

Nitrofuran derivatives of cellulose

X. 5-Nitrofurfurylidene derivatives of 2,4-dihydrazino-6-oxycelluloso-*s*-triazine and of 2,3-dihydrazinocellulose

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Reduction of 2,3-dicarbonylcellulose hydrazone gives rise to 2,3-deoxydihydrazinocellulose. Reaction of 2,4,6-trichloro-*s*-triazine with cellulose enables one to prepare 2,4-dichloro-6-oxycelluloso-*s*-triazine followed by 2,4-dihydrazino-6-oxycelluloso-*s*-triazine and after that by (2,4-dihydrazino-6-*s*-triazino)-2,3-dicarbonylcellulose, (2,4-dihydrazino-6-*s*-triazino)-2,3-dihydrazonocellulose and (2,4-dihydrazino-6-*s*-triazino)-2,3-deoxydihydrazinocellulose, respectively.

The dihydrazino derivatives give through condensation with 5-nitro-2-furaldehyde the appropriate 5-nitrofurfurylidene derivatives.

The behaviour of some of the selected materials being under thermogravimetric conditions is presented.

Посредством восстановления гидразона 2,3-дикарбонилцеллюлозы была получена 2,3-дезоксидигидразинцеллюлоза. Реакцией 2,4,6-трихлор-*s*-триазина с целлюлозой был получен 2,4-дихлор-6-оксицеллюлозо-*s*-триазин, из него 2,4-дигидразин-6-оксицеллюлозо-*s*-триазин, а далее (2,4-дигидразин-6-*s*-триазино)-2,3-дикарбонилцеллюлоза, (2,4-дигидразин-6-*s*-триазино)-2,3-дигидразонцеллюлоза и (2,4-дигидразин-6-*s*-триазино)-2,3-дезоксидигидразинцеллюлоза.

Из дигидразинпроизводных конденсацией с 5-нитро-2-фуральдегидом были получены соответствующие 5-нитрофурфурилиденовые производные.

Описано поведение некоторых избранных материалов в условиях термогравиметрии.

The synthesis of 5-nitrofurfurylidenehydrazone of both 2,3-dicarbonylcellulose (*I*) [1] and 2,4-oxycelluloso-6-(5-nitrofurfurylidenehydrazino)-*s*-triazine (*II*) [2] has been described previously. The derivative *I* was gained by condensation of 5-nitro-2-furaldehyde with 2,3-dicarbonylcellulose hydrazone. In this case, the 5-nitrofurfurylidene residue is bound to cellulose with a less stable azomethine bond. The derivative *II* with a degree of substitution ranging

between 0.008 and 0.019 was obtained by condensation of 2,4-dichloro-6-X-*s*-triazine (*III*) with cellulose; X represents a 5-nitrofurfurylidenehydrazine residue. The materials *I* and *II* possess some interesting antimicrobial properties [2, 3].

The paper is intended to describe a new synthesis of 2,4-dihydrazino-6-oxycelluloso-*s*-triazine, 2,3-deoxydihydrazinocellulose, and of various mixed hydrazinocellulose derivatives and corresponding 5-nitrofurfurylidene compounds.

Reaction of 2,3-dicarbonylcellulose with hydrazine hydrate yields almost quantitatively the dihydrazone. The reaction was considered to be suitable for the carbonyl groups determination in oxidized celluloses [4]. Upon condensation of 2,3-dicarbonylcellulose dihydrazone with 5-nitro-2-furaldehyde the 5-nitrofurfurylidene derivatives were formed under mild conditions, but with considerably lower degrees of substitution than it corresponds to hydrazone residues. This fact suggests that part of hydrazine hydrate is brought into reaction with 2,3-dicarbonylcellulose through both the amino groups [1], or else, part of carbonyl groups is not involved in the reaction at all [4]. From 2,3-dicarbonylcellulose with a degree of substitution 0.66 the 2,3-dihydrazone with a degree of substitution 0.40 was obtained. 2,3-Dihydrazone was converted by reduction with sodium borohydride into 2,3-deoxydihydrazinocellulose (*IV*). The latter was attained with a degree of substitution 0.27, which means that the reduction was accompanied by the elimination of hydrazone residues. The condensation of material *IV* with 5-nitro-2-furaldehyde gave rise to a deep-red material *V* having a degree of substitution 0.16. The lower degree of substitution suggests the lower number of free amino groups than it corresponds to the initial hydrazine *IV*.

