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Alkylation of Cyclic Mannich Bases, Derivatives of Thiourea and Simple Amino Acids

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Abstract—Aminomethylation of thiourea with aqueous formaldehyde and simple amino acids (glycine, β-alanine, γ-aminobutyric acid) have resulted in the formation of (4-thioxo-1,3,5-triazinan-1-yl)-substituted acetic, propionic, and butyric acids, respectively. By alkylation of these compounds corresponding *S*-methyl and *S*-ethyl iodides were obtained, and by the action of *tert*-butylamine, the corresponding salts. The same salts were obtained by the reaction of amine exchange between 5-*tert*-butyl-1,3,5-triazinan-2-thione and these amino acids in water. As a result of neutralization of *S*-methyl iodides with *tert*-butylamine in 2-propanol or aqueous 2-propanol zwitterionic [4-(methyl-sulfanyl)-3,6-dihydro-1,3,5-triazin-1(2*H*)-yl] derivatives of these acids were isolated. From aqueous solutions of *S*-methyl iodides and *tert*-butylamine ion associates of the corresponding zwitter-ions and *tert*-butylammonium iodide have crystallized. The same associates have formed at treating *S*-methyl iodides with *tert*-butylamine or diethylamine in the absence of a solvent.

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It was shown in [1] that 3-*tert*-butyl-6-(methylsulfanyl)-1,2,3,4-tetrahydro-1,3,5-triazine hydroiodide enters in the amine exchange reaction with glycine and β-alanine. In the case of glycine the final product of the exchange, [4-(methylsulfanyl)-5,6-dihydro-1,3,5-triaz-3-inium-1(2*H*)-yl] acetate, was isolated from the reaction mixture of transamination in the individual form. In this paper we describe the independent synthesis of this compound and its homologs by aminomethylation of thiourea with aqueous formaldehyde and simple amino acids and the subsequent methylation of thus obtained cyclic Mannich bases with methyl iodide followed by the neutralization of the resulting isothiuronium salts with *tert*-butylamine.

The scientific literature contains no data on the aminomethylation of thiourea (**I**) with amino acids as the amino component. There are a number of patents [2–6] describing use of cyclic Mannich bases **IIa–IIc**, the derivatives of thiourea and amino acids, as stabilizers of silver halide emulsion layers of the material for color photography, silver halide solvents for a photographic developer compositions and toners, the components of thermographic and photothermographic materials. The patent [2], which refers to several other patents and the work [7], describes a general method for the preparation of these compounds, but none of these sources does not contain their characteristics.

Indeed, as in the case of aminomethylation using simple aliphatic amines [7], thiourea (**I**) in aqueous formaldehyde easily enters into a similar reaction with the simplest amino acids like glycine, β-alanine, and γ-aminobutyric acid forming well-crystallized Mannich bases **IIa–IIc**. Probably, this reaction may be used to protect amino groups in peptide synthesis, just as it is suggested to do with the use of urea and formaldehyde [8].

In acetone or 2-propanol Mannich bases **IIa–IIc** readily in nearly quantitative yield are alkylated with simple alkyl halides forming a well-crystallized isothiuronium salts **IIIa–IIIc, IVa–IVc**. In 2-propanol or 2-propanol–water the action of an equivalent amount of *tert*-butylamine on the *S*-methyl iodides **IIIa–IIIc** converts the latter into zwitterionic structures **Va–Vc**, the first of which (**Va**) was obtained by us earlier as a result of "recrystallization" of its ion-associate with *tert*-butilammonium iodide (**VIa**), and by transamination of *tert*-butylamine analog of compound **IIIa** with glycine in 2-propanol or ethanol [1]. So, after neutralization with *tert*-butylamine of slightly heated solution of compound **IIIa** in aqueous 2-pro-

panol and subsequent cooling of the neutralized solution it crystallizes as a dihydrated zwitter-ion **Va**·$2H_2O$.

The zwitter-ion **Vc** can be isolated also by treating the corresponding ionic associate **VIc** with 2-propanol, that is, actually by washing out the *tert*-butylammonium iodide from the zwitter-ion **Vc** with this solvent.

From aqueous solutions of isothiuronium salts **IIIa–IIIc** mixed in equimolar ratio with *tert*-butylamine after complete evaporation of water the ion associates crystallized of the respective zwitter-ions **Va–Vc** and *tert*-butylammonium iodide, a kind of "quadrupole" **VIa–VIc**, which had been obtained earlier in the reaction of amine exchange (transamination) from the 3-*tert*-butyl-6-(methylsulfanyl)-1,2,3,4-tetrahydro-1,3,5-triazine hydroiodide and the corresponding amino acid in water [1].

We attempted to perform aminolysis of the isothiuronium derivatives **IIIb, IIIc** under mild conditions by keeping them at room temperature in the medium of the aliphatic amine: for 5 min in the case of derivatives **IIIb, IIIc** and *tert*-butylamine and for 2 h in the case of the derivative **IIIb** and diethylamine. In all three cases corresponding ion associates **VIb–VId** were identified. In the first two cases we confirmed the formation of associates **VIb, VIc** by coincidence of spectral characteristics of the samples isolated from the reaction mixture of aminolysis with those of the samples of compounds **VIb, VIc** obtained earlier in [1] and (or) in this study by the above way. In the third case the formation of ionic associate **VId** is suggested by analogy and needs to be confirmed by X-ray diffraction data, but we have not succeeded yet to grow a single crystal required for the XRD study.

At the attempted aminolysis of the glycine derivative **IIIa** by *tert*-butylamine, in the solid residue of the reaction mixture, alongside ionic associate **VIa** also another compound was detected by ^{1}H NMR spectroscopy. We failed to separate these two substances. Judging from the integral intensity of the signals in the NMR spectrum, it is presumable that this substance, formed in a twice less amount than associate **VIa**, is a cyclic urea, similar to cyclic thiourea **IIa**.

These results indicate that basicity of the aliphatic amine used is insufficient for the dehydroiodination of the isothiuronium salts **IIIa–IIIc**.

It was found in [1] that in the ^{1}H NMR spectra of DMSO solutions of zwitter-ion **Va** and its ionic associate with *tert*-butilammonium iodide **VIa** there was a difference in positions of the signals of methyl and cyclic methylene groups, obviously due to ionic interactions in the associate. Similar difference occurs in the spectra of the solutions of zwitter-ion **Vb** and its ionic associate with *tert*-butylammonium iodide **VIb** as well as zwitter-ion **Vc** and its ionic associate with *tert*-butylammonium iodide **VIc.** In the spectra of ionic associate **VIb** the signals of these groups are shifted by 0.08–0.09 ppm compared with the zwitter-ion **Vb**, while for the ionic associate **VIc** the shift is 0.04 ppm compared with zwitter-ion **Vc**, in both cases upfield.

Treating the cyclic thioureas **IIa–IIc** with *tert*-butylamine in ethanol results in the salts **VIIa–VIIc**. The salts **VIIa, VIIb** can be obtained in another way, in the reaction of the corresponding amino acid with the cyclic thiourea **VIII** in water that indicates the occurrence under these conditions of the reaction of amine exchange (transamination). A similar reaction between compound **VIII** iodomethylate and amino acids in water has been described earlier [1]. The driving force of amine exchange in these cases, in addition to protonation of *tert*-butylamine is, apparently, the fact that compound **VIII** and its iodomethylate bearing bulky substituents are less stable than compounds **II** and **V**, respectively, stabilized either by intramolecular hydrogen bonding and salt formation or by Coulomb interaction and ionic association, respectively.

