404. F.Ya.Perveev, Zhur.Obshch.Khim., 19, 1303 (1949).
405. F.Ya.Perveev, Zhur.Obshch.Khim., 19, 1309 (1949).
406. G.Englinton, E.R.H.Jones, G.H.Mansfield, and M.C.Whiting, J.Chem.Soc., 3197 (1954).
407. E.R.H.Jones, G.H.Whitham, and M.C.Whiting, J.Chem. Soc., 3201 (1954).
408. A.W.Nineham and R.A.Raphael, J.Chem.Soc., 118 (1949).
409. C.R.Lappin, J.Org.Chem., 16, 419 (1951).
410. E.R.H.Jones, G.H.Mansfield, and M.C.Whiting, J.Chem. Soc., 3208 (1954).
411. E.R.H.Jones, B.L.Shaw, and M.C.Whiting, J.Chem. Soc., 3212 (1954).
412. D.K.Black and S.R.Landor, J.Chem.Soc., Supplement No.6, 3503 (1963).
413. E.R.H.Jones, J.D.Lander, and M.C.Whiting, Proc.Chem. Soc., 180 (1960); Chem.Abs., 55, 4341 (1961).
414. B.S.Thyagaragan and K.K.Bolasubramanian, Tetrahedron Letters, No.21, 1398 (1964); Ref.Zhur.Khim., 6Zh, 47 (1964).
415. A.T.Babayan, M.G.Indzhikyan, A.A.Grigoryan, and R.V.Minasyan, Izv.Akad.Nauk Armyan.SSR, Khim.Nauki, 15, 567 (1962).
416. G.Opitz, Annalen, 650, 122 (1961).
417. A.N.Pudovik and I.M.Aladzheva, Zhur.Obshch.Khim., 33, 707 (1963).
418. A.N.Pudovik and I.M.Aladzheva, Zhur.Obshch.Khim., 33, 708 (1963).
419. A.N.Pudovik, I.M.Aladzheva, and N.A.Patrusheva, Zhur. Obshch.Khim., 34, 2907 (1964).
420. A.N.Pudovik, Zhur.Obshch.Khim., 20, 92 (1950).
421. A.P.Boisselle and N.A.Meinhardt, J.Org.Chem., 27, 1828 (1963).
422. B.I.Ionin and A.A.Petrov, Zhur.Obshch.Khim., 34, 1174 (1964).
423. B.I.Ionin and A.A.Petrov, Zhur.Obshch.Khim., 33, 432 (1963).

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U.D.C. 547.458.81

C-DERIVATIVES OF CELLULOSE AND OTHER POLYSACCHARIDES

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I. INTRODUCTION

From the time it was established that cellulose is a high-molecular-weight polysaccharide, the elementary unit of which contains alcoholic hydroxyls, investigations in the field of cellulose chemistry were directed mainly towards the study of the reactions involving replacement of the hydrogen atoms of the hydroxyl groups by acyl and alkyl radicals, that is, reactions of *O*-acylation and *O*-alkylation. The interest in obtaining cellulose ethers and esters is due to their widespread use in various products. Existing reviews and monographs mainly survey the progress in the field of the preparation and investigation of the properties of *O*-derivatives of cellulose. Even in the reviews which have appeared recently, in addition to such problems of cellulose chemistry as the dependence of the reactivity of cellulose on its physical structure and the comparative reactivity of the hydroxyl groups in alkylation and acylation, only problems arising in connection with the preparation of cross-linked cellulose macromolecules and graft copolymers of cellulose are considered[1,2].

The present review considers the development of the chemistry by the *C*-derivatives of cellulose, in which the hydroxyl groups are replaced by other functional groups. After the publication of the last monographs on cellulose chemistry[3,4] a number of new syntheses of aminodeoxy- and halogenodeoxy-celluloses have been effected. Hydrazino-, thiocyanato-, nitro-, mercapto-, and other new *C*-derivatives of cellulose have now been obtained.

The chemistry of the *C*-derivatives of cellulose is of great theoretical interest for the further study of the structure of cellulose. It allows a large number of reactions to be used for studying the glucopyranose unit. The investigation of the properties of *C*-derivatives of cellulose with a specified position of a substituent in the elementary unit allows information to be obtained about the carbon atom at which a given substituent is located. This will evidently facilitate an understanding of the complex problems of the mutual influence of groups in carbohydrates and the induction effects acting in them.

The practical interest in the chemistry of *C*-derivatives of cellulose consists both in the modification of cellulose materials with the aim of discovering new possibilities for their use, and also in the search for new ways of using cellulose as an organic raw material.

II. AMINO-DERIVATIVES OF CELLULOSE AND OTHER POLYSACCHARIDES

Attempts to replace the hydroxyl groups in cellulose and starch by amino-groups were made about 75 years ago[5], but the interest in this problem has never waned since then. Amination was carried out with the aim of increasing the dyeability of cellulose fibres[6,7], and for the production of

anion-exchange materials[8] or of analogues of chitosan and chitin[9].