During experiments [2], from 2,4,6-trichloro-*s*-triazine was prepared, by action of hydrazine hydrate, the 2,4-dichloro-6-hydrazino-*s*-triazine and from the latter one, by condensation with 5-nitro-2-furaldehyde, the 2,4-dichloro-6-(5-nitrofurfurylidenehydrazino)-*s*-triazine. The reaction of it with cellulose yielded 2,4-oxycelluloso-6-(5-nitrofurfurylidenehydrazino)-*s*-triazines (*II*) with their degrees of substitution, up to 0.02. In order to raise the degrees of substitution, the material *V* was prepared by the action of 2,4,6-trichloro-*s*-triazine upon alkali cellulose. The reaction was studied in the medium of various solvents. The highest degree of substitution 0.12 was attained in the xylene medium [2]. From the material *V*, after the action of hydrazine hydrate the dihydrazine *VI* with a degree of substitution 0.09 was obtained. The hydrazino derivative was condensed with 5-nitro-2-furaldehyde with formation of *XI* having a degree of substitution 0.082 and a canary-yellow colour.

From the material *VI*, the material *VII* was derived by periodate oxidation and from that, by action of hydrazine hydrate, the material *VIII*; from the latter

one, by reduction with sodium borohydride, the material *IX* was produced. From the material *VI*, the material *VII* was derived by periodate oxidation and from that, by action of hydrazine hydrate, the material *VIII*; from the latter one, by reduction with sodium borohydride, the material *IX* was produced. From hydrazines *IV*, *VI*, *VII*, and *IX* as well as from hydrazone *VIII*, the corresponding 5-nitrofurfurylidene derivatives *X*, *XI*, *XII*, *XIV*, and *XIII* were prepared by condensation with 5-nitro-2-furaldehyde under mild conditions.

The results obtained from the reactions indicate that the cellulosic hydrazino derivatives are convenient for carbonyl compounds binding. In our case, they served for the preparation of biologically efficient 5-nitrofurfurylidene derivatives.

The presence of hydrazine residues in the dihydrazone of 2,3-dicarbonyl-cellulose and in the materials *VII*, *VIII*, and *IX* is accompanied within the infrared spectra by wavenumbers of $\delta(\text{N—H})$ vibrations at 800 cm^{-1} and by complex vibrations $\nu(\text{C=N})$, $\nu(\text{C—N})$, and $\delta(\text{N—H}_2)$ in the region of 1750 to 1600 cm^{-1} . The presence of 5-nitrofurfurylidene residue is accompanied by the IR band positions of $\nu_{\text{as}}(\text{NO}_2)$ and $\nu_{\text{s}}(\text{NO}_2)$ vibrations at $\tilde{\nu} = 1530\text{ cm}^{-1}$ and 1365 cm^{-1} , respectively. In the case of material *V*, the wavenumbers of $\nu(\text{C—Cl})$ vibrations at 850 cm^{-1} are noticeable. The substitution of chlorine for a hydrazine residue causes that this band disappears and on the other hand, the wavenumbers of $\delta(\text{N—H})$ at 800 cm^{-1} and the indicated complex bands appear.

The antimicrobial substances which are chemically bound to cellulose show very frequently an unfavourable effect on the properties of cellulosic materials, limiting their application despite their favourable antimicrobial effects [5]. For these reasons, the stability of derivatives found under thermogravimetric conditions was observed. The thermogravimetric curves (Fig. 1) suggest that the cellulosic materials possess another thermal stability. They begin their thermal decomposing at the lower temperature than the cellulose does, however, their thermal decomposition proceeds at a lower rate leaving a residue which is highly resistant to the thermooxidative effect. The decomposition of nontreated cellulose proceeds in one stage until the decay at 600°C takes place. The cellulosic derivatives *V*, *VI*, and *XI* undergo the decomposition in two stages (Table 1), the first stage being found at the highest rate at $295\text{—}316^\circ\text{C}$ and the second one at $417\text{—}502^\circ\text{C}$. The maximum inhibitory effect on the derivative *V* is caused by the present chlorine atoms. The halo compounds are blocking the reactive radicals ($\text{HO}\cdot$, $\text{H}\cdot$) of flame combustion. The derivatives *XII* and *XIV*, containing the substituents in the open glucose unit, have three stages of decomposition. In comparison with materials *V*, *VI*, and *XI* they have, among others, the first stage of decomposition characterized by the maximum rate at $216\text{—}217^\circ\text{C}$, the second one by the maximum rate at $311\text{—}318^\circ\text{C}$, and the third stage — at $488\text{—}498^\circ\text{C}$ involving a lower resistant residue (R).

