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A THERMOCHEMICAL STUDY OF GAMMA IRRADIATED SERINE STEREOISOMERS

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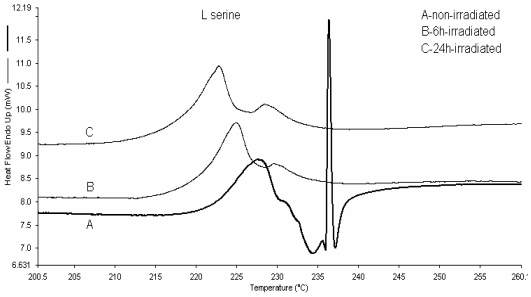
The behavior on heating of gamma irradiated L-, D-isomers and DL-racemic mixture of serine was investigated by means of differential scanning calorimetry (DSC). The results were compared with similar ones already obtained by us for the same non-irradiated compounds. The samples were irradiated at room temperature with gamma radiations using a ^{137} Cs source. The exposure doses ranged between 0.63-10 kGy. The transformation points (melting and decomposition) and the associated thermal effects were determined from the DSC curves in the temperature range between ambient to 350°C. The measurements have shown that after three compounds irradiation, the values of the melting/decomposition temperatures, enthalpies, heat capacities, weight loss and purity decrease. Fourier transform infrared spectroscopic studies were also made.



INTRODUCTION

The present paper is a continuation of the previous studies on the effect of γ rays upon some biological compounds such as aspartic acid isomers, monohydrated and anhydrous asparagine, amino butyric acid isomers and L-alanyl-glycine and carnosine.[1-6]

The use of ionizing radiations is one of the most promising methods for the sterilization of solid pharmaceuticals and foods. However, the radiosterilisation caused the appearance of new products which can induce a modification of the chemical structure and loss the biological activity of the materials.[7] Investigation of radiation effects on small biomolecules like amino acids would be helpful to understand the radiation effects on more complex biological system, such as proteins or even tissues and organisms.[8]

Amino acids are the building blocks of proteins and they exist as zwitterionic species in the crystalline state and in solution. When irradiated, radicals in a zwitterionic form can be formed and involved in many biological reactions.[9]

Serine is one of the naturally occurring proteinogenic amino acids. Only the L-stereoisomer appears in proteins. It is not essential to the human diet, since it is synthesized in the body from other metabolites including glycine. Serine is required for the metabolism of fat, tissue growth and the immune system as it assists in the production of immunoglobulins and antibodies. It is a constituent of brain proteins and nerve coverings and is also important in the formation of cell membranes.[10] Considering the use of serine as a stand-alone supplement or, more commonly, in combination amino acid supplements or as a natural moisturizing agent in many cosmetics and

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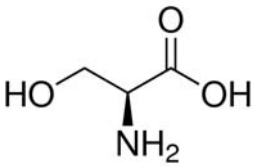
skin care preparations, products in whose preservation or sterilization the gamma radiations were often used, the understanding of chemical transformations caused by radiations is important.

Serine is like threonine one hydroxyl amino acid considered to be hydrophilic due to the hydrogen bonding capacity of the OH group.[11]

The thermal fragmentation of amino acids is a very complicated processes which involves many pathways such as: decarboxylation, decarbonylation, deamination, dehydration and condensation reactions, the extent of these reactions are dependent on structure.[12,13]

The aim of this contribution is highlighting the influence of gamma ionizing radiation on the serine isomers and racemic by tracking the variation of different properties obtained from thermal analysis methods. We watched the variation with dose rate of parameters associated with behavior on heating namely the temperatures and enthalpies of melting/decomposition heat capacities and the variation of the purity by DSC, the variation of the mass loss by TG. The results were compared to those for the same non-irradiated compounds, which have been the subject of a previous study.[14]

The structural formula of serine is:



Scheme 1 – The chemical structure of serine.

EXPERIMENTAL

1. Materials

L-, DL-, and D-serine studied in this work were obtained commercially from Sigma-Aldrich (DL- and D- isomers) mass fraction purities ≥98% and from Merck (L-serine) for biochemistry. The three compounds were used without further purification, but they were dried at 90^0C and preserved in a desiccator before use, in order to eliminate absorbed water.

2. Methods

Irradiation

A ^{137}Cs source with an activity of $3 \cdot 10^{13}$ Bq and a dose rate of $1.05 \cdot 10^2$ Gy h^{-1} was used for γ-irradiation of L, D and DL serine at room temperature. The exposure doses ranged between 0.63 and 10 kGy. The studied compounds were white fine crystallite powders prior to irradiation. No modification of the appearance of samples was observed after irradiation.

Differential scanning calorimetry

A Perkin Elmer power compensated DSC (model 8500) was used for the measurement of the enthalpies of the processes occurring during heating (fusion and decomposition). The calorimeter was calibrated with indium ($\Delta_{fus}H$ = 28.46 J g^{-1}). The areas of the peaks corresponding to the standard and studied substances were used to calibrate the instrument and calculate the thermal effects of the studied serines. The samples of about 1–2 mg of amino acid were sealed in standard aluminum pans. All samples were scanned in flowing nitrogen atmosphere (20 mL min^{-1}) from room temperature to a temperature exceeding the melting point. Three runs were performed for each isomer. The DSC experiments were done at a heating rate 10°C/min. and by using nitrogen with purity > 99.996% as carrier gas. The heat flow curves were processed with Pyris Software for Windows for calculating the thermal effects, namely melting/decomposition enthalpies, heat capacities and purity.

Thermogravimetry

The weight loss was measured using a TGA SETSYS EVOLUTION 17 instrument. The measurements were performed between ambient and 350^0C at a heating rate of 10^0C/min under argon flow using alumina crucibles.

Fourier transform infrared (FTIR) spectroscopic determinations

The IR spectra of serine isomers were recorded in solid state, at 298.15 K, in the wavenumber 625-4000 cm^{-1}, using Thermo Scientific Nicolet iS10 FT-IR spectrometer with an attenuated total reflection (ATR) method.