1. Reactions Used for Introducing Amino-Groups into Polysaccharides

Several reactions have been used for obtaining amino-derivatives of cellulose and other polysaccharides.

a. The action of ammonia on cellulose- and acetylcellulose-esters of sulphonic acids:

$$C_6H_7O_2(OH)_{3-x}(OSO_2R)_x \xrightarrow{NH_3} C_6H_7O_2(OH)_{3-x}(OSO_2R)_{x-y}(NH_2)_y.$$

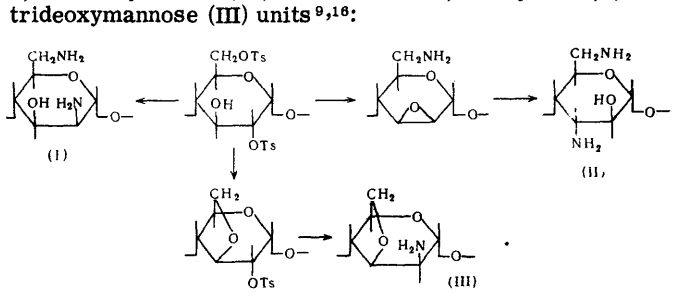
On boiling cellulose *p*-toluenesulphonate (tosylcellulose) with a concentrated solution of ammonia for 1 h at 100°C, Karrer and Wehrli[10] introduced 0.7–0.8% nitrogen into cellulose. On investigating the same reaction Sakurada[11,12] concluded that it only takes place to a slight extent. Gardner[13] also did not succeed in introducing an appreciable amount of nitrogen into cellulose by the action of ammonia on its mixed ester containing tosyl and acetyl groups. During the process the cellulose underwent considerable degradation.

By carrying out the reaction at room temperature or heating cellulose methanesulphonate (mesylcellulose) containing from 0.5 to 1 mesyl group per unit with an aqueous solution of ammonia (28–29%), part of the mesyl groups could be replaced. The products contained 0.5–4% nitrogen and 3–6% sulphur. A change in the reaction conditions did not yield a product free from sulphur[14]. An aminocellulose with 2.5–4.2% nitrogen, 12–14% sulphur, was obtained on treating mesyl cellulose (γ = 150–170) with a solution of ammonia in methanol[15].

b. Reaction of amylose *p*-toluenesulphonate with hydrazine or sodium hydrazide, with subsequent reduction:

$$C_6H_7O_2(OH)_{1.3}(OSO_2C_6H_4CH_3)_{1.7} \xrightarrow{NH_2NH_2} C_6H_7O_2(OH)_{1.6}(NHNH_2)_{1.4} \xrightarrow{NaNO_2} C_6H_7O_2(OH)_{1.6}(N_3)_{1.4} \rightarrow C_6H_7O_2(OH)_{1.6}(NH_2)_{1.4}.$$

The replacement of a considerable proportion of the hydroxyl groups in a polysaccharide by amino-groups was achieved in the reaction of tosylamylose (γ = 170) with hydrazine followed by reduction of the reaction product. To obtain the hydrazinoamylose, ditosylamylose was boiled for 7 days with anhydrous hydrazine under nitrogen. The hydrazinoamylose was reduced to aminoamylose in aqueous solution by Raney nickel for 24 h. The aminoamylose obtained (γ = 140) is an absolutely inhomogeneous product containing, in consequence of the reaction having proceeded in various directions, both 6-amino-6-deoxyglucopyranose and also 2,6-diamino-2,6-dideoxymannose (I), 3,6-diamino-3,6-dideoxyaltrose (II), and 2-amino-3,6-anhydro-2,3,6-trideoxymannose (III) units[9,16]:



6-Amino-6-deoxyamylose with a degree of substitution of 0.1–1 was obtained through the 6-amino-derivative with protected secondary hydroxyl groups by the following scheme[17]:

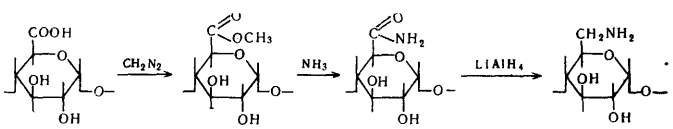
amylose
↓
6-*O*-tritylamylose
↓
6-*O*-tritylamylose 2,3-di-*O*-phenylcarbamate
↓
amylose 2,3-di-*O*-phenylcarbamate
↓
6-azido-6-deoxyamylose 2,3-di-*O*-phenylcarbamate
↓
6-amino-6-deoxyamylose.

c. Reduction of cellulose nitrate by sodium amide:

$$C_6H_7O_2(OH)(ONO_2)_2 \xrightarrow{NaNH_2} C_6H_7O_2(OH)_2(NH_2).$$

By reducing cellulose nitrate (11.7% nitrogen) with sodium amide in liquid ammonia for 9 h, Scherer and Feild[18] obtained monoaminocellulose, with 8.35% total and 7.94% amine nitrogen, which was evidently extensively degraded, as it was extremely soluble in water.

d. Reduction of the amide of an alginic acid:



A new attempt was recently made to introduce an amino-group into a polysaccharide by making use of the reduction of an acid amide. The degree of esterification of the alginic acid and the number of amido-groups introduced were sufficiently high but the product obtained on reducing the amide with lithium tetrahydroaluminate only contained 12 amino-groups per 100 glucose residues[19].