The action of γ-aminobutyric acid on cyclic thiourea **VIII** in water also results in transamination, but in contrast to similar reactions with glycine and β-alanine, where the products of amine exchange **IIa, IIb** could be isolated only in the form of *tert*-butylammonium salts **VIIa**, **VIIb**, in this case, the product of amine exchange **IIc** precipitates directly from the reaction solution as large crystals, without binding with the *tert*-butylamine.

Salt **VIIc** at the attempted recrystallization from 96% ethanol hydrolyzed to the cyclic thiourea **IIc**. It was shown in [1] that iodomethylates **VI** behave similarly turning into zwitter-ions **V** at the recrystallization from aqueous 2-propanol.

In 85% aqueous ethanol cyclic thiourea **VIII** does not undergo the amine exchange with amino acids, and can be identified unchanged in the dry residue of the reaction mixture (according to NMR spectrum of its solution in DMSO-d_6).

The structure of **IIa** is a six-membered heterocycle that forms an *envelope*, whose five atoms, including the sulfur atom, lie in one plane and the N^1 atom is out

Table 1. Bond lengths (*d*) and bond angles (ω) in compound **IIa**

Bond	*d*, Å	Angle	ω, deg
S^1–C^4	1.713(4)	$C^4N^2C^3$	123.1(3)
N^2–C^4	1.330(5)	$C^5N^1C^3$	108.0(3)
N^2–C^3	1.472(5)	$C^2N^1C^3$	112.9(3)
O^1–C^1	1.202(5)	$C^2N^1C^5$	112.2(3)
O^2–C^1	1.325(4)	$C^5N^3C^4$	121.4(3)
N^1–C^5	1.459(5)	$N^2C^4S^1$	120.4(3)
N^1–C^2	1.457(5)	$N^3C^4S^1$	121.3(3)
N^1–C^3	1.453(5)	$N^3C^4N^2$	118.3(3)
N^3–C^4	1.324(5)	$O^1C^1C^2$	125.0(3)
N^3–C^5	1.462(5)	$O^2C^1C^2$	110.7(3)
C^1–C^2	1.508(5)	$O^2C^1O^1$	124.3(3)
		$N^3C^5N^1$	110.6(3)
		$N^1C^2C^1$	112.5(3)
		$N^1C^3N^2$	110.4(3)

of the plane, so that the N^1–C^2 bond is almost perpendicular to the plane. The plane of the carboxy group is almost perpendicular to the plane of the heterocyclic fragment. The oxygen atoms of the carboxy group (hydrogen atom at O^2 of the carboxy group is not localized), the sulfur atom and all nitrogen atoms of the heterocycle are involved into the intermolecular hydrogen bonding.

The length of S^1=C^4 bond is 1.713 Å (Table 1), intermediate between those for double (1.61 Å) and single bonds (1.81 Å) [9]. The same, but to a lesser extent, is characteristic of the bonds N^2–C^4 (1.330 Å) and N^3–C^4 (1.324 Å) (the C=N and C–N bond lengths are 1.27 and 1.47 Å, respectively [9]). This indicates a significant contribution of the thiol canonical form with separate charges into the structure of the compound **IIa**, in other words, a significant shift occurs of electron density from the nitrogen atoms N^2 and N^3 to the sulfur atom. This, in turn, leads to a significant decrease in the basicity of the nitrogen N^1 (due to the destabilization of the form protonated at the atom N^1 and the stabilization of the non-protonated form) and explains the existence of the glycine fragment of compound **IIa** in a neutral, rather than zwitter-ionic form, as show the bond lengths O^1=C^1 1.202 Å and O^2–C^1 1.325 Å (1.22 Å for C=O and 1.43 Å for C–O [9]). Some shortening of the O^2–C^1 bond is due to the hydrogen bonding C^1–O^2H···S^1=C^4 (Fig. 1).

The six-membered heterocycle conformation in the structure **IIIa**·H_2O, is an *envelope*, like in the case of compound **IIa**, with the N^1 atom significantly deviated out of the plane of the rest ring atoms. Just as in the structure **IIa**, the N^1–C^2 bond is almost perpendicular to the flat fragment of the ring. Neighboring molecules are connected in pairs by hydrogen bonds (the O^2···O^1 distance is 2.645 Å) through the carboxy groups in the dimeric fragments. In addition, the oxygen O^1 of the carboxy group is involved in hydrogen bonding with the oxygen of the hydration water O^3. The O^3 atom is involved in an intermolecular hydrogen bond with the H atom at the nitrogen N^3 (the hydrogen atom at the O^2 atom of the carboxy group and one of the hydrogens at the oxygen of hydration water O^3 are not localized). Thus, the hydration water molecules combine the dimeric fragments by hydrogen bonds into the endless bands, which, in turn, are combined by van der Waals contacts in the three-dimensional framework. Iodide ion is linked by a hydrogen bond with N^2 atom of the heterocycle. In contrast to structure **IIa**, in the structure **IIIa**·H_2O in the hydrogen bonds only two nitrogen atoms of the heterocycle are involved (Fig. 2).

The bonds N^2–C^4 1.32 Å and N^3–C^4 1.29 Å (Table 2) are almost double bonds, and their asymmetry is due to the involvement of the nitrogen atoms N^2 and N^3 in various hydrogen bonds, N^2H···I and N^3H···O^3 (Table 3). What has been said about non-zwitter-ionic structure of the glycine fragment of compound **IIa** is even more true for the glycine fragment of compound **IIIa**, because the positive charge of its isothiuronium fragment even more stabilizes the non-protonated form and destabilizes the form protonated at the N^1 atom (second protonation of the ring). The bond lengths in the carboxy fragment O^1=C^1 1.21 Å and O^2–C^1 1.32 Å do not differ from those in the compound **IIa**. The O^2–C^1 bond is also shortened due to the hydrogen bond C^1–O^2H···O^1=C^1 (Table 3).

The XRD study of compounds **Va**, **VIa** [1], and **IIIa** showed that these glycine derivatives crystallize as mono- or dihydrates. The presence of hydration water in the samples is also seen in the appearance of the respective vibration bands in the IR spectra. For β-alanine and γ-aminobutyric homologues of these compounds, as well as for iodoethylates **IVa–IVc**, which were not studied by XRD, the conclusion about

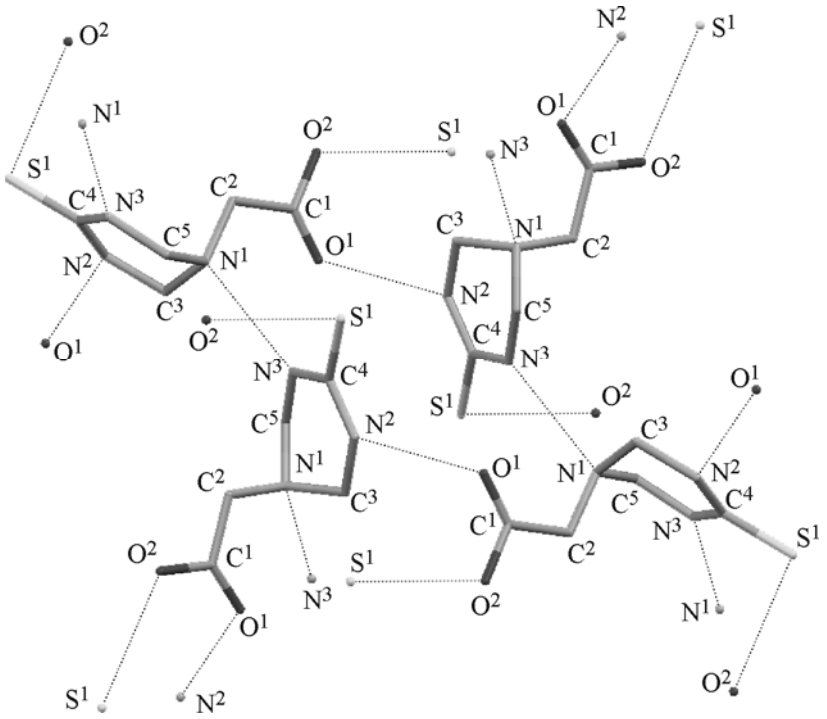


Fig. 1. Structure of the molecule and the hydrogen bonds in the crystal of **IIa** by X-ray diffraction data.