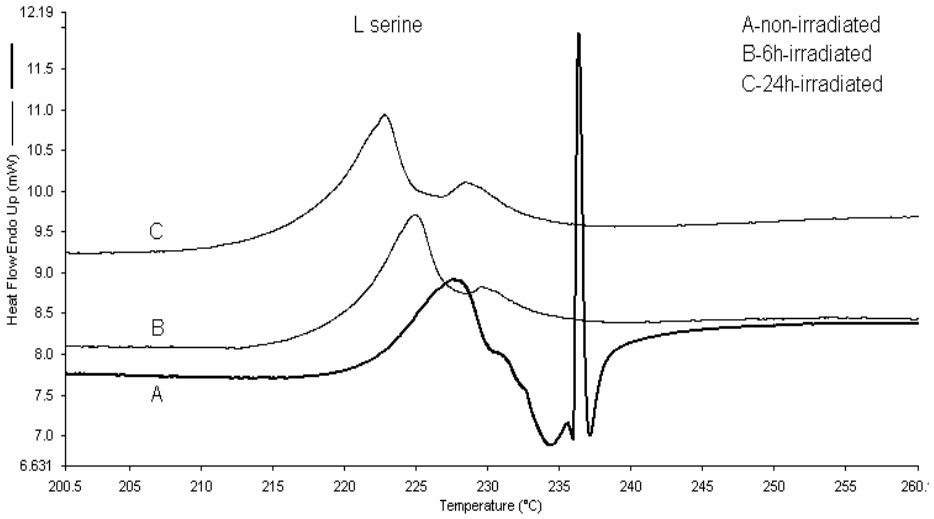
RESULTS AND DISCUSSION

Thermal analysis methods, namely DSC and thermogravimetry, were used to highlight the effect of irradiation on the studied compounds.

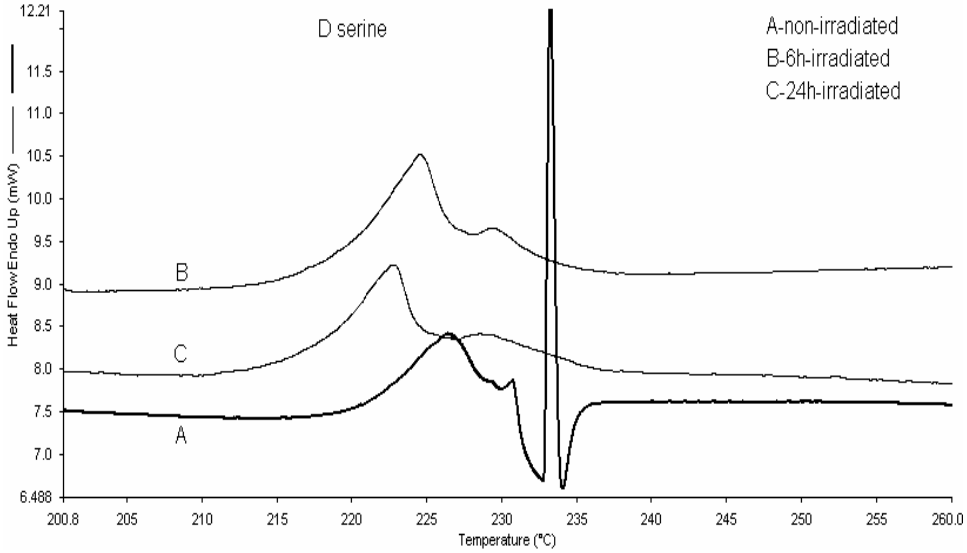
The recorded DSC curves of non-irradiated and irradiated L-, D-, DL-serine present the same thermal behavior[14] (Fig. 1) except that in the case of irradiated samples the recorded peaks are shifted towards lower temperatures with increasing irradiation dose (Fig. 1).

By analyzing the DSC curves one can observed that the three optical isomers have both similarities and differences regarding their thermal behavior. A similarity consists of the endothermic thermal effect for all three non-irradiated and irradiated isomers extending on a wide temperature range between 215-250°C.

The two endothermic effects from Fig. 1 are close to one another and are attributed to melting accompanied by decomposition. There are two main processes which belong to decomposition of the amino acids, namely: deamination and decarboxylation.



a)



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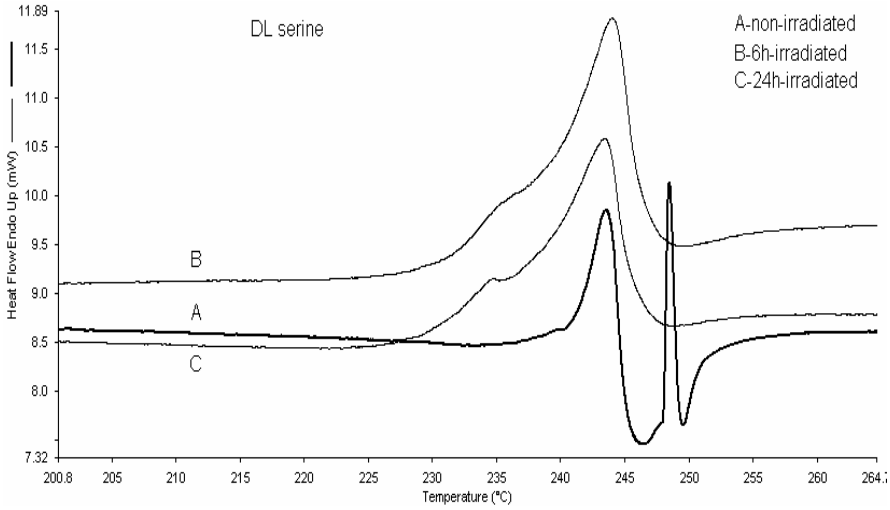


c)

Fig. 1 – a) The curves of L serine samples: non-irradiated (A) and irradiated: 6 h (0.63 kGy) (B), 24 h (2.52 kGy) (C); b) D serine samples: non-irradiated (A) and irradiated: 6 h (0.63 kGy) (B), 24 h (2.52 kGy) (C) and c) DL serine samples: non-irradiated (A) and irradiated: 6 h (0.63 kGy) (B), 24 h (2.52 kGy) (C).

