

Synthesis and Characterization of N-acylation and N-alkylation Derivatives of 4-azasebacic Acid and Diethyl-4-azasebacate

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In this paper there are presented the synthesis and characterization of new N-acyl and N-alkyl derivatives of 4-azasebacic acid and diethyl-4-azasebacate. The obtained products have been characterized by various methods: IR, UV-VIS, $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, elemental analysis, TLC, m.p. (Boethius).

Keywords: 4-azasebacic acid, N-acylation, N-alkylation, surfactants

Recently, the strategy of surfactants manufacturing has moved beyond conventional conceptions of amphiphiles made from petroleum [1]. Most of ionic surfactants used for a long time have been alkyl and alkyl-aryl sodium sulphates and sulphonates, but these compounds are hardly biologically decomposed. The variety of available bio surfactants includes naturally occurring compounds such as glycolipids, acyl peptides, phospholipids, proteins and liposaccharides [2-8].

Generally, N-acylated amino acids can be used as surfactants, but also they can be used in pharmaceutical and cosmetic industry. [8, 9] Both amino acids and peptides derived from naturally raw materials can be used for the synthesis of reminded products [10 - 12]. Classically N-acylation techniques, with strong alkaline bases

solutions, present the great risk of secondary reactions [7]. In this paper, there were obtained N-acylation and N-alkylation derivatives synthesized in presence of anhydrous pyridine; in this way, the secondary undesired reactions were avoided and the yields of the main products obtaining were also higher than in case of traditional methods used in these cases. [7,11,14,15] The present work describes the syntheses of new N-acylation and N-alkylation derivatives of 4-azasebacic acid, which is a hydrolysis degradation product from N-(β -cianoethyl)- ϵ -caprolactam and also, of diethyl-4-azasebacate. The obtained products have been characterized by various methods: FTIR, UV-VIS, $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, elemental analysis, TLC, m.p. (Boethius). The reaction schemes of the synthesized compounds are presented in figures 1, 2.

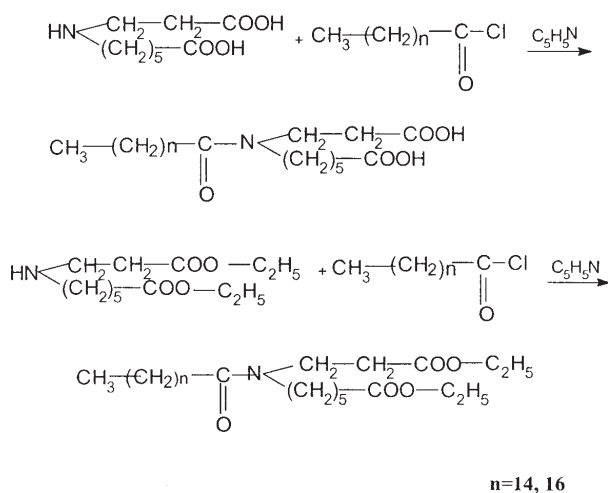


Fig. 1. N-acylation of 4-azasebacic acid and of diethyl-4-azasebacate, in presence of pyridine

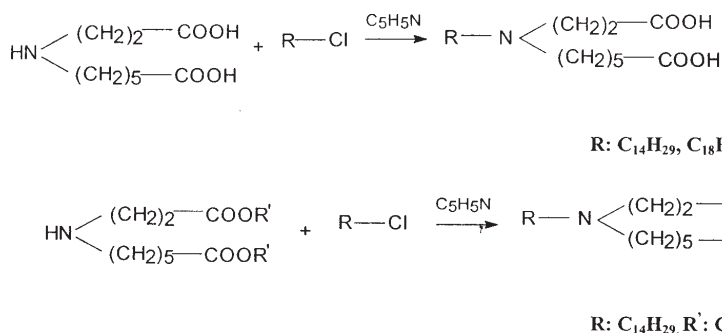


Fig. 2. N-alkylation of 4-azasebacic acid and of diethyl-4-azasebacate, in presence of pyridine

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Experimental part

The synthesis of 4-azasebacic acid was performed as described in literature [13]. Diethyl-4-azasebacate was synthesized by using a classical technique- the esterification with an inferior alcohol in presence of gaseous chlorhidric acid, at reflux. All the other chemicals were of reagent grade, purchased from Fluka and used without further purification.