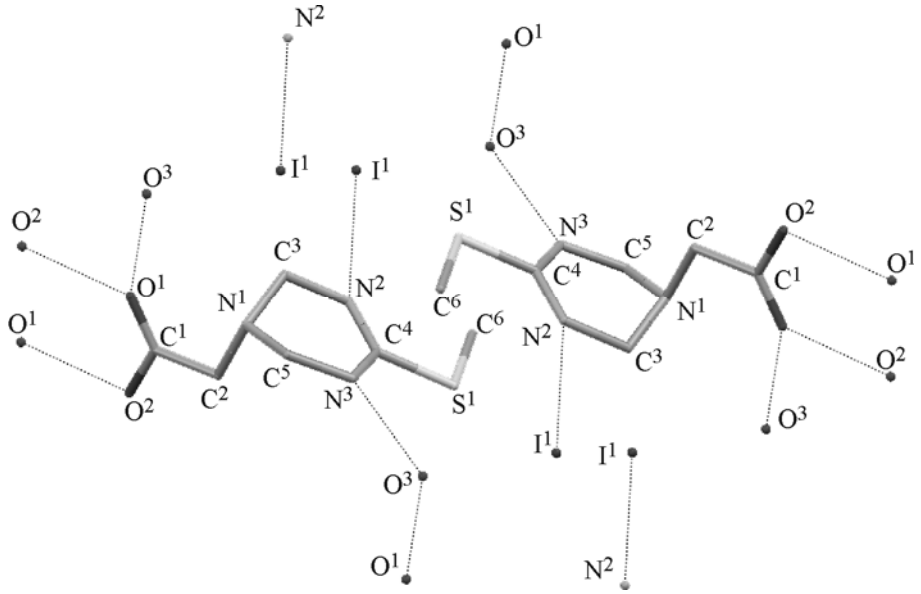


Fig. 2. Structure of the molecule and the hydrogen bonds in the crystal of **IIIa**·H_2O by X-ray diffraction data.

the presence or absence of hydration water in samples was made on the basis of elemental analysis, and by comparison of shortwave regions of their IR spectra with the corresponding regions of the IR spectra of the hydrates **Va**·$2H_2O$, **VIa**·H_2O, and **IIIa**·H_2O.

According to elemental analysis, the samples of compounds **IIIb**, **IIIc** and **IVa–IVc** do not contain water. The non-hydration nature of the iodomethylates **IIIb**, **IIIc** and iodoethylates **IVa–IVc** is consistent with the fact that their IR spectra do not include the

Table 2. Bond lengths (*d*) and bond angle (ω) in compound **IIIa**·H_2O

Bond	*d*, Å	Angle	ω, deg
$S^1–C^4$	1.77(1)	$C^6S^1C^4$	102.5(6)
$S^1–C^6$	1.79(1)	$C^4N^2C^3$	119.0(9)
$N^2–C^4$	1.32(1)	$C^5N^1C^3$	109(1)
$N^2–C^3$	1.49(1)	$C^2N^1C^3$	112.8(9)
$O^1–C^1$	1.21(1)	$C^2N^1C^5$	112.8(8)
$O^2–C^1$	1.32(2)	$C^5N^3C^4$	120(1)
$N^1–C^5$	1.44(2)	$N^2C^4S^1$	120.7(8)
$N^1–C^2$	1.47(2)	$N^3C^4S^1$	116.3(8)
$N^1–C^3$	1.44(2)	$N^3C^4N^2$	122(1)
$N^3–C^4$	1.29(2)	$O^1C^1C^2$	125(1)
$N^3–C^5$	1.49(2)	$O^2C^1C^2$	112(1)
$C^1–C^2$	1.49(2)	$O^2C^1O^1$	122(1)
		$N^3C^5N^1$	111.8(9)
		$N^1C^2C^1$	111.4(9)
		$N^1C^3N^2$	111.1(8)

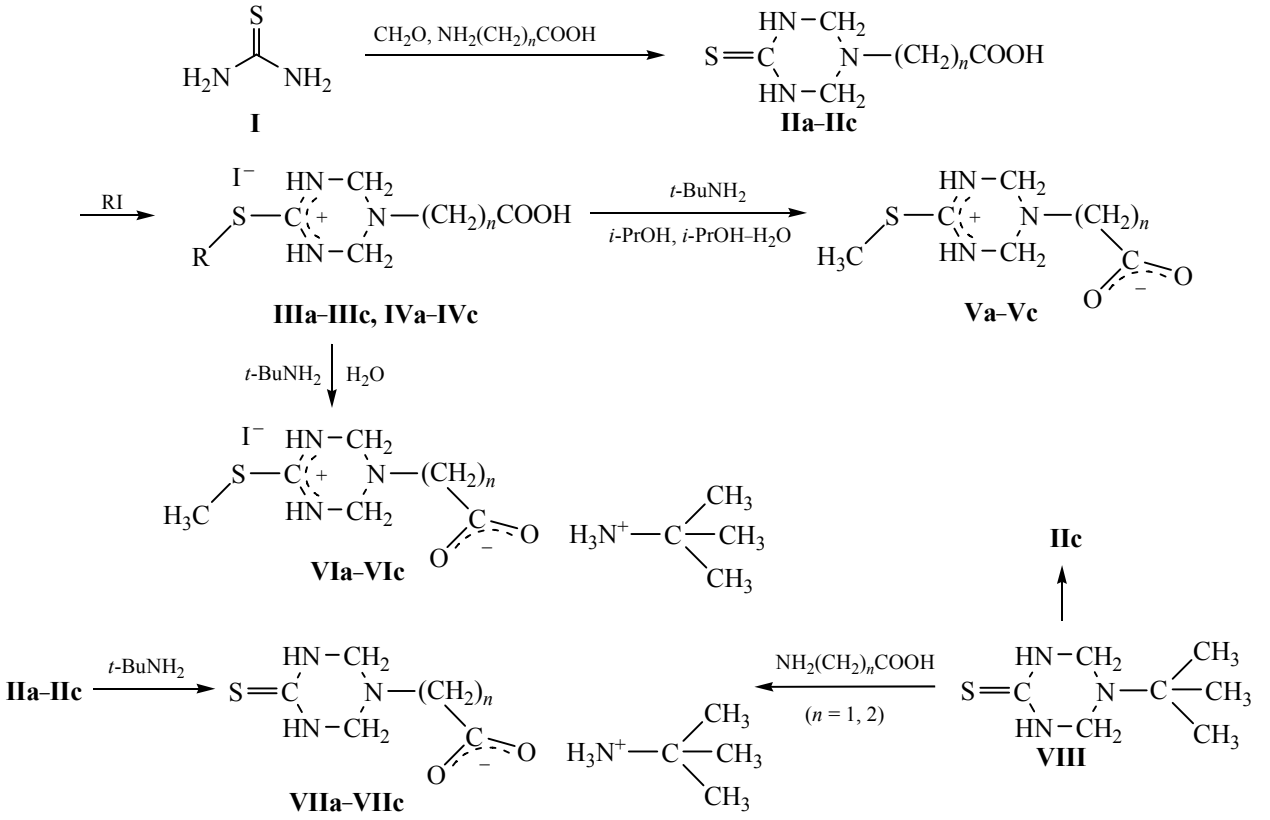
Table 3. Parameters of hydrogen bonds in the crystal of **IIIa**·H_2O

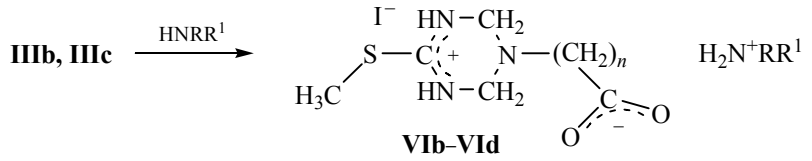
Bond (D–H···A)	*d* (D···A), Å
$O^2···O^1$	2.645
$O^3···O^1$	2.853
$N^3···O^3$	2.803
$N^2···I$	3.516
$O^3···I^a$	3.522

[a] Not shown in Fig. 2.

absorption bands characteristic of stretching vibrations of hydration water, whereas in the IR spectrum of the hydrated iodomethylate **IIIa**·H_2O (XRD data) it is detected by an intense ν(O–H) band at 3510 cm^{-1}.