Yablokov[15] have observed that the decomposition of serine yields only CO_2 and formation of volatile and liquid substances below its melting point which explains the registration of several endothermic processes as in the case of our recorded curves.

The temperatures of the onset ($t_{onset,}$°C) and peaks maxima (t_{max1}, t_{max2},°C) were determined, as well as the enthalpy of the recorded processes (ΔH), for each isomer.

In Fig. 2 are shown the variation of the first peak maxima temperature (t_{max1}, °C) (a) and second peak maxima temperature (t_{max2}, °C) (b) versus irradiation dose for the three isomers of serine.

The effect of γ radiation upon the serine isomers is sustained by the decrease of melting – decomposition peaks, t_{max1} and t_{max2} (Figs. 2a and 2b) towards lower temperatures with the increase of the irradiation dose. From Figs. 2a, 2b it can be remarked that the effect of radiations on the decrease of t_{max1}, t_{max2} is significant for all three isomers, at low doses; a tendency towards a plateau is observed at higher doses. The same comment was formulated by Varshney[16] following the plot of the alanine decomposition temperature versus the irradiation dose. A similar diminishing in the melting enthalpy caused by irradiation has been observed earlier for some antibiotics and steroids.[17,18]

This behavior is due to the formation of radiolysis products of amino acids. The presence of radiolytic products in the irradiated samples of amino acids even in small concentration has the same effect as the presence of impurities: they modify the crystalline structure of the substance and produce the decrease of the above-mentioned parameters. All temperature values t_{onset}, $t_{max1,}$ t_{max2} and the enthalpies ΔH on the DSC curves decrease with the irradiation dose. We consider that the weight of this reaction in the overall decomposition process increases with the irradiation dose.

Reaching a plateau is due to the accumulation of radiolysis products with increasing irradiation dose. As a consequence, the irradiation products have a protective effect on the amino acid parent molecule. The values of the temperatures t_{onset}, $t_{max1,}$ t_{max2}, calculated for a wide range of irradiation doses from 0.63 to 10 kGy are listed in Table 1.

An increase of the four temperatures t_{onset}, $t_{max1,}$ t_{max2} is noticed in the order D-Ser < L-Ser < DL-Ser isomers for both non-irradiated and irradiated. A decrease of the decomposition enthalpy with irradiation dose is noticed for all three isomers. The decomposition enthalpy was calculated for each recorded thermal effect. Deconvolution procedure was used in order to separate the recorded peaks. Thus, the recorded data were imported in PeakFit v. 4.12 software. Therefore, this procedure allowed us calculating ΔH_1 and ΔH_2 The obtained results are presented in Table 2.

The differences found in the decreasing of the temperatures and melting-decomposition enthalpies on the serines irradiated samples are due to the physical and chemical effects produced by ionizing radiation. Physical effects consist in producing the crystalline lattice defects. It is known that the high gamma radiation energy produces the breaking of the covalent bonds and disturb the interactions that stabilize the amino acid crystalline lattice.

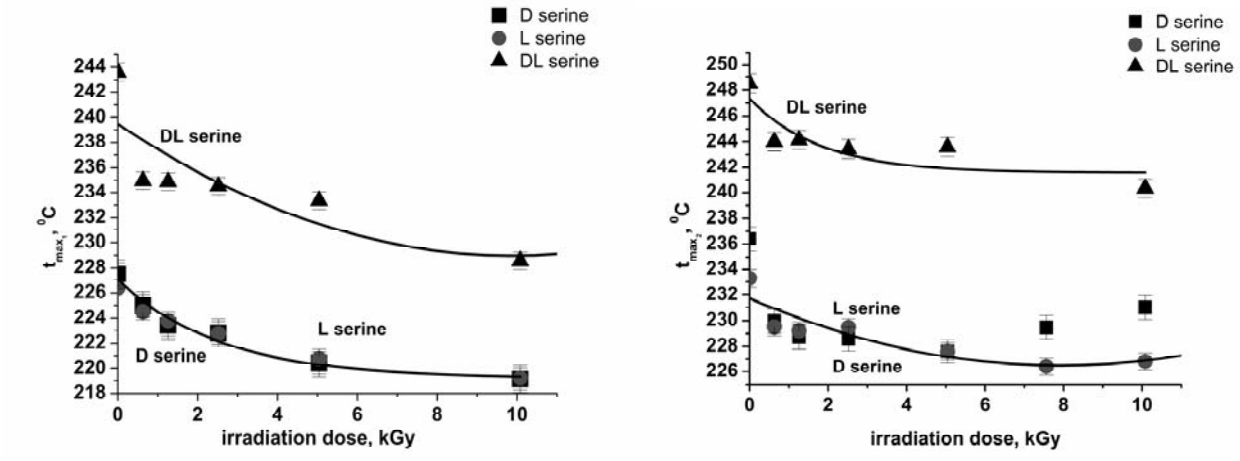


Fig. 2 – Variation of the peaks maxima temperature versus irradiation dose.