Melting points of the obtained products were determined by using an apparatus KSP II Krüss Optronic. Thin layer chromatograms were performed on Merck plates with silica gel, by using as solvent *sec*-BuOH: HCOOH: H₂O = 75:15:10, usually for 10 h; unitary spots were developed with a UV lamp ($\lambda = 254$ nm and 365 nm).

Electronic spectra were obtained using a UV-VIS JASCO-V550 spectrophotometer, in domain 190-900 nm, with MgO as reference. FT-IR spectra were recorded in the in domain 4000-400 cm⁻¹, by using a Varian Resolutions Pro 3100 spectrophotometer. NMR spectra were recorded on a Varian Gemini 300 spectrometer operating at 300 MHz (¹H-NMR) and 75 MHz (¹³C-NMR) respectively, in CDCl₃ and DMSO-d₆, with tetramethylsilane (TMS) as the internal standard. For elemental analysis there was used a COSTECH ECS 4010 CHNSO analyzer.

N-acylation of 4-azasebacic acid –in presence of pyridine

To 4-azasebacic acid there were added fatty acid chloride- stearoyl chloride or palmitoyl chloride (molar ratio acid/fatty acid chloride = 1.2/1) and anhydrous pyridine (5 × 10⁻² mol). The mixture was refluxed at 90°C, for 5 h, at constant stirring. After cooling, the reaction mixture was treated with a solution of HCl 2N, until a pH < 3. The mixture precipitates and then is filtered off, dried (yield 80-82%) and purified by recrystallization from absolute ethanol. These *N*-acylation compounds are white powders; they are soluble in acetone, ethanol, *sec* butanol, formic acid, DMSO, water-at heating.

***N*-stearoyl 4-azasebacic acid:** ¹H-NMR δ (ppm): 0.83 (m, 3H, CH₃-(CH₂)₁₆), 1.23 (m, 32 H, CH₂), 2.20 (m, 2H (N-CH₂-CH₂-CH₂-CH₂-CH₂)), 2.50 (m, 2H, N-CH₂-CH₂-CH₂-CH₂-CH₂), 3.35 (t, 2H, N-CH₂-CH₂-CH₂-CH₂-CH₂), 4.57 (t, 2H, N-CH₂-CH₂-CH₂-CH₂-CH₂), 7.53 (t, 2 H, N-CH₂-CH₂), 12.07 (s, 1H, -COOH);

¹³C-NMR δ (ppm): 13.88 (CH₃-(CH₂)₁₆), 21.76 (CH₂-CH₂COOH), 24.04 (N-CH₂-CH₂-CH₂-CH₂-CH₂), 28.97 (N-CH₂-CH₂-CH₂-CH₂-CH₂), 38.94 [(CH₂)₁₆], 49.03 (N-CH₂-CH₂-CH₂-CH₂-CH₂), 63.35 (CH₂-CH₂N), 132.92 (N-CO), 173.01 ((CH₂)_nCOOH).

***N*-palmitoyl 4-azasebacic acid:** ¹H-NMR δ (ppm): 0.85 (m, 3H, CH₃-(CH₂)₁₄), 1.23 (m, 28 H, CH₂), 2.23 (m, 2H, (N-CH₂-CH₂-CH₂-CH₂-CH₂)), 2.56 ((m, N-CH₂-CH₂-CH₂-CH₂-CH₂)), 3.38 (t, N-CH₂-CH₂-CH₂-CH₂-CH₂), 4.50 (t, 2H, N-CH₂-CH₂-CH₂-CH₂-CH₂), 7.53 (t, 2H, N-CH₂-CH₂) 12.35 (s, 1H, -COOH);

¹³C-NMR δ (ppm): 13.06 (CH₃-(CH₂)₁₄), 21.70 (CH₂-CH₂COOH), 24.50 (N-CH₂-CH₂-CH₂-CH₂-CH₂), 31.79 (N-CH₂-CH₂-CH₂-CH₂-CH₂), 38.31 [(CH₂)₁₄], 49.86 (N-CH₂-CH₂-CH₂-CH₂-CH₂), 64.17 (CH₂-CH₂N), 134.09 (N-CO), 174.81 ((CH₂)_nCOOH).

