $CaCl_2$ on it, and a thermometer in the other mouth, were added 40 mL of acetic anhydride and then 15 g (0.075 mol) of *N*-phthaloyl-α-glutamic acid were added. The mixture was refluxed in a water bath at 90 ℃ for 20-30 minutes. A solution was formed in which a slight opalescence (turbidity) appeared for a short time. The solution was left in the refrigerator for 2-3 hours when the reaction product formed in the form of shiny white crystals. The anhydride formed was filtered, washed with ether and dried in a desiccator over KOH for 4-5 days. $C_{13}H_9NO_5$ (**2**), White solid; MW = 259.2143; Yield 93%, mp = 198-200 ℃; (Lit. [14]199-201℃); TLC analysis yielded a single spot (R_f = 0.53) (ethanol:acetone = 3:1 (*v*/*v*) (visualization in UV at λ = 245 nm); Elemental Analysis (%) Calcd. (Found) C: 60.24 (60.13), H: 3.50 (3.78), N: 5.40 (5.82); ^{1}H-NMR (DMSO-d_6, 600MHz, δ/ppm): 7.99-7.81 (4H, m); 3.41 (2H, t); 3.17(1H, t); 2.96 (2H, m); ^{13}C-NMR (DMSO, 150MHz, δ/ppm): 167.2; 166.8; 135.3; 131.6; 123.9; 48.1; 29.9; 20.8. HRMS (*m/z*): 282.0366 $[M+Na]^+$.

Synthesis of N-phthaloyl-γ-L-glutamylcyclohexylamide (3)

A suspension consisting of 0.01 mol of *N*-phthaloyl-*L*-glutamic acid anhydride (**2**), 0.01 mol of cyclohexylamine and a few particles of *p*-toluenesulfonic catalyst in 35 mL of 1,4-dioxane was refluxed at 98-100 ℃ for 15 hours. The mixture was left overnight at room temperature, where the reaction product obtained was separated by filtration, washed with ether and dried.

Synthesis of γ-L-cyclohexylglutamylamide (4)

A suspension consisting of 0.007 mol of *N*-phthaloyl-*γ*-*L*-glutamylcyclohexylamide (**3**) in 30 mL of ethanol was treated with 0.7-0.8 mL of 100% hydrazine hydrate. The mixture was refluxed, with stirring, for 1 hour at 76-78 ℃ and left overnight at room temperature. The solvent was removed by rotavapor and 10 mL of 1N HCl was added to the residue, stirred with a magnetic stirrer for 1 h at room temperature, and the undissolved phthaloylhydrazide was filtered. The solution was treated with a 1M Na_2CO_3 aqueous solution at pH = 6 where *γ*-*L*-glutamylcyclohexylamide (**4**) was separated. The product was filtered, washed with water, acetone and ether and dried in a desiccator. $C_{11}H_{20}N_2O_3$ (**4**) White solid; MW = 228.2881; Yield: 62% (Overall yield 41%); mp. = 219-221 ℃; TLC analysis yielded a single spot (R_f = 0.53) (1-propanole:acetic acid:water = 8:1:1 (*v*/*v*) visualization with ninhydrin spray); Elemental Analysis (%) Calcd. (Found) C: 57.87 (57.13), H: 8.83 (8.11), N: 12.27 (11.93); HRMS (*m/z*): 229.1552 $[M+H]^+$; Exact Mass: 228.1474; ^{1}H-NMR (Acetic acid-d_4, 600MHz, δ(ppm)): 4.23 (s, 1H, H_6). 3.79 (t, J=8.2Hz, 1H, H_2); 2.71 (s, 2H, H_4); 2.40 (s, 2H, H_3); 1.72-2.01 (overlapped signals, 5H from cyclohexyl rest); 1.29-1.51 (m, 5H from cyclohexyl rest); ^{13}C-NMR (Acetic acid-d_4, 150MHz, δ(ppm)): C_1 overlapped with solvent (178.9) C_5 (175.1). C_6 (50.7); C_2 (33.9); C_7, C_{11} (33.8); C_4 (33.5); C_3 (27.7); C_8, C_{10} (26.9); C_9 (26.3). Thermal Analysis: 30 ℃ (Endo) (TGexp. = 0.31%); 100 ℃ (Endo) (TGexp = 0.91%); 220 ℃ (Exo) (TGcalcd. = 32.44%, TGexp. = 35.22%); 270 ℃ (Exo) (TGcalcd. = 36.35%, TGexp. = 34.19%); 523 ℃ (Exo) (TGcalcd. = 31.21%, TGexp. = 29.37%).

4. Conclusions

The *γ*-*L*-Cyclohexyl glutamylamide (**4**) has been alluded to in the literature but not *via* a mild phthaloylation [12-16]. For this purpose, the amide bond formation protocol was used, from the peptide synthesis, starting from an *N*-terminal amino acid. The overall yield beginning from *L*-Glutamic acid increased to 41% under this route compared to synthesis started from *N*-(Benzyloxycarbonyl)-*L*-Glutamic acid (overall yield 27% [14]). The identity of the compounds (**1-4**) was confirmed by elemental, spectral analysis and thermogravimetric studies. Mass spectra in high resolution were also recorded for all compounds (**1-4**), confirming the proposed structures

Elemental and thermal analysis leads to the idea that the organic compound could act as a bidentate ligand, thus coordination involving the carboxylate oxygen and the nitrogen atom belonging to the free amino group of the *L*-Glutamic acid rest.

During heating in air atmosphere in the 20-800 °C temperature range, the ligand decomposes in multistage, and some of the stages are weakly separated one from another.

The results are in good agreement with the corresponding formulas: $C_{13}H_{11}NO_6$ (**1**), $C_{13}H_9NO_5$ (**2**), $C_{19}H_{22}N_2O_5$ (**3**), $C_{11}H_{20}N_2O_3$(**4**).

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