Table 1

DSC temperatures for serines non-irradiated and irradiated with different doses

Dose, kGy	The melting/decomposition temperatures of serines.								
	L-Ser			D-Ser			DL-Ser		
	t_{onset},°C	$t_{max1,}$ °C	t_{max2}, °C	t_{onset},°C	$t_{max1,}$ °C	t_{max2}, °C	t_{onset},°C	$t_{max1,}$ °C	t_{max2}, °C
0	223.0±0.2	227.5±0.34	236.4±0.27	218.33±0.23	226.36±0.1	233.27±0.15	240.7±0.3	243.6±0.11	248.5±0.22
0.63	213.0±0.1	224.9±0.23	229.9±0.13	212.01±0.25	224.5±0.17	229.5±0.22	232.0±0.4	234.9±0.34	244.0±0.12
1.26	212.9±0.12	223.4±0.18	228.7±0.14	211.9±0.10	223.7±0.31	229.2±0.18	229.9±0.33	234.8±0.6	244.1±0.29
2.52	209.4±0.21	222.8±0.35	228.5±0.37	210.06±0.26	222.7±0.44	229.4±0.33	229.44±0.2	234.5±0.41	243.4±0.14
5.04	209.0±0.15	220.5±0.10	227.6±0.31	207.5±0.41	220.7±0.20	227.6±0.23	229.2±0.26	233.3±0.15	243.5±0.34
7.56	205.1±0.3	219.4±0.44	229.4±0.28	208.29±0.39	219.3±0.11	226.3±0.1	229.0±0.4	232.2±0.5	243.1±0.23
10.08	205.0±0.11	219.0±0.29	231.0±0.22	208.6±0.2	219.2±0.19	226.8±0.1	227.7±0.29	232.8±0.3	241.9±0.40

Table 2

Decomposition enthalpy for serine isomers non-irradiated and irradiated with different doses

Dose, kGy	The decomposition enthalpies, ΔH, (kJ mol^{-1})					
	L-Ser		D-Ser		DL-Ser	
	ΔH_1, (kJ mol^{-1})	ΔH_2, (kJ mol^{-1})	ΔH_1, (kJ mol^{-1})	ΔH_2, (kJ mol^{-1})	ΔH_1, (kJ mol^{-1})	ΔH_2, (kJ mol^{-1})
0	28.33±0.6	10.37±0.80	39.68±0.53	12.12±0.9	36.16±0.2	57.73±0.56
0.63	19.15±0.65	9.28±0.08	17.60±0.79	8.15±0.13	3.21±0.05	55.16±0.6
1.26	17.54±0.55	8.71±0.43	17.55±0.1	5.32±0.11	0.90±0.03	53.64±0.65
2.52	17.25±0.89	7.74±0.06	16.76±0.70	2.75±0.01	0.82±0.01	52.76±0.78
5.04	16.85±0.46	2.37±0.14	16.27±0.17	2.07±0.04	0.74±0.04	27.56±0.8
7.56	16.12±0.5	2.33±0.16	16.21±0.64	0.61±0.02	0.71±0.02	9.13±0.02
10.08	15.46±0.8	0.75±0.05	15.80±0.66	0.34±0.01	0.69±0.01	2.70±0.011

The significant changes of the values of the melting-decomposition enthalpy relative to the initial value, as a result of irradiation could be explained by the cleavage of the amino acids bond, as well as by changes in the crystal structure and the implication of decomposition products. The decomposition as a result of radiolysis affects the physico-chemical properties of the compound.[17]

The solid state irradiation of the amino acids causes the formation of free radicals in the molecular crystal followed by the decomposition of the pristine amino acid for instance by a deamination or a decarboxylation reaction.[19]

Thus, the continuous radiolysis causes a steady decomposition but occurring in the solid state, the radiolysis products are not so mobile and cannot escape easily, especially large molecular fragments remain trapped in the crystalline structure of the amino acids causing a reduction of the melting point. The higher the amount of radiolysis products and larger is the reduction in the melting enthalpy.[20,21]