N-acylation of diethyl-4-azasebacate– in presence of pyridine

To diethyl 4-azasebacate were added fatty acid chloride- stearoyl chloride or palmitoyl chloride (molar ratio ester/fatty acid chloride = 1/1) and pyridine in excess (5 × 10⁻² moles). The mixture was refluxed at 90°C, for 6 h, at constant stirring. After cooling, the reaction mixture was treated with a solution of HCl 2N, until a pH < 3. The mixture

precipitates and then is filtered off, dried (yield 82-85%) and purified by recrystallization from absolute ethanol. These compounds are white powders; they are soluble in acetone, ethanol, *sec* butanol, formic acid, DMSO, water-at heating.

***N*-stearoyl diethyl-4-azasebacate** ¹H-NMR: δ (ppm): 0.93 (m, 3H, CH₃-(CH₂)₁₆), 1.01 (t, 2H, N-CH₂-CH₂-COOR and N-(CH₂)₄-CH₂-COOR), 1.23 (t, 3H, CH₃-CH₂), 1.63 (q, 2H, CH₃-CH₂), 2.27 (m, 2H, N-CH₂-CH₂-CH₂-CH₂-CH₂COOR), 2.32 (t, 2H, N-CH₂-CH₂-COOR), 4.10 (m, 2H, N-CH₂-(CH₂)₄-COOR);

¹³C-NMR: δ (ppm): 25.18 (CH₃-CH₂), 29.50 (CH₃-CH₂), 34.44 (N-CH₂-CH₂-COOR and N-(CH₂)₄-CH₂-COOR), 39.91 [(CH₂)₄], 60.58 (N-CH₂-CH₂-CH₂-CH₂-CH₂COOR), 77.01 (N-CH₂-CH₂-COOR and N-CH₂-(CH₂)₄-COOR), 138.19 (N-CO), 174.49 (-COOR).

***N*-palmitoyl diethyl-4-azasebacate** ¹H-NMR: δ (ppm): 0.90 (m, 3H, CH₃-(CH₂)₁₄), 1.05 (t, 2H, N-CH₂-CH₂-COOR and N-(CH₂)₄-CH₂-COOR), 1.45 (t, 3H, CH₃-CH₂), 1.60 (q, 2H, CH₃-CH₂), 2.27 (m, 2H, N-CH₂-CH₂-CH₂-CH₂-CH₂COOR), 2.57 (2H, N-CH₂-CH₂-COOR), 4.12 (t, 2H, N-CH₂-(CH₂)₄-COOR);

¹³C-NMR: δ (ppm): 24.70 (CH₃-CH₂), 29.07 (CH₃-CH₂), 34.08 (N-CH₂-CH₂-COOR and N-(CH₂)₄-CH₂-COOR), 37.89 [(CH₂)₄], 61.70 (N-CH₂-CH₂-CH₂-CH₂-CH₂COOR), 78.05 (N-CH₂-CH₂-COOR and N-CH₂-(CH₂)₄-COOR), 139.06 (N-CO), 176.08 (-COOR).

N-alkylation of 4-azasebacic acid –in presence of pyridine

To 4-azasebacic acid (1 mmol; 0,203 g) there were added cetyl chloride or stearyl chloride (1 mmol) and pyridine (5 mmol; 0.3495 g). This mixture was refluxed at 85-90°C, for 6 hours. The reaction mixture was treated after cooling with a HCl solution 1N until pH < 3, then it was filtered, dried (yield 79-81%) and purified by recrystallization from absolute ethanol. These compounds are pale yellow powders; they are soluble in acetone, ethanol, *sec* butanol, formic acid, DMSO, water-at heating.

