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UREA DERIVATIVES OF ISOCYANURIC ACID

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Interaction of monomethylol urea with isotsianuric acid has been investigated at different molar rations. Mono-, di- and tris-substituted derivatives of isotsianuric acid have been obtained. The compounds have been studied by IR, PMR spectroscopy and elemental analysis.

Keywords: monomethylol urea, derivatives, isotsianuric acid, IR spectroscopy, PMR spectroscopy, elemental analysis.

Introduction. Both in theoretical and practical applications cyanuric acid and its keto form isocyanuric acid and their functional derivatives are of great interest. There are a number of derivatives of isocyanuric acid, differ with high thermal-physical and physical-mechanical parameters and are recommended as a modifiers to create different composite materials to be applied [1–3]. Some isocyanuric acid derivatives exhibiting biological activity are used in pharmacology [4]. Isocyanuric acid derivatives reveal fungicidal, bactericidal, flame retardants and other important properties [5].

This report describes the new mono-, di-, and tris-substituted isocyanuric acid, which can be used as a basis for the synthesis of polymers and resins applied destination. Urea isocyanuric acid derivatives are obtained by interaction of monomethylol urea (MMU) with isocyanuric acid (ICA). Depending on the molar ratio of MMU/ICA the compounds I–III were synthesized.

When the interaction of 1 *mol* of ICA with 6 *mol* MMU brings to the approximate structure IV.

Compounds I–IV the IR, PMR spectroscopy and elemental analysis are studied, the mass of compounds I, II and IV in the form of their salts were determined by sodium cryoscopy. Treating by aqueous solution of NaOH were obtained sodium salts of I, II and IV. It should be noted that, from the compounds listed above only III is not involved in salt formation. This is apparently due to the fact that compound III is not exposed to keto-enol transformations.

The structure of the sodium salts of compounds I, II and IV can be submitted to V–VII respectively.

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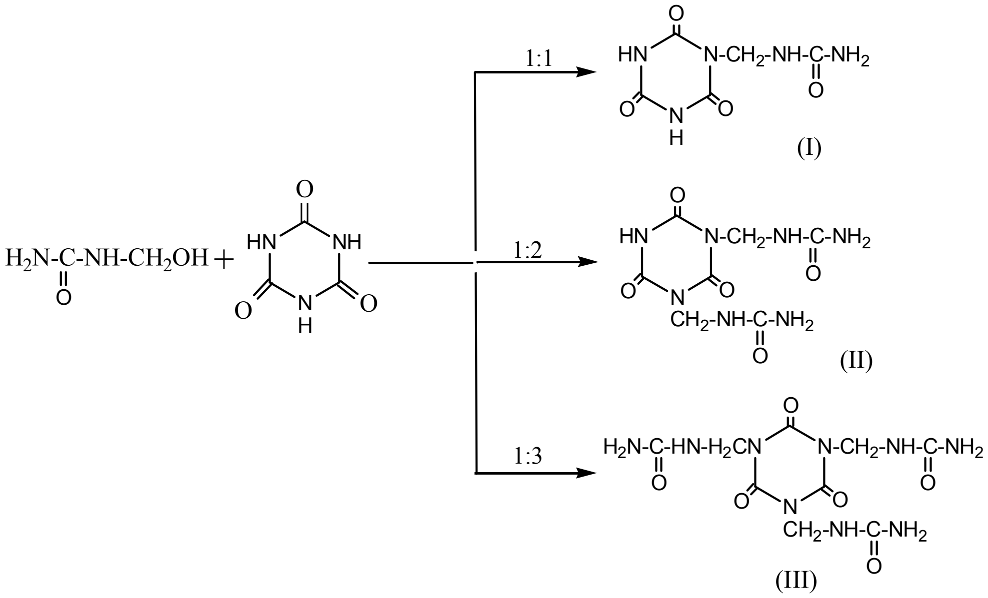
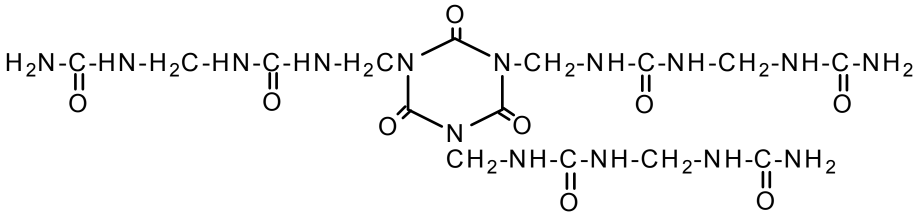
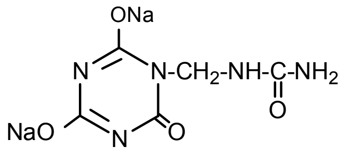
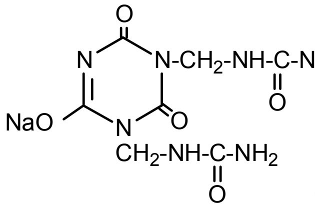