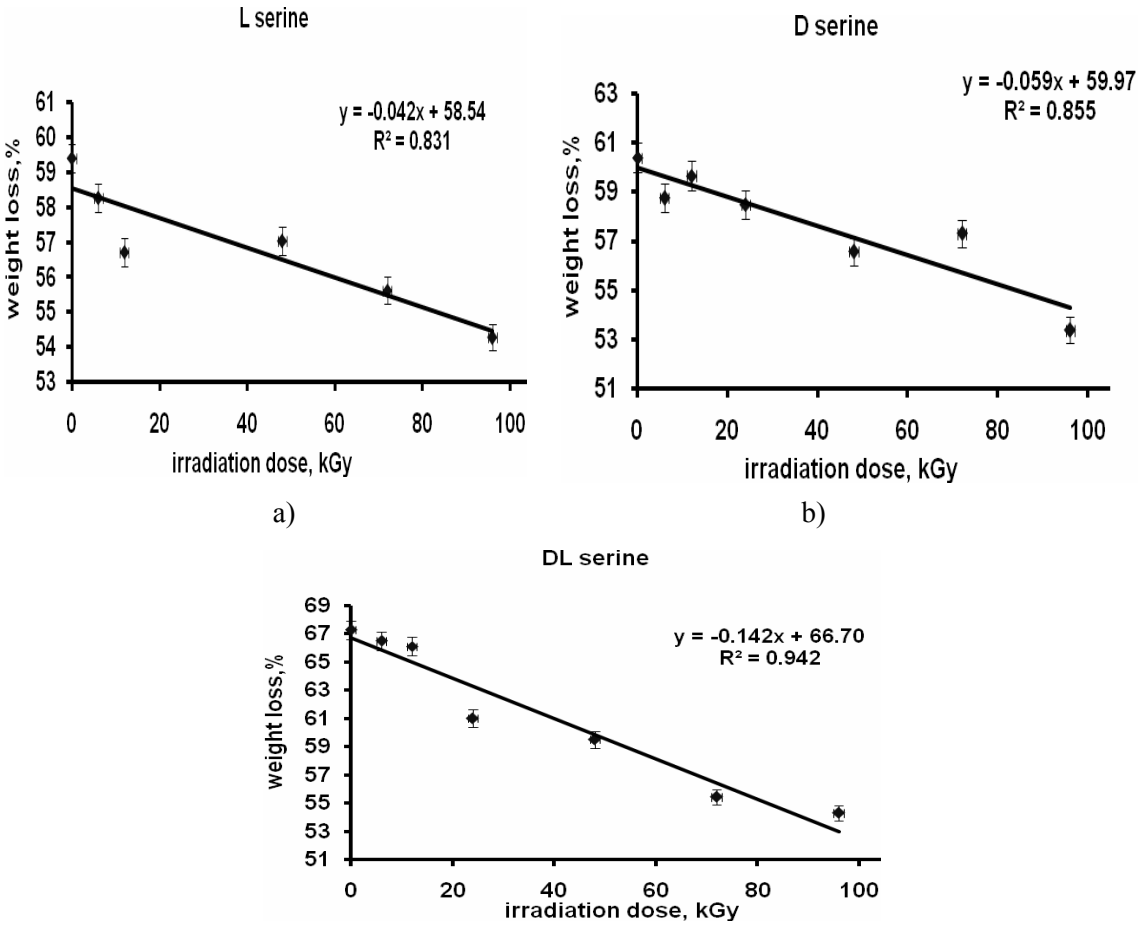


Fig. 3 – Dependence of the weight loss of L serine (a), D serine (b) and DL serine (c) on heating to 350°C, on irradiation dose (kGy).

On the recorded DSC curves is observed that the reduction of the melting enthalpy after radiolysis is always accompanied by a shift in the onset and in the melting peak of the transition toward lower temperature.

All the effects observed including a decrease of the melting point and of the values of the enthalpies of decomposition and melting of serine after irradiation are due to the break of covalent bonds produced by the high energy ionizing radiation. Weaker interactions stabilizing the crystal lattice are also perturbed in this way and as a result defects are appearing in the crystal lattice.

In order to establish the influence of radiations upon the thermal behavior of serines the weight losses of the irradiated and non-irradiated samples were measured using thermogravimetric method. Ionizing radiations cause a decrease of the mass loss of serines with increasing the dose. This behavior is illustrated in Figs. 3a), b) and c) for L, D and DL serine.

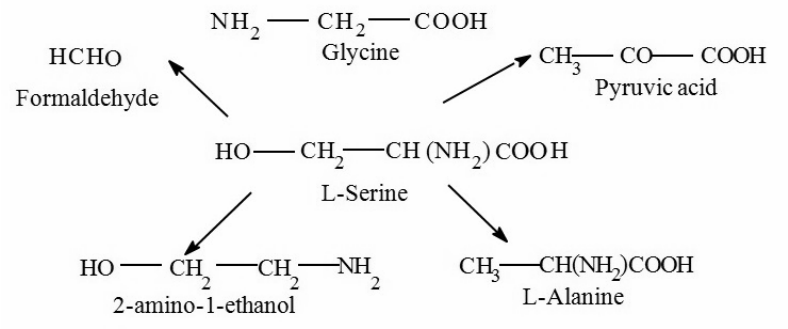
Decomposition mechanism

The position and the nature of the side chain brings about changes in thermal stability and decomposition process. The presence of a hydroxylic group in the side chain does not cause "sublimation" when it is bonded to a primary carbon (Ser), while "sublimation" does occur when it is bonded to a secondary carbon (Thr). Usually, their effect is stabilizing.[22]

The main reaction in the thermal decomposition process of serine is considered to be decarboxylation[15] with ethanolamine as the reaction product.

The reaction occurs in living organisms, as well, this compound being an important component of phospholipids found in biological membranes. However, authors[23] have observed a weight loss of about 60 %, between 230 and 270^{0}C (in agreement with our data) which means that other processes take place.

Possible decomposition pathways are shown in the scheme below.[24]



Scheme 2 – Thermal decomposition of serine.

Determination of the heat capacities

To highlight the effect of ionizing radiations on the studied serines, heat capacities were also measured using DSC 8500 calorimeter between -20-150 °C temperature range.

Heat capacity is one of the fundamental parameters describing thermodynamic properties of a system. The heat capacity at a constant pressure, Cp, can be defined as a temperature derivative of one of the basic thermodynamic parameters describing the state of a macroscopic system, the enthalpy, $H(T)_p$:

$$C_p = \frac{dH(T)_p}{dT}, \qquad (1)$$

where Cp is the sample's heat capacity (J/g°)
dH is the change in heat absorbed (J/g)
and
dT is the change in temperature (°C)

Heat capacity for D and DL serine were reported by Drebushchak[25] in the temperature range 5.5 to 300 K. Similar heat capacity measurements were carried out for L serine by Makhatadze[26] in the temperature range 10 K-310.15K and Hutchens[27] in the range of 11 to 305 K and no phase transitions or even irregularities in function Cp(T) were found.

In this work the results of our calorimetric study focused on the determination of heat capacity for serines in a wider range of temperatures (from -20°C up to melting temperature of the sample) are presented both for non-irradiated and irradiated samples. Our experimental heat capacities values of L, D and DL serine non-irradiated and 24h (2.52 kGy) and 72 h (7.56 kGy) irradiated are presented in Table 3.

In Fig. 4 the temperature dependence of the specific heat capacity of non-irradiated, 24 h (2.52 kGy) and 72h (7.56 kGy)-irradiated DL serine is exemplified.