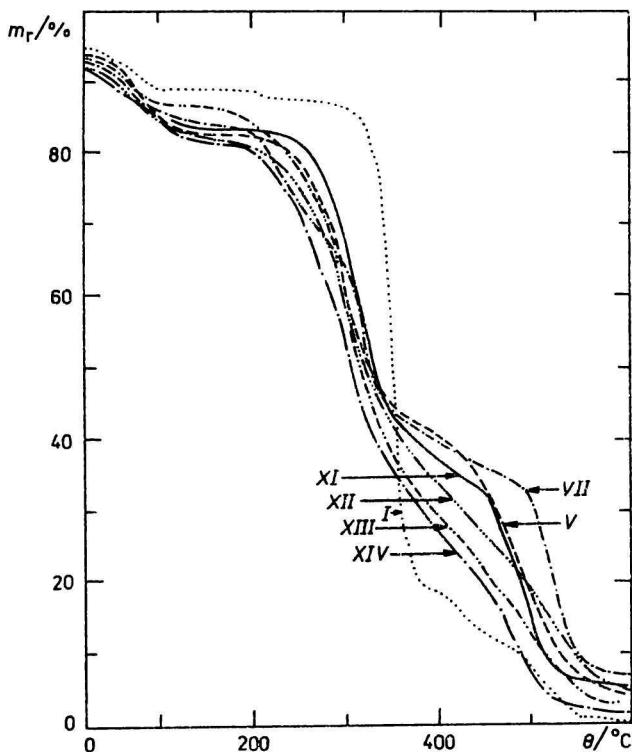


Fig. 1. Thermogravimetry of cellulose (I) and of materials V, VII, and XI to XIV.

Experimental

During experiments, a dissolving pulp of the Rauma Repola firm (Finland) was used. 5-Nitro-2-furaldehyde was prepared in accordance with Ref. [6, 7]. 2,4-Dichloro-6-oxycelluloso-*s*-triazine (V) with a degree of substitution 0.12 was prepared by reaction of 2,4,6-trichloro-*s*-triazine with alkali cellulose according to [8] in the xylene medium.

The degrees of substitution were assessed either from the nitrogen content determined by Kjeldahl's method or from the chlorine content.

The infrared absorption spectra of the materials under investigation were measured on a double-beam UR 20 spectrometer (Zeiss, Jena), in the KBr tablets with a content of 2.2 mg material/300 mg KBr, in the range $\tilde{\nu} = 500\text{--}3600\text{ cm}^{-1}$.

The thermal analysis was made on the Thermoanalyzer-2 apparatus (Mettler). Within the analysis, the air flow of $7\text{ dm}^3\text{ min}^{-1}$ and the heating rate of $10^\circ\text{C min}^{-1}$ were used. The sensitivity of thermogravimetry was $1\text{ mg}/25.4\text{ mm}$. For the differential thermal analysis, both the Pt/Rh thermocouples and freshly annealed aluminium oxide as a standard were applied.

Table 1

The results of thermal analysis of cellulose and of synthesized derivatives

Material	Degradation									R/%
	1st degree 150—250°C			2nd degree 250—420°C			3rd degree 420—550°C			
	t_{\max} °C	r_{\max} mg min ⁻¹	m_r %	t_{\max} °C	r_{\max} mg min ⁻¹	m_r %	t_{\max} °C	r_{\max} mg min ⁻¹	m_r %	
Cellulose	—	—	—	350	1.13	85.12	—	—	—	—
V	—	—	—	295	0.43	45.72	502	0.46	32.84	8.58
VII	—	—	—	325	0.49	46.35	475	0.27	32.96	7.12
XI	—	—	—	316	0.49	46.29	467	0.30	35.13	7.15
XII	216	0.15	18.57	311	0.46	51.42	488	0.21	24.28	0.71
XIII	—	—	14.20	318	0.63	53.97	496	0.19	25.56	1.42
XIV	217	0.24	14.28	311	0.57	47.14	498	0.17	25.71	4.28

2,3-Deoxydihydrazinocellulose (IV)

20 g (0.112 mol) of 2,3-dicarbonylcellulose hydrazone [I] with a degree of substitution 0.40 were suspended in the 400 cm³ ethanol—water mixture (volume ratio = 2 : 1), then the pH was adjusted to 9 by sodium carbonate and the 3.51 g (0.09 mol) solution of sodium borohydride was added into the 150 cm³ ethanol—water mixture. The reaction mixture was agitated for 2 h and left standing for 20 h at the laboratory temperature. The fibres were separated, washed with 0.1 M-CH₃COOH (1000 cm³) and distilled water until the neutral reaction. Thus the material *IV* with a degree of substitution 0.27 was attained.

2,4-Dihydrazino-6-oxycelluloso-s-triazine (VI)

40 cm³ of hydrazine hydrate was gradually added at 0°C to the suspension of 20 g (0.064 mol) of material *V* in the 450 cm³ dioxan—water mixture (volume ratio = 1 : 1), and the resultant mixture was agitated for 2 h at the same temperature. After that time the temperature was increased up to 80°C and kept at the same level during intense stirring for 1 h. The fibres were separated, washed by water until the neutral reaction, and purified by extraction in Soxhlet's apparatus. In such a way the material *VI* with a degree of substitution 0.09 was produced.