***N*-cetyl 4-azasebacic acid:** ¹H-NMR: δ (ppm): 0.88 (m, 3H, CH₃-(CH₂)₁₂), 1.20 (m, 26H, (CH₂)₁₂), 2.28 (m, 2H, (N-CH₂-CH₂-CH₂-CH₂-CH₂)), 2.58 (m, 2H, (N-CH₂-CH₂-CH₂-CH₂-CH₂)), 3.37 (t, 2H, N-CH₂-CH₂-CH₂-CH₂-CH₂), 4.51 (t, 2H, N-CH₂-CH₂-CH₂-CH₂-CH₂), 7.21 (t, N-CH₂-CH₂), 12.08 (s, 1H, -COOH);

¹³C-NMR: δ (ppm): 13.30 (CH₃-(CH₂)₁₂), 21.13 (CH₂-CH₂COOH), 24.82 (N-CH₂-CH₂-CH₂-CH₂-CH₂), 29.07 (N-CH₂-CH₂-CH₂-CH₂-CH₂), 38.07 [(CH₂)₁₂], 49.88 (N-CH₂-CH₂-CH₂-CH₂-CH₂), 63.87 (CH₂-CH₂N), 173.87 ((CH₂)_nCOOH).

***N*-stearyl-4-azasebacic acid:** ¹H-NMR: δ (ppm): 0.89 (m, 3H, CH₃-(CH₂)₁₇), 1.28 (m, 34, CH₂), 2.29 (m, 2H, (N-CH₂-CH₂-CH₂-CH₂-CH₂)), 2.59 (m, 2H, (N-CH₂-CH₂-CH₂-CH₂-CH₂)), 3.81 (t, 2H, N-CH₂-CH₂-CH₂-CH₂-CH₂), 4.57 (t, 2H, N-CH₂-CH₂-CH₂-CH₂-CH₂), 7.21 (t, 2H, N-CH₂-CH₂), 12.16 (s, 1H, -COOH);

¹³C-NMR: δ (ppm): 13.90 (CH₃-(CH₂)₁₇), 21.78 (CH₂-CH₂COOH), 24.87 (N-CH₂-CH₂-CH₂-CH₂-CH₂), 29.37 (N-CH₂-CH₂-CH₂-CH₂-CH₂), 38.80 [(CH₂)₁₇], 49.96 (N-CH₂-CH₂-CH₂-CH₂-CH₂), 63.89 (CH₂-CH₂N), 174.09 ((CH₂)_nCOOH).

N-alkylation of diethyl-4-azasebacate–in presence of pyridine

To diethyl-4-azasebacate (1 mmol; 0,2602 g) there were added cetyl chloride (1 mmol) and pyridine (5 mmol; 0.3495 g). This mixture was refluxed at 85-90°C, for 5 h. The reaction mixture was treated after cooling with a HCl solution 1N until pH < 3, then it was filtered off, dried (yield 82-83%) and purified by recrystallization from absolute ethanol. There was obtained a pale yellow powder. This

compound is soluble in acetone, ethanol, *sec* butanol, formic acid, DMSO, water-at heating.

N-cetyl diethyl-4-azasebacate: ¹H-NMR: δ (ppm): 0.89 (m, 3H, CH₃-(CH₂)₁₂), 1.20 (m, 26H, CH₂)₁₂), 1.43 (t, 3H, CH₂-CH₃), 1.58 (q, 2H, CH₂-CH₃), 2.33 (m, 2H, (N-CH₂-CH₂-CH₂-CH₂-CH₂)), 2.90 (m, 2H, (N-CH₂-CH₂-CH₂-CH₂-CH₂)), 3.97 (t, 2H, N-CH₂-CH₂-CH₂-CH₂-CH₂), 4.58 (t, 2H, N-CH₂-CH₂-CH₂-CH₂-CH₂), 7.31 (t, N-CH₂-CH₂);

¹³C-NMR: δ (ppm): 13.36 (CH₃-(CH₂)₁₂), 21.16 (CH₂-CH₂COOR), 24.37 (CH₂-CH₂), 25.38 (N-CH₂-CH₂-CH₂-CH₂-CH₂), 27.89 (N-CH₂-CH₂-CH₂-CH₂-CH₂), 29.38 (CH₃-CH₂), 38.32 [(CH₂)₁₃], 49.38 (N-CH₂-CH₂-CH₂-CH₂-CH₂), 63.37 (CH₂-CH₂N), 174.36 ((CH₂)_nCOOR).