Table 3

Experimental heat capacities of serine isomers non-irradiated and 24h (2.52 kGy), 72h (7.56 kGy)-irradiated (formula mass=105.093 $gmol^{-1}$)

Temperature, °C	Heat capacities of serines irradiated and non-irradiated (J/g°C)								
	L-Ser			D-Ser			DL-Ser		
	Non-irradiated	2.52 kGy irradiated	7.56 kGy irradiated	Non-irradiated	2.52 kGy irradiated	7.56 kGy irradiated	Non-irradiated	2.52 kGy irradiated	7.56 kGy irradiated
-20	1.129	1.084	1.023	1.09	0.954	0.8	1.1	0.944	0.801
-10	1.172	1.14	1.093	1.175	1.089	0.932	1.116	1	0.877
0	1.213	1.175	1.13	1.22	1.124	0.975	1.144	1.035	0.912
10	1.261	1.211	1.155	1.266	1.183	1.031	1.183	1.069	0.94
20	1.293	1.255	1.188	1.299	1.22	1.068	1.221	1.111	0.973
30	1.329	1.285	1.225	1.329	1.251	1.1	1.26	1.142	1.01

Table 3 (continued)

40	1.381	1.317	1.249	1.361	1.284	1.141	1.297	1.176	1.039
50	1.415	1.344	1.291	1.394	1.317	1.172	1.338	1.203	1.074
60	1.445	1.371	1.318	1.433	1.349	1.204	1.378	1.231	1.102
70	1.477	1.404	1.351	1.463	1.386	1.24	1.415	1.264	1.135
80	1.525	1.448	1.376	1.496	1.421	1.273	1.451	1.307	1.161
90	1.564	1.479	1.409	1.529	1.454	1.299	1.487	1.339	1.194
100	1.614	1.508	1.436	1.562	1.492	1.34	1.522	1.368	1.221
110	1.651	1.548	1.474	1.599	1.524	1.375	1.555	1.406	1.259
120	1.685	1.577	1.505	1.633	1.562	1.41	1.588	1.437	1.29
130	1.716	1.608	1.532	1.668	1.596	1.44	1.619	1.468	1.316
140	1.758	1.635	1.56	1.706	1.622	1.468	1.651	1.495	1.345
150	1.8	1.669	1.589	1.739	1.649	1.495	1.684	1.529	1.378

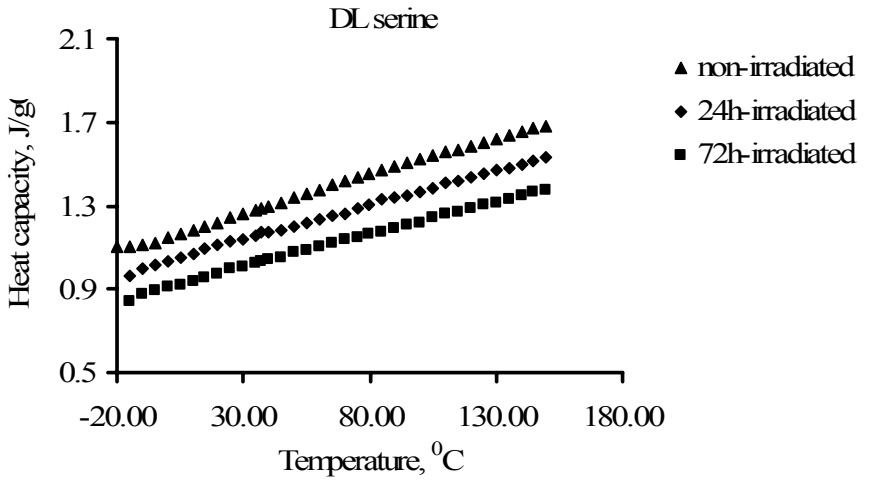


Fig. 4 – Plot of heat capacity of the non-irradiated and irradiated samples of DL serine.

From Fig. 4 we ascertained that the specific heat capacity of the irradiated DL serines decrease with irradiation dose. The same behavior was also observed for D and L serine (non-Fig.d).

Determination of purity by DSC

The PerkinElmer Pyris DSC purity analysis software permits the assessment of purities for samples which undergo simultaneous degradation during melting. The purity of a sample for which only the molecular weight and sample weight are known can be ascertained by a simple mathematical treatment of the data from a DSC scan.

This method has an excellent feature not found in other methods – it can accurately determine the total amount of impurities, including the unknown species.[28]

In Fig. 5 is plotted the purity using Pyris software for L-serine 6h-irradiated (0.63 kGy).

In the T vs $1/F_s$ curve, the corrected data points are shown as black circles and the line drawn through them shows how the data fit the Van't Hoff relationship Eq. (2). The black boxes represent the uncorrected values calculated for $1/F_s$ (fraction melted) at given temperatures (Fig. 6).

$$1/F_S \quad [\ H/R\ ]\ [T_o - T_S]/T_o^2\ \ [1/X_2] \qquad (2)$$

T_s – sample temperature and the melting temperature, K
T_0 – the melting temperature of the pure substance
ΔH – heat of melting of the pure material, J/g
X_2 – mole fraction of impurity in the sample
R – constant (8,314 J/mole·K)
F_s – fraction of sample melting at temperature T_s

$$F_S = \frac{A_S}{A_t}$$

A_s – area of the melting endotherm up to temperature T_s
A_t – total area of melting endotherm