The results of elemental analysis of the zwitter-ions **Vb**, **Vc** indicate their dihydrate structure. The presence in the IR spectra of these compounds of broad low intensity bands at 3425 and 3432 cm^{-1}, respectively, does not contradict this conclusion, since in the IR spectrum of the zwitter-ion **Va**·$2H_2O$, whose dihydrate structure is unambiguously determined by XRD study





VIb–**VId**

n = 1 (**a**), 2 (**b**), 3 (**c**); **III**, R = CH_3; **IV**, R = C_2H_5; **VIb**, *n* = 2, R = H, R^1 = *t*-Bu; **VIc**, *n* = 3, R = H, R^1 = *t*-Bu; **VId**, *n* = 2, R = R^1 = Et.

[1], the absorption of hydration water appears as a broad intense band ν(O–H) at 3380 cm^{-1}.

The IR spectrum of the associate **VIa** with determined by X-ray data hydrate structure [1] includes a strong band at 3466 cm^{-1}, which can be attributed to the stretching vibrations of O–H bonds of the hydration water. In the IR spectra of compounds **VIb**, **VIc** such a characteristic band is not observed, but there are broad bands of moderate intensity in the range 3430–3440 cm^{-1}. It is impossible to attribute them definitely to vibrations of the O–H or N–H bonds. Elemental analysis indicates anhydrous (non-hydrated) form of compound **VIb** and hydrated form of **VIc**.

EXPERIMENTAL

^{1}H NMR spectra were recorded on a Bruker AM-400 (400 MHz) and Bruker AM-200 (200 MHz) instruments, solvents DMSO-d_6 and D_2O. IR spectra were recorded on a Shimadzu FTIR-8400S spectrophotometer from KBr tablets. Elemental analysis was performed on a Leco CHNS (O) 942 analyzer. TLC was performed on Silufol UV-254 plates, eluent chloroform–ethanol, 1:10. Acetone (commercial) was dried and purified by the method of [10]. 2-propanol of chemically pure grade was used without purification.

The XRD analysis was performed on a single-crystal automatic diffractometer IPDS 2T STOE (MoK_α-radiation). The structure was solved and refined using the SIR software package.

The structure **IIa** crystallizes in the monoclinic system, space group $P2_1/c$, cell dimensions: *a* 7.138(2), *b* 9.118(2), *c* 12.268(3) Å, β 102.26(2)°, *V* 780.25(34), *Z* 4. A set of 1080 reflections ($F > 4\sigma$), collected in the angular range 2θ 0–60, was obtained from a colorless crystal of the size 0.27×0.32×0.41 mm, *R* 0.42.

The structure **IIIa**·H_2O crystallizes in the triclinic space group $P\bar{1}$, cell dimensions: *a* 8.014(2), *b* 8.657(2), *c* 9.562(2) Å, α 91.68(2), β 105.11(2), γ 105.89(3)°, *V* 612.40(26), *Z* 2. A set of 2121 reflections ($F > 4\sigma$), collected in the angular range 2θ 0°–60°, was obtained from a colorless crystal of the size 0.22×0.24×0.37 mm, *R* 0.64.

Images of crystal structures were obtained using the Mercury 2.2 [11] and Chem3D Ultra 10.0 software.

(4-Thioxo-1,3,5-triazinan-1-yl)acetic acid (IIa). To a mixture of 7.61 g (100 mmol) of thiourea and 15.0 ml of 37% aqueous formaldehyde (186.7 mmol) was added at vigorous stirring 7.51 g (100 mmol) of glycine, and stirring was continued for another 15 min until it dissolved. A day latter, the precipitate was filtered off and recrystallized from a mixture of 2-propanol–water (1:1). Yield 13.40 g (76.5%), mp 176–178°C. IR spectrum (thin film), ν, cm^{-1}: 1550 (C–N, δ_{NH}), 1721 (C=O), 2484, 2618 (NH), 2889, 2934 (CH_2), 3063, 3205 (NH), 3379 (OH). ^{1}H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm: 3.31 s (2H, CH_2COO), 4.04 s (4H, C^2H_2, C^6H_2), 7.98 s (2H, N^3H, N^5H), 12.40 s (1H, COOH). Found, %: C 34.86, H 5.14; N 24.46. $C_5H_9N_3O_2S$. Calculated, %: C 34.28; H 5.18; N 23.98.

3-(4-Thioxo-1,3,5-triazinan-1-yl)propanoic acid (IIb) was prepared similarly. Yield 16.30 g (86.1%), mp 116–118°C. IR spectrum (thin film), ν, cm^{-1}: 1554 (C–N, δ_{NH}), 1692 (C=O), 2556, 2614 (NH), 2888, 2932 (CH_2), 3214, 3278 (NH), 3363 (OH). ^{1}H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm: 2.37 t (2H, $NCH_2C\underline{H}_2COO$, *J* 6.9 Hz), 2.76 t (2H, $NC\underline{H}_2CH_2COO$, *J* 6.9 Hz), 3.98 s (4H, C^2H_2, C^6H_2), 7.94 s (2H, N^3H, N^5H). Found, %: C 38.46, H 6.39; N 21.72. $C_6H_{11}N_3O_2S$. Calculated, %: C 38.08; H 5.86; N 22.21.

4-(4-Thioxo-1,3,5-triazinan-1-yl)butanoic acid (IIc). *a*. The preparation was the same as for compound **IIa**. Yield 14.80 g (72.8%), mp 148–152°C. IR spectrum (thin film), ν, cm^{-1}: 1540 (C–N), 1560 (δ_{NH}), 1698 (C=O), 2503, 2587, 2633 (NH), 2884, 2946, 3075 (CH_2), 3174, 3288 (NH), 3380 (OH). ^{1}H NMR

spectrum (400 MHz, DMSO-d_6), δ, ppm: 1.66 m (2H, $NCH_2C\underline{H_2}CH_2COO$), 2.22 t (2H, $NCH_2CH_2C\underline{H_2}COO$, *J* 6.9 Hz), 2.53 t (2H, $NC\underline{H_2}CH_2CH_2COO$, *J* 6.9 Hz), 3.97 s (4H, C^2H_2, C^6H_2), 7.91 s (2H, N^3H, N^5H), 11.87 s (1H, COOH). Found, %: C 41.87, H 6.35; N 21.32. $C_7H_{13}N_3O_2S$. Calculated, %: C 41.36; H 6.45; N 20.67.