Results and discussion

For N-acylation derivatives, there were observed characteristic IR bands for amidic compounds: a sharp absorption band at 1652-1675 cm⁻¹ characteristic to the group -C=O („amide band I”), at 1564-1550 cm⁻¹ for „amide band II”, and at 1298-1360 cm⁻¹ there appeared vibrations of O -C -N, as weak bands, for „amide band III”. The carbonyl group absorption band of amides occurs at lower frequencies than normal carbonyl absorption, due to the resonance effect. [6, 18] After N-acylation, the bands corresponding to -C=O group from diethyl-4-azasebacate (at 1738 cm⁻¹) and from stearoyl chloride (1780 cm⁻¹) disappeared and there could be observed an intense absorption band at 1652-1675 cm⁻¹ corresponding to the carbonyl stretching of amide band I. For N-alkylation derivatives there were observed intense bands at 1736-1739 cm⁻¹ assigned to -C=O group from -COOH or -COOR and in region 1374-1465 cm⁻¹ there appeared bands specific to -C -O groups [6, 19]. In domains 2971-2920 cm⁻¹ and 2851-2855 cm⁻¹ there appeared -CH₂ and -CH₃ specific stretch vibrations.

UV-VIS analysis of N-acylation derivatives showed an intense band from 230-232 nm, characteristic to -C=O amidic group, for n→π* transitions [6,13]. For N-alkylation derivatives, there were observed characteristic bands to -C=O group from -COOH or -COOR groups, in domain 198-232 nm, due to n→π* transitions.

NMR spectra of N-acylation and N-alkylation compounds confirmed also their structure, as the assignments showed. For N-acylation compounds, there were observed intense signals as multiplets, in the domain 1.23-1.33 ppm, because of protons from -(CH₂)₁₆ and -(CH₂)₁₄. For N-alkylation derivatives there were also observed signals as multiplets for protons from -(CH₂)₁₃ and -(CH₂)₁₇, in the domain 0.89-0.99 ppm. Carboxylic protons for N-stearoyl and N-palmitoyl 4-azasebacic acid, N-cetyl and N-stearyl 4-azasebacic acid presented signals as singlet, in domain 12.04 -12.35 ppm, the characteristic region for this type of protons [6]. At the frequency of 300 MHz some methylene groups are overlapped like N-CH₂-CH₂-CH₂-CH₂-CH₂; these protons are strongly coupled and they action as a conglomerate of spins. For N-acylation derivatives of diethyl-4-azasebacate, methylene protons linked to -COO group are deshielded. For N-acylation derivatives, the signal of the proton from nitrogen (-NH group) at 2.97 ppm disappeared, because of amidation process.

In ¹³C-NMR spectra of N-acylation derivatives, because of nitrogen and carbon atoms from -(CH₂)_n (n=14,16) groups, the chemical shift for carbon in C=O-N is 132.92 - 134.09 ppm, with a difference of about 30-35 ppm compared to an esteric group [6]. In N-acyl and N-alkyl 4-azasebacic acid derivatives carbon atoms from carboxylic groups give characteristic signals at 173.01 -174.81 ppm. All carbon atoms from -(CH₂)_n groups in these compounds give signals in the interval 28.01 - 29.89 ppm, as multiplets. Carbon atoms from -C=O groups give signal in domain