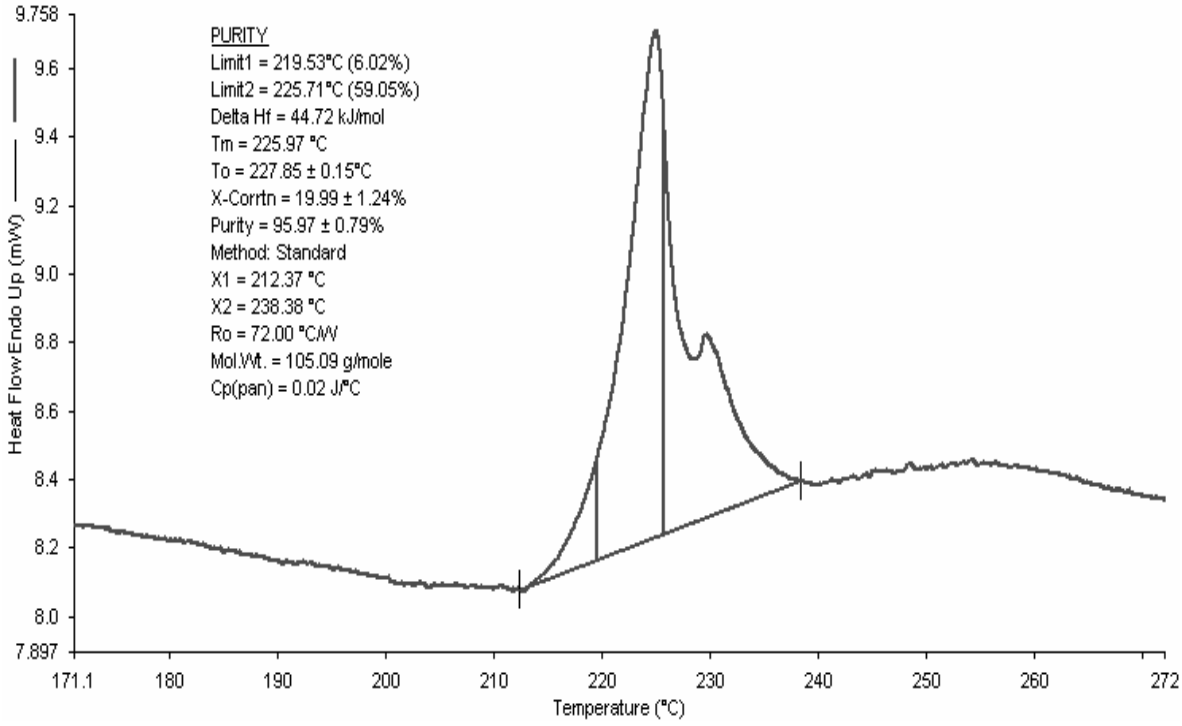


Fig. 5 – Determination of purity using Pyris software for L-serine 6h-irradiated (0.63 kGy).

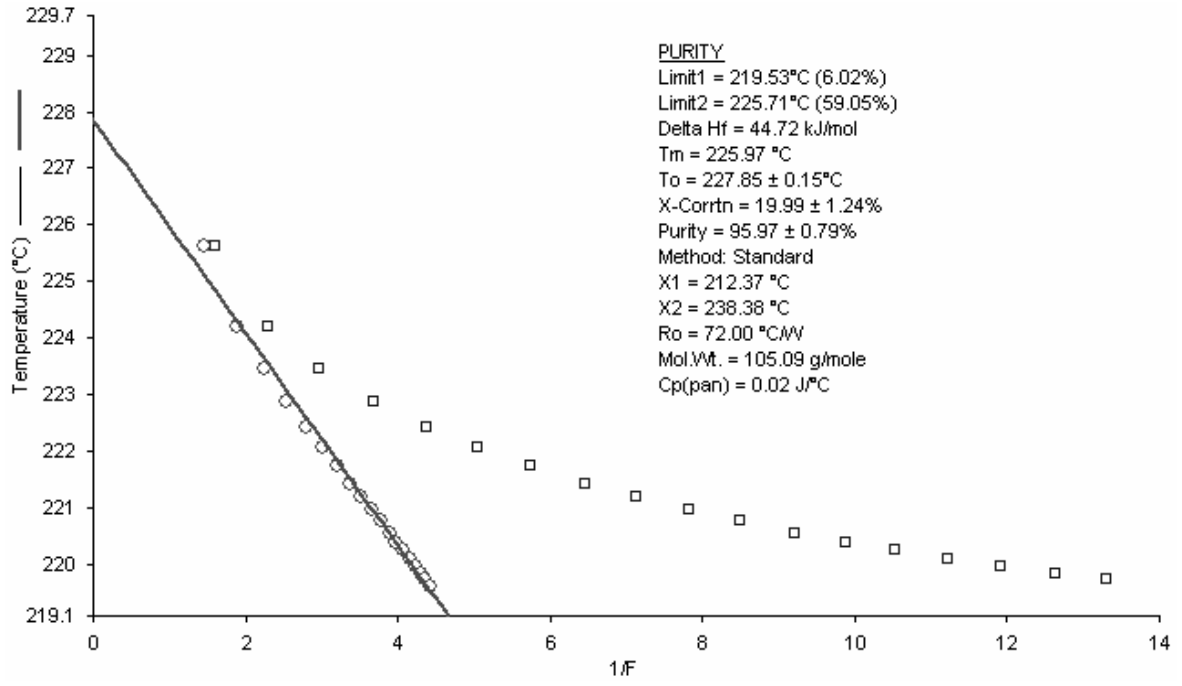


Fig. 6 – Van't Hoff plot for 6h-irradiated (0.63 kGy) L-serine.

Data of Table 4 indicate the decreasing of purity for serines with increasing irradiation dose.

The presence in the irradiated samples of radiolytic products of the serines, even in a small concentration, has the same influence as the presence of impurities: damages the crystalline structure of the amino acid and produces the decrease of the experimental parameters presented.

Small changes were noted in the IR spectra of L serine 24h-irradiated (2.52 kGy), relative to the spectrum of non-irradiated compound (Fig. 7). The changes were detected in the intensity of some peaks, while the character of the spectrum did not change.