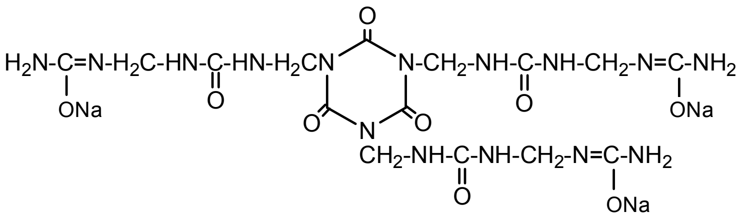
(IV)



(V)



(VI)



(VII)

Physico-chemical parameters of the compounds I–VII are given in Tab. 1.

Table 1

Comp.	Temp. swim, *K*	IR spectr., *ν*, *cm*$^{-1}$	NMR spectr., *δ*, m. d.	The Elemental Composition Found / Calculated, %			
				C	H	N	Na
I	240±0.5	763 (simm. triaz.), 1420 (〉NC(O)N〈), 1645(〉C=O simm. triaz.) 2850–2930 (–CH$_2$–) 3060–3200 (N–H–)	4.43–4.5 d (2H, NCH2) 6.41–6.48 s (1H, NH) 8.98 d (2H, NH2)	29.7 29.85	3.53 3.48	34.9 34.82	
II	210±0.5	763 (simm. triaz), 1415–1425(〉NC(O)N〈), 1695–1705 (〉C=O simm. triaz.) 2850–2900 (–CH$_2$–) 3100–3210 (N–H–)	4.42–4.52 d (4H, NCH$_2$) 6.43–6.81 s (2H, NH) 8.85–8.95 d (4H, NH$_2$)	30.6 30.77	3.9 4.03	35.7 35.89	
III	160±0.5	763 (simm. triaz), 1420 (〉NC(O)N〈), 1695 (〉C=O simm. triaz.) 2870–2920 (–CH$_2$–) 3060–3200 (N–H–)	4.42–4.51 d (6H, NCH$_2$) 6.42–6.88 s (3H, NH) 8.95–8.98 d (4H, NH$_2$)	31.1 31.36	4.5 4.65	35.7 35.89	
IV	190±0.5	763 (simm. triaz.), 1420 (〉NC(O)N〈), 1695–1720 (〉C=O simm. triaz)	4.41–4.55 d; 4.35–4.39 d (12H, NCH$_2$) 6.4–6.42 s; 6.43–6,5 s (3H, NH), 8.98 d (4H, NH$_2$)	32.2 32.08	4.7 4.81	37.5 37.40	
V		763, 860 (simm. triaz.), 1425 (〉NC(O)N〈), 1635–1655 (C=N simm. triaz) 1690–1700 (〉C=O simm. triaz.) 2850–2930 (–CH$_2$–) 3060–3200 (N–H–)	4.45–4.55 d (2H,NCH$_2$) 6.41–6.75 s (1H, NH) 8.9–9.98 d (2H, NH$_2$)	24.3 24.49	2.0 2.04	28.6 28.57	18.6 18.77
VI		765, 860 (simm. triaz), 1420 (〉NC(O)N〈), 1630–1650(C=N simm. triaz.) 1695–1705 (〉C=O simm. triaz.) 2850–2910 (–CH$_2$–) 3060–3210 (NH–)	4.43–4.55 d (4H, NCH$_2$) 6.41–6.5 s (2H, NH) 8.99 d (4H, NH$_2$)	28.6 28.47	3.2 3.39	33.1 33.22	7.7 7.79
VII		763, 860 (simm. triaz.), 1415–1420 (〉NC(O)N〈), 1615 (C=N simm. triaz.) 1690–1700 (〉C=O simm. triaz.) 2850–2930 (–CH$_2$–) 3060–3220 (NH–)	4.47–4.55 d; 4.58–4.61 d (12H, NCH$_2$) 6.41–6.54 s; 6.43–6.5 s (6H, NH), 8.82–8.98 d (12H, NH$_2$)	28.6 28.71	3.9 3.83	33.4 33.49	11.1 11.0

Molecular weight of the compounds V–VII are provided in Tab. 2.