b. Hydrolysis of salts **VIIc**. 1.319 g (4.77 mmol) of compound **VIIc** was boiled a few min in 5 ml of 96% ethanol, the solution was cooled, and the precipitate was filtered off. Yield 0.732 g. Crystallization was repeated once more, mp 157–158°C. IR spectrum (thin film), ν, cm^{-1}: 1539 (C–N), 1561 (δ_{NH}), 1702 (C=O), 2505, 2583, 2626 (NH), 2886, 2945, 3072 (CH_2), 3178, 3290 (NH), 3381 (OH). ^{1}H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm: 1.67 m (2H, $NCH_2C\underline{H_2}$· CH_2COO), 2.24 t (2H, $NCH_2CH_2C\underline{H_2}COO$, *J* 7.4 Hz), 2.54 t (2H, $NC\underline{H_2}CH_2CH_2COO$, *J* 6.9 Hz), 3.98 s (4H, C^2H_2, C^6H_2), 7.95 s (2H, N^3H, N^5H .) Found, %: C 40.77, H 6.00; N 20.09. $C_7H_{13}N_3O_2S$. Calculated, %: C 41.36; H 6.45; N 20.67.

c. From 1,733 g (10 mmol) of compound **VIII** in 30 ml of water and 1.031 g (10 mmol) of γ-amino butyric acid in 10 ml of water at 45°C similarly to the preparation of compounds **VIIa** and **VIIb** by the method *b* (see below). 15 min after mixing the reagents dissolved. The reaction mixture was left at room temperature. In 2 days large crystals precipitated, which were washed with water and dried first in air and then in a vacuum desiccator over $CaCl_2$. Yield 1.323 g (65.1%), mp 163–167°C. IR spectrum (thin film), ν, cm^{-1}: 1540 (C–N), 1560 (δ_{NH}), 1702 (C=O), 2518, 2583, 2628 (NH), 2884, 2946, 3072 (CH_2), 3171, 3289 (NH), 3375 (OH). ^{1}H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm: 1.66 m (2H, $NCH_2C\underline{H_2}$· CH_2COO), 2.23 m (2H, $NCH_2CH_2C\underline{H_2}COO$), 2.53 m (2H, $NC\underline{H_2}CH_2CH_2COO$), 3.98 s (4H, C^2H_2, C^6H_2), 7.92 s (2H, N^3H, N^5H), 11.79 br.s (1H, COOH). Found, %: C 40.70, H 6.09; N 20.20. $C_7H_{13}N_3O_2S$. Calculated, %: C 41.36; H 6.45; N 20.67.

3-(2-Carboxyethyl)-6-(methylsulfanyl)-2,3,4,5-tetrahydro-1,3,5-triazin-1-ium iodide (IIIa), **hydrate**. To a mixture of 1.750 g (9.99 mmol) of compound **IIa** and 30 ml of 2-propanol under vigorous stirring was added at room temperature 2.1 ml (4.786 g, 33.72 mmol) of methyl iodide. The precipitate of the starting material completely dissolved, but after 30 min on the flask wall started to form precipitate of the product. A day latter, the resulting precipitate was filtered off and washed with a small amount of 2-propanol. Yield 3.2 g (60.6%), mp 160–162°C (2-propanol). IR spectrum (thin film), ν, cm^{-1}: 1565, 1602 (C–N, δ^+_{NH}), 1706 (C=O, δ^+_{NH}), 2929, 2978 (CH_2, CH_3), 3048, 3148, 3173, 3254 (NH), 3403 (OH), 3510 (H_2O). ^{1}H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm: 2.57 s (3H, CH_3), 3.45 s (2H, CH_2COO), 4.41 s (4H, C^2H_2, C^4H_2), 9.90 br.s (NH, OH). Found, %: C 22.07, H 4.14, N 13.08. $C_6H_{12}IN_3O_2S{\cdot}H_2O$. Calculated, %: C 21.50; H 4.21; N 12.54.

3-(2-Carboxyethyl)-6-(methylsulfanyl)-2,3,4,5-tetrahydro-1,3,5-triazin-1-ium iodide (IIIb). *a*. To a mixture of 1.890 g (9.99 mmol) of compound **IIb** and 30 ml of acetone under vigorous stirring at room temperature was added 2.1 ml (4.786 g, 33.72 mmol) of methyl iodide. The starting material completely dissolved, but after 30 min on the flask wall started to form a precipitate. After 1 day the precipitated product was filtered off and washed with a small amount of acetone. Yield 2.202 g (63.1%), mp 142–144°C. IR spectrum (thin film), ν, cm^{-1}: 1545, 1597 (C–N, δ^+_{NH}), 1728 (C=O, δ^+_{NH}), 2872, 2923, 2969, 2990 (CH_2, CH_3), 3045, 3110, 3149 (NH), 3351 (OH). ^{1}H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm: 2.47 t (2H, NCH_2CH_2COO, *J* 6.9 Hz), 2.57 s (3H, CH_3), 2.85 m (2H, NCH_2CH_2COO, *J* 6.9 Hz), 4.35 s (4H, C^2H_2, C^4H_2), 9.80 br.s (NH, OH). Found, %: C 25.97, H 4.10; N 13.28. $C_7H_{14}IN_3O_2S$. Calculated, %: C 25.39; H 4.26; N 12.69.

b. To a mixture of 1.890 g (9.99 mmol) of compound **IIb** and 30 ml of 2-propanol under vigorous stirring was added at room temperature 2.1 ml (4.786 g, 33.72 mmol) of methyl iodide. Within 15 min the initial material completely disappeared, and after 10 min the product began to precipitate. After 2 h the precipitate formed was filtered off and washed with a small amount of 2-propanol. Yield 2.35 g (67.3%), mp 140–144°C.

3-(3-Carboxypropyl)-6-(methylsulfanyl)-2,3,4,5-tetrahydro-1,3,5-triazin-1-ium iodide (IIIc). *a*. The preparation was the same as for compound **IIIb** from 2.030 g (9.99 mmol) of compound **IIc** and 2.1 ml (4.786 g, 33.72 mmol) of methyl iodide in 30 ml of acetone. Yield 2.226 g (64.5%), mp 98–100°C. IR spectrum (thin film), ν, cm^{-1}: 1546, 1596 (C–N, δ^+_{NH}), 1697 (C=O, δ^+_{NH}), 2924, 3051 (CH_2, CH_3), 3115, 3151, 3235 (NH), 3446 (OH). ^{1}H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm: 1.73 m (2H, $NCH_2C\underline{H_2}CH_2COO$), 2.26 t (2H, $NCH_2CH_2C\underline{H_2}COO$, *J* 6.9 Hz), 2.57 s (3H,

CH_3), 2.62 t (2H, NC<u>H</u>$_2$CH$_2$CH$_2$COO, *J* 6.9 Hz), 4.34 s (4H, C^2H_2, C^4H_2), 9.78 br.s (NH, OH). Found, %: C 28.35, H 4.55; N 12.71. $C_8H_{16}IN_3O_2S$. Calculated, %: C 27.83; H 4.67; N 12.17.

b. The preparation was the same as for compound **IIIb** from 2.030 g (9.99 mmol) of compound **IIc** and 2.1 ml (4.786 g, 33.72 mmol) of methyl iodide in 30 ml of 2-propanol. Yield 2.44 g (70.8%), mp 101–103°C.