Table 1
MAIN PROPERTIES OF THE SYNTHESIZED COMPOUNDS

Compound	TLC (R _f)	m.p. (°C)	Elemental analysis	
			Calculated (%)	Found (%)
N-stearoyl 4-azasebacic acid	0,51	84-85	C 68.27%, H 11.15%, N 3.06%	C 68.35%, H, 11.13%, N 3.19%,
N-palmitoyl 4-azasebacic acid	0,46	80-81	C 70.24%, H 10.73%, N 3.41 %	C 70.12%, H 10.88%, N 3.47%
N-stearoyl diethyl-4-azasebacate	0.55	75-76	C 69.90%, H 11.84%, N 2.71%	C 69.77%, H 11.72%, N 2.59%
N-palmitoyl diethyl-4-azasebacate	0,61	78-79	C 72.35% , H 11.43% , N 2.91%	C 72.84 % , H 11.93 % , N 2.82 %
N-cetyl 4-azasebacic acid	0,58	62-63	C 69.00%, H 11.50%, N 3.50%	C 68.53%, H 11.16%, N 3.23%
N-stearyl-4-azasebacic acid	0,56	65-66	C 71.05%, H11.84%, N 3.07%	C 70.72%, H 11.04%, N 3.11%
N-cetyl diethyl-4-azasebacate	0,64	67	C 72.62 % , H 9.83% , N 3.13%	C 72.44 % , H 9.58% , N 3.21%

Compound	Assignments, ν_{\max} (cm^{-1})			
	ν (C=O)	ν (C–O) sym., assym.	ν (CH ₂), ν (CH ₃), assym., sym.	δ (CH ₂), δ (CH ₃)/ γ (CH ₂), γ (CH ₃)
N-stearoyl 4-azasebacic acid	1695 ("amide band I")	1087 1044	2913 2847	941 723
N-palmitoyl 4-azasebacic acid	1699, ("amide band I")	1085 1042	2922 2842	934 798
N-stearoyl diethyl-4-azasebacate	1730 (esteric band) 1704 ("amide band I") 1469 (–N–C=O, "amide band II")	1376 ("amide band III") 1103	2920 2851	945
N-palmitoyl diethyl- 4-azasebacate	1736 (esteric band) 1703 ("amide band I") 1463, (–N–C=O, "amide band II")	1380 ("amide band III") 1178	2914 2848	903 804
N-cetyl 4-azasebacic acid	1736	1274 1215	2971 2851	879
N-stearyl-4-azasebacic acid	1739	1265	2963 2855	808
N-cetyl diethyl-4-azasebacate	1738	1465 (–C–O esteric band); 1200	2920 2851	898 797

Table 2
IR CHARACTERIZATION (4000-400
 cm^{-1}) OF SYNTHESIZED
COMPOUNDS

Table 3
UV-VIS CHARACTERIZATION OF SYNTHESIZED COMPOUNDS

Compound	λ (nm)	Assignment
N-stearoyl 4-azasebacic acid	232	$n \rightarrow \pi^*$ (C=O)
N-palmitoyl 4-azasebacic acid	230	$n \rightarrow \pi^*$ (C=O)
N-stearoyl diethyl-4-azasebacate	231	$n \rightarrow \pi^*$ (C=O)
N-palmitoyl diethyl-4-azasebacate	230	$n \rightarrow \pi^*$ (C=O)
N-cetyl 4-azasebacic acid	198	$n \rightarrow \pi^*$ (C=O)
N-stearyl-4-azasebacic acid	230	$n \rightarrow \pi^*$ (C=O)
N-cetyl diethyl-4-azasebacate	202 232	$n \rightarrow \pi^*$ (C=O)

150-185 ppm [6]; substituents and electrons spinning effects are approximately similar to those of ketones. Alkyl substituents at nitrogen atoms in amides give rise to a small displacement to right for the carbon atom signal of carbonyl group, at about 180 ppm.

Elemental analyses results correspond to proposed structures for the synthesized derivatives (table 1).

Conclusions

There have been synthesized 7 new N-acylation and N-alkylation derivatives of 4-azasebacic acid and diethyl 4-azasebacate.

Due to the simple method of synthesis in the presence of pyridine, the undesired secondary reactions do not appear, this fact being demonstrated by the results of the thin layer chromatography and of the spectrophotometric analyses.

The purification of the synthesized compounds is very simple and also, it is not expensive.

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