Table 2

Connection	V	VI	VII
Average mol. weight, *M*	240±15	290±15	630±20

Experimental Part. IR and NMR spectra of the compounds I–VII were recorded by spectrophotometer Spekord-75IR and the unit Varian Mercury-300 respectively. IR spectra of the above compounds are removed from the paste and obtained by smear and liquid paraffin. As a solvent for NMR spectroscopy DMSO is used. Isocyanuric acid is used after overcrystallization of water. 38% aqueous solution of formaldehyde is used. MMU is obtained as in [6]. The molecular weight of compounds V–VII is determined by cryoscopy [7]. As a solvent for cryoscopic measurements distilled water (K=1.863) is used:

$$M = K\frac{m_2 10^3}{m_1 \Delta T},$$

where m_1 and m_2 are the compound V (or IV, or VII) and water weights respectively, ΔT is the temperature difference between freezing solution and solvent.

1-Monokarbamidilmethyl Isocyanurate (I). In 25 *ml* water dissolved 2.7 *g* (0.03 *mol*) MMU and stirring the solution the temperature was adjusted to 65^0C. Then injected 3.87 *g* (0.03 *mol*) isocyanuric acid and reaction mixture pH was adjusted to 6.5–7.5. While stirring at the temperature of $80–85^0C$, interaction between these agents spend 6.5–7 *h*. And the reaction mass is transferred to ethanol and filtered. White precipitate was repeatedly washed with acetone. In order to separate the reaction product from unreacted isocyanuric acid precipitate was dissolved in DMSO, which is removed by vacuum filtration (1.5–2 *mm* Hg) at $50–55^0C$. White crystalline solid was washed with acetone and dried under vacuum (10–15 *mm* Hg) at $80–85^0C$ to constant weight with 57% output. Purity of the product was checked by TLC on plates Silufol UV-254 in system DMSO–acetone at volumetric ratio of 3:1 developer $KMnO_4$.

1,3-Karbamidilmethyl Isocyanurate (II). 5.4 *g* (0.06 *mol*) of MMU was dissolved in 25 *ml* water and stirring the solution the temperature was adjusted to 65^0C. Then injected 3.87 *g* (0.03 *mol*) isocyanuric acid and reaction medium pH was adjusted to 6.5–7.5. The temperature of the reaction mixture was adjusted to 85^0C, at this temperature stirring continued for 6.5–7 *h*. After that the reaction product from unreacted starting solid matter was precipitated in ethanol and filtered. The white precipitate was repeatedly washed with acetone. Then it was dissolved in DMSO and filtered. From the filtrate under vacuum (1.5–2 *mm* Hg) at $55–60^0C$ DMSO was removed. White crystalline solid was washed with acetone and dried under vacuum with 71% output. Purity of the product was checked by TLC on plates Siluful UV-254 in systems of DMSO–acetone at volumetric ratio of 3:1 developer $KMnO_4$.

Tris-1,3,5-Karbamidilmethyl Isocyanurate (III). The reaction between 8.1 *g* (0.09 *mol*) of MMU and 34.87 *g* (0.03 *mol*) ICA and separation of the reaction product is carried out similarly to the above example. Output was 76.5%. Purity of the product was checked by the method described above.

Product IV. The reactor was charged with 1.8 *g* (0.03 *mol*) of urea, 3.45 *g* (0.01 *mol*) of tris-1,3,5-karbamidilmethyl isocyanurate and stirring temperature is increased to $75–85^0C$. During the interaction intensively ammonia was released. After cooling the reaction mixture was washed several times with ethanol and then with acetone, and dried to constant weight. A white mat shade product was gain with 87% output.

Compounds V, VI and VII. In 25 *ml* (0.06 *mol*) of an aqueous solution of NaOH 0.02 *mol* of compound II (or IV, or VII) was administered, and with vigorous stirring the temperature was adjusted to 75^0C, and the stirring was continued until complete dissolution of the compound II (or IV, or VII). Under vacuum (10–15 *mm* Hg) at the temperature range of 35–45^0C reducing the water a white substance was isolated. The resulting compound V (or VI, or VII) repeatedly were washed with warm ethanol, then with acetone to remove the unreacted NaOH. Dried under vacuum (10–15 *mm* Hg) at 65–70^0C it comes to constant mass.

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