3-(Carboxymethyl)-6-(ethylsulfanyl)-2,3,4,5-tetrahydro-1,3,5-triazin-1-ium iodide (IVa). To a solution of 1.750 g (9.99 mmol) of compound **IIa** in 30 mL of ethanol at 45°C under vigorous stirring was added 2.4 ml (4.639 g, 29.8 mmol) of ethyl iodide. The reaction mixture was stirred for 1 h to cool to room temperature. 0.035 g of precipitated glycine was filtered off (data of NMR spectroscopy in D_2O) and the filtrate was placed in a Petri dish to evaporate the solvent. The large yellow crystals formed within a day were washed with 2-propanol, filtered off and dried in a vacuo over $CaCl_2$. Yield 1.101 g (33.3%), mp 110–114°C. IR spectrum (thin film), ν, cm^{-1}: 1562, 1597 (C–N, δ^+_{NH}), 1703, 1719 (C=O, δ^+_{NH}), 2728, 2882, 2960, 2983 (CH_2, CH_3), 3100 3141, 3201 (NH), 3389 (OH). ^{1}H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm: 1.30 t (3H, C<u>H</u>$_3$CH$_2$, *J* 7.4 Hz), 3.15 q (2H, CH$_3$C<u>H</u>$_2$, *J* 7.9 Hz), 3.45 s (2H, CH$_2$COO), 4.43 s (4H, C^2H_2, C^4H_2). Found, %: C 25.02, H 4.26; N 12.36. $C_7H_{14}IN_3O_2S$. Calculated, %: C 25.39; H 4.26; N 12.69.

3-(2-Carboxyethyl)-6-(ethylsulfanyl)-2,3,4,5-tetrahydro-1,3,5-triazin-1-ium iodide (IVb). The preparation was the same as for compound **IIIb** by the method *a* from 1.890 g (9.99 mmol) of compound **IIb** and 2.4 ml (4.639 g, 29.8 mmol) of ethyl iodide. Yield 1.33 g (38.6%), mp 102–105°C. IR spectrum (thin film), ν, cm^{-1}: 1550, 1594 (C–N, δ^+_{NH}), 1724 (C=O, δ^+_{NH}), 2856, 2896, 2946 (CH_2, CH_3), 3019, 3252 (NH) , 3420 (OH). ^{1}H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm: 1.29 t (3H, C<u>H</u>$_3$CH$_2$, *J* 6.9 Hz), 2.47 t (2H, NCH$_2$C<u>H</u>$_2$COO, J 6.4 Hz), 2.82 t (2H, NC<u>H</u>$_2$CH$_2$COO, *J* 6.4 Hz), 3.11 q (2H, CH$_3$C<u>H</u>$_2$, *J* 6.9 Hz), 4.33 s (4H, C^2H_2, C^4H_2), 9.70 br.s (2H, N^1H, N^5H). Found, %: C 28.40, H 4.88; N 12.78. $C_8H_{16}IN_3O_2S$. Calculated, %: C 27.83; H 4.67; N 12.17.

3-(2-Carboxypropyl)-6-(ethylsulfanyl)-2,3,4,5-tetrahydro-1,3,5-triazin-1-ium iodide (IVc). To a mixture of 2.030 g (9.99 mmol) of compound **IIc** and 30 ml of acetone under vigorous stirring at room temperature was added 2.4 ml (4.639 g, 29.8 mmol) of ethyl iodide. After 5 h the starting material completely dissolved. The reaction solution was left to stand at room temperature. After 2 days at the bottom of the flask formed a transparent film, which over 2 days has turned into a solid white precipitate. Yield 1,987 g (55.4%), mp 98–100°C. IR spectrum (thin film), ν, cm^{-1}: 1544, 1601 (C–N, δ^+_{NH}), 1731 (C=O, δ^+_{NH}), 2865, 2924, 2954 (CH_2, CH_3), 3106, 3162 (NH) , 3447 (OH). ^{1}H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm: 1.29 t (3H, C<u>H</u>$_3$CH$_2$, *J* 7.2 Hz), 1.72 m (2H, NCH$_2$C<u>H</u>$_2$·CH$_2$COO), 2.26 t (2H, NCH$_2$CH$_2$C<u>H</u>$_2$COO, *J* 6.9 Hz), 2.60 t (2H, NC<u>H</u>$_2$CH$_2$CH$_2$COO, *J* 6.9 Hz), 3.14 q (2H, CH$_3$C<u>H</u>$_2$, J 7.2 Hz), 4.35 s (4H, C^2H_2, C^4H_2), 9.84 br.s (2H, N^1H, N^5H), 11.91 br.s [1H, C(O)OH]. Found, %: C 30.63, H 4.73; N 12.18. $C_9H_{18}IN_3O_2S$. Calculated, %: C 30.09; H 5.05; N 11.70.

[4-(Methylsulfanyl)-5,6-dihydro-1,3,5-triazin-3-ium-1(2*H*)-yl] acetate (Va) dihydrate. A mixture of 0.317 g (0.946 mmol) of compound **IIIa**·H_2O recrystallized from ethanol, and 0.105 ml (0.073 g, 0.999 mmol) of *tert*-butylamine in 5 ml of 2-propanol–water (9:1) was refluxed at 40–45°C for ~10 min to complete dissolution of compound **IIIa.** The precipitate formed after cooling the reaction mixture was filtered off, washed with a small amount of 2-propanol, and dried in a vacuum desiccator. Yield 0.068 g (31.9%), mp 158–160°C (125°C [1]). IR spectrum (thin film), ν, cm^{-1}: 1589 (C–N, δ^+_{NH}, CO_2^-), 1646 (δ^+_{NH}), 2890, 2931 (CH_2, CH_3), 3193 (NH), 3380 (H_2O). ^{1}H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm: 2.24 (3H, SCH_3), 3.27 s (2H, CH_2COO), 4.13 s (4H, C^2H_2, C^6H_2). Found, %: C 32.58, H 6.54; N 18.68. $C_6H_{11}N_3O_2S·2H_2O$. Calculated, %: C 31.99; H 6.71; N 18.65.

3-[4-(Methylsulfanyl)-5,6-dihydro-1,3,5-triazin-3-ium-1(2*H*)-yl] propanoate (Vb) dihydrate. Prepared similarly from 0.331 g (1.00 mmol) of compound **IIIb** and 0.105 ml (0.0731 g, 1.00 mmol) of *tert*-butylamine. Yield 0.113 g (55.6%), mp 136°C. IR spectrum (thin film), ν, cm^{-1}: 1567, 1595 (C–N, δ^+_{NH}, CO_2^-), 1710 (δ^+_{NH}), 2915, 2973, 3031, 3083 (CH_2, CH_3), 3137, 3425 (NH) ^{1}H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm: 2.37 s (3H, CH_3), 2.41 t (2H, NCH$_2$C<u>H</u>$_2$COO, *J* 7.4 Hz), 2.81 t (2H, NC<u>H</u>$_2$CH$_2$·COO, *J* 7.4 Hz) , 4.19 s (4H, C^2H_2, C^6H_2). Found, %: C 34.60, H 6.82; N 16.96. $C_7H_{13}N_3O_2S·2H_2O$. Calculated, %: C 35.13; H 7.16; N 17.56.

4-[4-(Methylsulfanyl)-5,6-dihydro-1,3,5-triazin-3-ium-1(2*H*)-yl] butyrate (Vc) dihydrate. *a*. The

preparation was the same from 0.345 g (1.00 mmol) of compound **IIIc** in 5 ml of 2-propanol. Yield 0.1058 g (48.7%), mp 140–142°C (2-propanol). IR spectrum (thin film), ν, cm^{-1}: 1569 (C–N, δ^{+}_{NH}), 1612 (CO_2^-), 1721 (δ^{+}_{NH}), 2856, 2912, 2937 (CH_2, CH_3), 3069, 3164, 3252, 3432 (NH). ^{1}H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm: 1.70 m (2H, $NCH_2C\underline{H}_2CH_2COO$), 2.25 t (2H, $NCH_2CH_2C\underline{H}_2COO$, *J* 6.9 Hz), 2.37 s (3H, CH_3), 2.58 t (2H, $NC\underline{H}_2CH_2CH_2COO$, *J* 5.9 Hz), 4.18 s (4H, C^2H_2, C^6H_2). Found, %: C 37.34, H 7.01; N 16.16. $C_8H_{15}N_3O_2S{\cdot}2H_2O$. Calculated, %: C 37.93; H 7.56; N 16.59.

b. To 0.389 g (0.930 mmol) of compound **VIc** was added 30.0 ml of 2-propanol, insoluble precipitate was filtered off and dried in vacuo over $CaCl_2$. Yield 0.111 g (55.0%), mp 142–144°C.