Table 4

Variation of the purity, % versus irradiation dose for serines

Compound	Dose, kGy	Purity, %
L-serine	0	98.81±2.23
	0.63	95.97±0.79
	1.26	95.21±0.6
	2.52	94.69±1.12
	5.04	94.32±4.65
	7.56	89.35±9.34
	10.08	88.25±8.66
D-serine	0	95.57±1.15
	0.63	94.58±1.02
	1.26	94.25±0.96
	2.52	94.16±1.34
	5.04	91.20±5.33
	7.56	87.49±5.23
	10.08	86.78±4.84
DL-serine	0	98.68±0.21
	0.63	89.47±0.92
	1.26	87.44±0.86
	2.52	76.92±5.29
	5.04	76.64±3.72
	7.56	75.73±2.24
	10.08	68.32±5.69

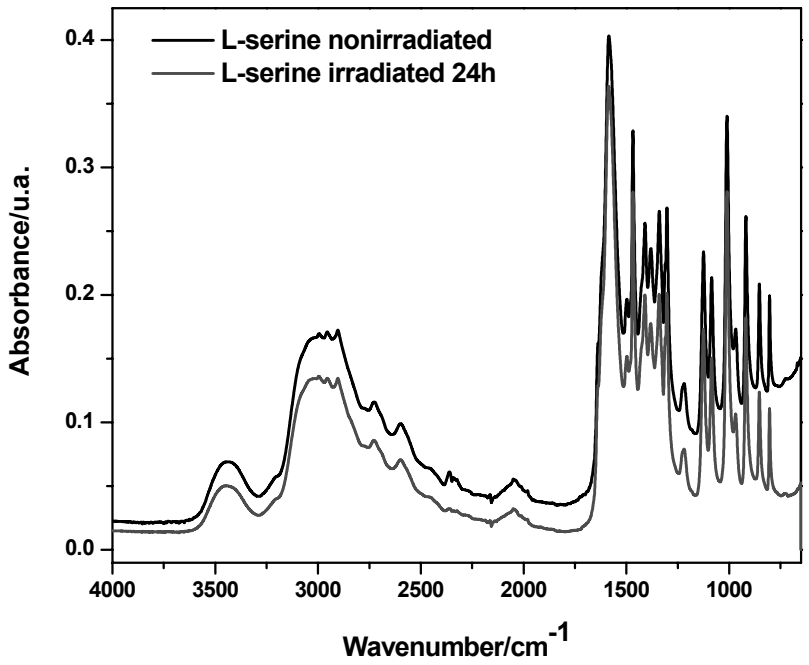


Fig. 7 – FTIR spectra of 24h (2.52 kGy) -irradiated and non-irradiated L serine.

Table 5

IR band positions and band assignments for the L-serine over 625-3500 cm^{-1} spectral range

Band assignments	*Non-irradiated L serine*	*2.52 kGy (24h) irradiated L serine*
νOH[29,30]	3429	3429
$\nu_a(NH_3^+)$[30]	3206	3201
$\nu_a(CH_2)$[30]	2995	2995
$\nu_s(CH_2)$[29-31]	2955	2955
$\nu(CH)$[30]	2903	2903
Overtone and combination bands[29]	2772 2727 2598 2450 2363 2340 2323	2770 2727 2598 2450 2361
$\nu(NH\cdots O)$?	2188 2164 2138	2186 2164 2138
$\delta(NH_3^+) + \tau(NH_3^+)$[29]	2037	2057
?	2011 1980 1858 1822	2011 1979 1854 1822
$\nu(C=O)$[11,31]	1797 1778 1764 1753 1737 1723 1709 1704 1691 1687	1764 1731
$\delta_{as}(NH_3^+)$[29,30]	1637	1637
$\nu_{as}(COO^-)$[30]	1585	1585
$\delta_s(NH_3^+)$[30]	1498	1497
$\delta(CH_2)$[29,32]	1468	1467
$\nu_{as}(COO^-)$[30,32]	1411	1411
$\omega(CH_2)$[30]	1380	1382
δ (CH)[30]	1339	1339
γ (CH)[30]	1303	1303
δ (COH)[30]	1219	1219
γ (NH_3^+)[30]	1124	1124
ν (CO)[30]	1085	1085
γ (CH_2)[29,30]	1010	1011
ν (CN)[30]	968	968
ν(CC)[30]	920 852	918 852
γ (COO^-)[29,30,11]	806 726	806 728
δ (CO)[11]	667	667

ν_s – symmetrical stretching, ν_a – asymmetrical stretching, δ – deformation, δ_a – asymmetric deformation, ρ – rocking, ω – wagging, τ – torsion, γ – out of plane bending

The functional groups of L-serine were identified by FT-IR spectroscopy analysis. The observed IR spectra of non-irradiated L-serine and 24h (2.52 kGy) irradiated L-serine, at room temperature, are presented in Fig. 7. After irradiation we observed a decrease of intensity of

the bands ascribed to 24h (2.52 kGy) irradiated L-serine. The 24h irradiated sample was highlighted because in this case the irradiation effect seems to be a significantly one (see the DSC results). A comparison between the non-irradiated L-serine and 24h irradiated L-serine revealed that their vibrational spectra reflect well the different characteristics of zwiterion. The spectral intensity region decrease after irradiation, thus supporting the assignement of the 727 cm^{-1} band corresponding to the γCOO^- rocking (out-of-plane) and band at 2363 cm^{-1} attributed to combinations of NH_3^+ degenerate deformation mode with the C–N stretching mode or NH_3^+ rocking mode.[11,29] The assigned frequencies characteristic zwitterion groups appear in both the irradiated and non-irradiated sample spectrum, the largest difference being found for COO^- and it can be attributed to partial decarboxylation caused by irradiation.

CONCLUSIONS

The decomposition of L- and D- isomers of serine and of their racemic mixture proceeds in two steps. This is proved by the existence of two endothermic peaks at close temperatures, on the DSC curves.

The temperature values (t_{onset}, t_{max1}, t_{max2}) from the DSC curves of the three irradiated compounds show a similar tendency as those of non-irradiated ones increasing in the following order: D-Ser< L-Ser<DL-Ser.

Although the general properties of the isomers L-, D and DL-Ser are known to be the same, the present DSC study showed a different thermal behavior. These differences were found for both non-irradiated and irradiated isomers and are assigned to the difference in morphology of the enantiomers crystals.

The weight loss due to the thermal decomposition is lower for the irradiated samples than the non-irradiated ones and is more pronounced at low doses.

The values obtained for purity and heat capacities for all the three irradiated serines are smaller than the non-irradiated ones and decrease with increasing irradiation dose.

The obtained results are also expected to be relevant for studies of other classes of organic molecules containing similar functional substituents.

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