(2,4-Dihydrazino-6-s-triazino)-2,3-dicarbonylcellulose (VII)

Solution of 17.18 g (0.088 mol) of periodic acid in 100 cm³ of water was added to the 2% suspension of 20 g (0.075 mol) of material *VI* in water. Within stirring, the medium was adjusted to pH = 5 by sodium acetate solution and the reaction mixture was agitated for 1 h and left standing for 10 h at the laboratory temperature. After that time the fibres were separated and washed by water until the neutral reaction. The content of carbonyl groups was determined from the nitrogen content after their reduction to oxime. The compound *VII* with a degree of substitution 0.11 was thus obtained.

(2,4-Dihydrazino-6-s-triazino)-2,3-dihydrazonocellulose (VIII)

Solution of 30 cm³ of hydrazine hydrate in 200 cm³ of ethanol was added to the suspension of 20 g (0.075 mol) of material *VII* in 200 cm³ of ethanol and the mixture was stirred for 2 h at the laboratory temperature. The fibres were separated and purified by washing with distilled water. In such a way the material *VIII* with a degree of substitution 0.08 was gained.

(2,4-Dihydrazino-6-s-triazino)-2,3-dihydrazinocellulose (IX)

Solution of 0.89 g (0.023 mol) of sodium borohydride in 150 cm³ of ethanol—water mixture was added to the suspension of 20 g (0.076 mol) of material *VIII* in 400 cm³ of ethanol—water mixture (volume ratio = 2 : 1) adjusted to pH = 9 by sodium carbonate. The mixture was agitated for 2 h and left standing for 10 h at the laboratory temperature. The separated fibres were purified by washing with water. Consequently, the material *IX* with a degree of substitution 0.06 was gained.

5-Nitrofurfurylidenehydrazino derivatives of cellulose (X—XIV)

4.29 g (0.03 mol) of 5-nitro-2-furaldehyde in 100 cm³ of ethanol was added to the suspension of 20 g (0.112 mol) of materials *IV*, *VI*, *VII*, and *VIII* or *IX* in 250 cm³ of ethanol. The mixture was heated on the water bath for 2 h at the temperature of 70°C. The fibres were separated, washed by water and ethanol, and purified by extraction in Soxhlet's apparatus.

2,3-Di(5-nitrofurfurylidenehydrazino)cellulose (*X*) of deep-red colour with a degree of substitution 0.16 was derived from the material *IV* with a degree of substitution 0.27; 2,4-di(5-nitrofurfurylidenehydrazino)-6-oxycelluloso-*s*-triazine (*XI*) with a degree of substitution 0.082 was produced from the material *VI* with a degree of substitution 0.09; [2,4-di(5-nitrofurfurylidenehydrazino)-6-*s*-triazino]-2,3-dicarbonylcellulose (*XII*) with a degree of substitution 0.093 was gained from the material *VII* with a degree of substitution 0.09 for a 2,4-dihydrazino-6-*s*-triazine residue; [2,4-di(5-nitrofurfurylidenehydrazino)-6-*s*-triazino]-2,3-di(5-nitrofurfurylidenehydrazono)cellulose (*XIII*) with corresponding degrees of substitution 0.08 and 0.075 was obtained from the material *VIII* with a degree of substitution 0.09 for a 2,4-dihydrazino-6-*s*-triazine residue and 0.08 for a 2,3-dihydrazone residue; [2,4-di(5-nitrofurfurylidenehydrazino)-6-*s*-triazino]-2,3-di(5-nitrofurfurylidenehydrazono)cellulose (*XIV*) with degrees of substitution 0.08 and 0.05 was produced from the material *IX* with degrees of substitution 0.09 for a 2,4-dihydrazino-6-*s*-triazine residue and 0.06 for a 2,3-dihydrazine residue, respectively.

References

1. Krkoška, P. and Godó, Š., *Sborník prác Chemickotechnologickej fakulty SVŠT.* (Collection of Scientific Papers of the Faculty of Chemical Technology, Slovak Technical University.) P. 277, Bratislava, 1972.
2. Krkoška, P., Blažej, A., Kiss, V., Zemanová, M., and Zoborová, R., *Cell. Chem. Technol.* 14, 19 (1980).
3. Krkoška, P., Ebringer, L., Ondrišová, M., and Remenár, M., *Cell. Chem. Technol.* 10, 155 (1976).

4. Norsted, I. and Samuelson, O., *Sv. Papperstidn.* 69, 44 (1966).
5. Volf, L., Polishchuk, B. O., and Kotetskii, V. V., *Cell. Chem. Technol.* 7, 417 (1973).
6. Gilman, H. and Wright, G. F., *J. Amer. Chem. Soc.* 52, 2550 (1930).
7. Gilman, H. and Wright, G. F., *J. Amer. Chem. Soc.* 52, 4160 (1930).
8. Summer, H. H., *J. Soc. Dyers Colour.* 76, 672 (1966).

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