[4-(Methylsulfanyl)-5,6-dihydro-1,3,5-triazin-3-ium-1(2*H*)-yl] acetate associate with *tert*-butylammonium iodide (1:1) (VIa) hydrate. A mixture of 0.335 g (1.000 mmol) of compound **IIIa·H_2O** in 7 ml of water and 0.15 ml (0.104 g, 1,427 mmol) of *tert*-butylamine was stirred for 2 h at room temperature and then poured into a Petri dish for evaporation of the solvent. After 5 days solid shiny single crystals formed, which were dried in vacuo over $CaCl_2$. Yield 0.304 g (74.4%), mp 125–128°C (127–129°C [1]). IR spectrum (thin film), ν, cm^{-1}: 1593 (C–N, δ^{+}_{NH}, CO_2^-), 2884, 2926, 2978 (CH_2, CH_3), 3049 (NH), 3432 (H_2O). ^{1}H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm: 1.25 s [9H, $C(CH_3)$ 3], 2.35 s (3H, SCH_3), 3.20 s (2H, CH_2COO), 4.22 s (4H, C^2H_2, C^6H_2). Found, %: C 29.62, H 5.90; N 13.80. $C_6H_{11}N_3O_2S{\cdot}C_4H_{12}IN{\cdot}H_2O$. Calculated, %: C 29.42, H 6.17; N 13.72.

3-[4-(Methylsulfanyl)-5,6-dihydro-1,3,5-triazin-3-ium-1(2*H*)-yl] propanoate associate with *tert*-butylammonium iodide (1:1) (VIb). *a*. The preparation was the same from 0.348 g (1.051 mmol) of compound **IIIb** and 0.15 ml (0.104 g, 1.427 mmol) of *tert*-butylamine in 3 ml of water. Yield 0.311 g (73.2%), mp 130–133°C (127–130°C [1]). IR spectrum (thin film), ν, cm^{-1}: 1536, 1566 (C–N, δ^{+}_{NH}), 1606 (CO_2^-), 2923, 2967 (CH_2, CH_3), 3160 sh, 3439 (NH). ^{1}H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm: 1.25 s [9H, $C(CH_3)_3$], 2.28 s (3H, SCH_3), 2.33 t (2H, $NCH_2C\underline{H}_2COO$, *J* 7.4 Hz), 2.76 t (2H, $NC\underline{H}_2CH_2COO$, *J* 7.4 Hz), 4.11 s (4H, C^2H_2, C^6H_2). Found, %: C 32.84, H 5.94; N 13.76. $C_7H_{13}N_3O_2S{\cdot}C_4H_{12}IN$. Calculated, %: C 32.68, H 6.23; N 13.86.

b. A mixture of 0.331 g (0.999 mmol) of compound **IIIb** and 10 ml of *tert*-butylamine was stirred with a magnetic stirrer at room temperature to form a gelatinous slurry. After 5 min the suspension was transferred to a Petri dish for evaporation of the amine. After 3 days the solid residue was crushed and dried in a vacuum. Yield 0.318 g (79.4%), mp 121–124°C (127–130°C [1]). IR spectrum (thin film), ν, cm^{-1}: 1536, 1562, 1583 (C–N, δ^{+}_{NH}), 1608 (CO_2^-), 2878, 2926, 2967 (CH_2, CH_3), 3160 sh, 3425 (NH). ^{1}H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm: 1.26 s [9H, $C(CH_3)_3$], 2.23 s (3H, SCH_3), 2.34 t (2H, $NCH_2C\underline{H}_2COO$, *J* 6.9 Hz), 2.77 t (2H, $NC\underline{H}_2CH_2COO$, *J* 6.9 Hz), 7.4 s (4H, C^2H_2, C^6H_2). Found, %: C 31.96, H 6.47; N 13.94. $C_7H_{13}N_3O_2S{\cdot}C_4H_{12}IN$. Calculated, %: C 32.68, H 6.523; N 13.86.

4-[4-(Methylsulfanyl)-5,6-dihydro-1,3,5-triazin-3-ium-1(2*H*)-yl] butanoate associate with *tert*.-butylammonium iodide (1:1) (VIc) hydrate. *a*. The preparation was the same as for compound **VIa** from 0.363 g (1.052 mmol) of compound **IIIc** and 0.15 ml (0.104 g, 1,427 mmol) of *tert*-butylamine in 5 ml of water. Yield 0.298 g (67.7%), mp 134–138°C. IR spectrum (thin layer), ν, cm^{-1}: 1563, 1571 (C–N, δ^{+}_{NH}), 1607, 1718 (CO_2^-), 2934, 2976 (CH_2, CH_3), 3066, 3173, 3431 (NH). ^{1}H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm: 1.25 s [9H, $C(CH_3)_3$], 1.67 m (2H, $NCH_2C\underline{H}_2CH_2COO$), 2.22 t (2H, $NCH_2CH_2C\underline{H}_2COO$, *J* 6.9 Hz), 2.25 s (3H, CH_3), 2.54 t (2H, $NC\underline{H}_2CH_2{\cdot}CH_2COO$, *J* 6.9 Hz), 4.08 s (4H, C^2H_2, C^6H_2). ^{1}H NMR spectrum (400 MHz, D_2O), δ, ppm: 1.36 s [9H, $C(CH_3)_3$], 1.80 m (2H, $NCH_2C\underline{H}_2CH_2COO$), 2.22 t (2H, $NCH_2CH_2C\underline{H}_2COO$, *J* 7.4 Hz), 2.56 s (3H, CH_3), 2.72 t (2H, $NC\underline{H}_2CH_2CH_2COO$, *J* 7.4 Hz), 4.44 s (4H, C^2H_2, C^6H_2). Found, %: C 32.50, H 6.22; N 12.69. $C_8H_{15}N_3O_2S{\cdot}C_4H_{12}IN{\cdot}H_2O$. Calculated, %: C 33.03, H 6.70; N 12.84.

b. To 0.345 g (0.999 mmol) of compound **IIIc** was added while stirring 10 ml of *tert*-butylamine. After a few seconds the initial compound dissolved, and an amorphous precipitate began to form in the entire volume of the reaction mixture. The reaction mixture was left overnight. In the flask formed a finely dispersed suspension, which was transferred to a Petri dish for evaporation of the amine excess. After 2 months the whole mass solidified. Yield 0.183 g (42.0%), mp 102–104°C. IR spectrum (thin film), ν, cm^{-1}: 1562 (C–N, δ^{+}_{NH}), 1609, 1712 (CO_2^-), 2878, 2913, 2978 (CH_2, CH_3), 3002, 3056, 3153, 3257, 3418 (NH). ^{1}H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm:

1.25 s [9H, $C(CH_3)_3$], 1.67 m (2H, $NCH_2C\underline{H}_2\cdot CH_2COO$), 2.21 t (2H, $NCH_2CH_2C\underline{H}_2COO$, *J* 6.9 Hz), 2.30 s (3H, CH_3), 2.54 t (2H, $NC\underline{H}_2CH_2CH_2COO$, *J* 6.9 Hz), 4.12 s (4H, C^2H_2, C^6H_2). Found, %: C 32.04, H 5.95; N 12.63. $C_8H_{15}N_3O_2S\cdot C_4H_{12}IN\cdot H_2O$. Calculated, %: C 33.03; H 6.70; N 12.84.

3-[4-(Methylsulfanyl)-5,6-dihydro-1,3,5-triazin-3-ium-1(2*H*)-yl] propanoate associate with diethylammonium iodide (1:1) (VId). A mixture of 0.331 g (0.999 mmol) of compound **IIIb** and 10 ml of diethylamine was stirred with a magnetic stirrer at room temperature for 30 min, the dissolution was not observed. After 2 h the upper liquid layer (diethylamine) was decanted, and a syrupy suspension at bottom was transferred to a Petri dish for the amine evaporation. After 3 days the solid residue was crushed and dried in a vacuum. Yield 0.287 g (71.7%), mp 108–110°C. IR spectrum (thin film), ν, cm^{-1}: 1562 (C–N, δ^+_{NH}), 1611 (CO_2^-), 2813, 2859, 2910, 2959, 2988 (CH_2, CH_3), 3048, 3218, 3418 sh (NH). ^1H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm: 1.19 t (6H, $CH_2C\underline{H}_3$, *J* 7.4 Hz), 2.35 t (2H, $NCH_2C\underline{H}_2COO$, *J* 6.9 Hz), 2.38 s (3H, SCH_3), 2.77 t (2H, $NC\underline{H}_2CH_2\cdot COO$, *J* 6.9 Hz), 2.91 q (4H, $C\underline{H}_2CH_3$, *J* 7.4 Hz), 4.19 s (4H, C^2H_2, C^6H_2). Found, %: C 32.12, H 6.15; N 13.70. $C_{11}H_{25}IN_4O_2S$. Calculated, %: C 32.68, H 6.23; N 13.86.

2-Methylpropane-2-ammonium(4-thioxo-1,3,5-triazinane-1-yl) acetate (VIIa). *a*. To 0.333 g (1.9 mmol) of compound **IIa** in 50 ml of ethanol at 45–50°C at vigorous stirring was added 0.139 g (0.20 ml, 1.9 mmol) of *tert*-butylamine. After 1 day the precipitate was filtered off, washed with ethanol, and dried in a vacuum desiccator over $CaCl_2$. Yield 0.334 g (70.8%), mp 185–186°C. IR spectrum (thin film), ν, cm^{-1}: 1528 (C–N), 1571 (δ^+_{NH}), 1630 (CO^{2-}), 2533, 2622, 2834, 2874, 2934, 2982 (CH_2, CH_3), 3030 3243, 3418 (NH). ^1H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm: 1.22 s [9H, $C(CH_3)_3$], 2.98 s (2H, CH_2COO), 4.05 s (4H, C^2H_2, C^6H_2), 7.92 (2H, NH). Found, %: C 44.02, H 8.41; N 23.04. $C_9H_{20}N_4O_2S$. Calculated, %: C 43.53, H 8.12; N 22.56.

b. To a suspension of 1.733 g (10 mmol) of compound **VIII** in 30 ml of water was added with stirring a solution of 0.751 g (10 mmol) of glycine in 10 ml of water. The reaction mixture was heated to 60°C and kept at this temperature for 1.5 h, after which the solution was left to stand for 1 day at room temperature, and then was poured into a Petri dish. After 2 days the resulting crystals were dried in a vacuum over $CaCl_2$ and recrystallized from ethanol. Yield 0.982 g (39.5%), mp 180–183°C. IR spectrum (thin film), ν, cm^{-1}: 1529 (C–N), 1562 (δ^+_{NH}), 1630 (CO_2^-), 2532, 2622, 2730, 2835, 2872, 2934, 2982 (CH_2, CH_3), 3030, 3242, 3416 (NH). ^1H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm: 1.22 s [9H, $C(CH_3)_3$], 3.01 s (2H, CH_2COO), 4.06 s (4H, C^2H_2, C^6H_2), 7.89 (2H, NH). Found, %: C 43.81, H 7.76; N 22.97; S 12.35. $C_9H_{20}N_4O_2S$. Calculated, %: C 43.53, H 8.12; N 22.56; S 12.91.

2-Methylpropane-2-ammonium(4-thioxo-1,3,5-triazinane-1-yl) propanoate (VIIb). *a*. The preparation was the same as for compound **VIIa** from 0.360 g (1.9 mmol) of compound **IIb** and 0.139 g (0.20 ml, 1.9 mmol) of *tert*-butylamine in 20 ml of ethanol. Yield 0.456 g (91.5%), mp 157–160°C. IR spectrum (thin film), ν, cm^{-1}: 1543 (C–N, δ^+_{NH}), 1629 (CO_2^-), 2543, 2616, 2732, 2845, 2885, 2931, 2975 (CH_2, CH_3), 3079, 3196, 3415 (NH). ^1H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm: 1.19 s [9H, $C(CH_3)_3$], 2.14 br.s (2H, $NCH_2C\underline{H}_2COO$), 2.70 br.s (2H, $NC\underline{H}_2CH_2COO$), 3.97 s (4H, C^2H_2, C^6H_2), 7.95 (2H, NH). Found, %: C 45.28, H 7.92; N 21.93. $C_{10}H_{22}N_4O_2S$. Calculated, %: C 45.78, H 8.45; N 21.35.

b. The preparation was the same as for compound **VIIa** from 1.733 g (10 mmol) of compound **VIII** and 0.891 g (10 mmol) of β-alanine. Yield 1.129 g (43.0%), mp 159–162°C. IR spectrum (thin film), ν, cm^{-1}: 1528 (C–N), 1630 (CO_2^-), 2543, 2627, 2738, 2844, 2890, 2930, 2978 (CH_2, CH_3), 3007, 3199, 3340 (NH). ^1H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm: 1.20 with [9H, $C(CH_3)_3$], 2.15 br.s (2H, NCH_2CH_2COO), 2.70 br.s (2H, NCH_2CH_2COO), 3.97 s (4H, C^2H_2, C^6H_2), 7.94 (2H, NH). Found, %: C 46.22, H 7.91; N 21.74; S 11.63. $C_{10}H_{22}N_4O_2S$. Calculated, %: C 45.78, H 8.45; N 21.35; S 12.22.

2-Methylpropane-2-ammonium(4-thioxo-1,3,5-triazinane-1-yl) butanoate (VIIc). The preparation was the same as for compound **VIIa** from 0.386 g (1.9 mmol) of compound **IIb** and 0.139 g (0.20 ml, 1.9 mmol) of *tert*-butylamine in 10 ml of ethanol at 65°C. Yield 0.495 g (94.3%), mp 138–140°C. IR spectrum (thin film), ν, cm^{-1}: 1551 (C–N, δ^+_{NH}), 1637 (CO_2^-), 2534, 2614, 2846, 2925, 2975 (CH_2, CH_3), 3044, 3186, 3389 (NH). ^1H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm: 1.16 s [9H, $C(CH_3)_3$], 1.62 m (2H, $NCH_2C\underline{H}_2CH_2COO$), 2.03 t (2H, $NCH_2CH_2C\underline{H}_2COO$, *J* 6.9 Hz), 2.51 t (2H, $NC\underline{H}_2CH_2CH_2COO$, *J* 6.9 Hz),

3.97 s (4H, C^2H_2, C^6H_2), 7.94 (2H, NH). Found, %: C 48.44, H 9.00; N 20.83. $C_{11}H_{24}N_4O_2S$. Calculated, %: C 47.80, H 8.75; N 20.27.

5-*tert*-Butyl-1,3,5-triazinan-2-thione VIII was obtained by the method of [7].

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