e. Action of ammonia on halogenodeoxycellulose:

$$C_6H_7O_2(OH)_{3-x}(hal)_x \xrightarrow{NH_3} C_6H_7O_2(OH)_{3-y}(NH_2)_y.$$

It has proved impossible to introduce into cellulose an appreciable amount of nitrogen by treating acetyl-6-iodo-6-deoxytosylcellulose with ammonia in organic solvents; a little nitrogen (0.3%) was introduced into it on using sodium amide in liquid ammonia[13]. Recently, Polyakov and Rogovin[8] reinvestigated this reaction. As a result of treating chlorodeoxycellulose with ammonia in alcoholic solution at 160°C they succeeded in introducing 23 amino-groups per 100 glucose residues, which corresponded with 2.25% nitrogen. Under the action of aqueous ammonia saponification of the chlorine occurred in addition to the substitution.

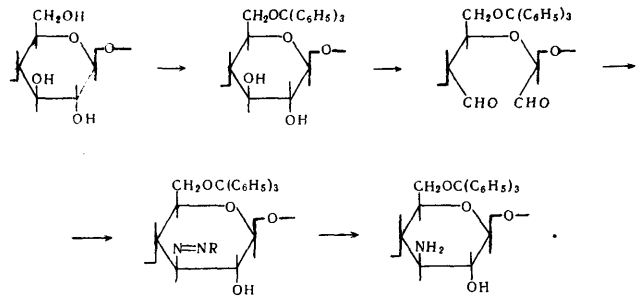
f. Phthalimide synthesis.

An attempt was made to replace a tosyl group in cellulose and acetylcellulose by a phthalimide residue. It was suggested that on saponification of the phthaloyl derivative an aminocellulose and phthalic acid would be obtained.

Only 25% of the tosyl groups in 2,3-di-*O*-acetyl-6-*O*-tosylcellulose could be replaced. In acetyltosylcelluloses with 1.85 acetyl and 0.43 tosyl groups per elementary unit of the cellulose, the tosyl groups were replaced stoichiometrically by the phthalimido-groups. However, it was

found impossible to remove the phthalic acid residues and obtain aminocellulose in this way[20].

g. Condensation of 2,3-dialdehydo-6-*O*-tritylcellulose with *p*-tolylhydrazine and reduction of the condensation product[21,22]:



The condensation of 2,3-dialdehydo-6-*O*-tritylcellulose with *p*-tolylhydrazine in pyridine solution for 24 h gave partially and completely substituted 3-deoxy-3-*p*-tolylazo-6-*O*-tritylcellulose. Reduction of the condensation product in the presence of Raney nickel at a hydrogen pressure of 150 atm and 90°C yielded 3-amino-3-deoxy-6-*O*-tritylcellulose with various amino-group contents, for example:

$$C_6H_7C_2(CH)_{1.46}(NH_2)_{0.62}[CC(C_6H_5)_3]_{0.92}.$$

Hence despite the many stages in the processes, the incompleteness of the reactions, and the great difficulty in proving the structure of the products obtained, the search for new syntheses of aminopolysaccharides is still continuing. The greatest degree of conversion into aminopolysaccharides was reached during the introduction of hydrazido- or azido-groups into tosylamylose and their subsequent reduction. Of all the reactions used, only the condensation of 2,3-aldehydo-6-*O*-tritylcellulose with *p*-tolylhydrazine and subsequent reduction of the product allows an amino-group to be introduced into the glucopyranose chain of cellulose in a definite position: at the third carbon atom.

2. Properties of Aminodeoxypolysaccharides

Aminocellulose is soluble in water, capable of being diazotised and of forming dyes on combination with 1-naphthol, 2-naphthol, aniline, resorcinol, phenol, *o*-cresol, 1-naphthylamine, 2-naphthylamine, etc. It is uncertain, however, whether the dyes produced have the diazo-structure since they are stable to reduction and nitration[23].

Deacetylated chitin and desulphated heparin are deaminated under the action of nitrous acid[24,25].

The exchange capacity of aminocellulose with a high concentration of amino-groups is 2.5 mg-equiv. g^{-1}.[8]

The chemical properties of the glucoside bond and of hydroxyl groups when amino-groups are present in the polysaccharide have been studied in detail, by the example of chitosan and chitin[26]. Danilov and Plisko investigated the action of acids and alkalis on chitin and also its reactivity in etherification and alkylation. The chitin is dissolved in dilute organic and mineral acids after swelling in 8–10% sodium hydroxide at −40°C. Glyceryl, hydroxyethyl, ethyl, and carboxymethyl ethers of chitin were obtained[27–30]. Note that chitin is less reactive than cellulose (as was shown earlier[31–33]) in the reactions for the formation of ethers and esters[34].

N-alkyl and *N*-aryl derivatives of aminocellulose were obtained indirectly[6,7,8,20,35–40]. They dissolve in organic solvents[36] and dilute solutions of acetic acid, and are capable of forming fibres with the best dyability with acid dyes. There are indications that it may be possible to use them as finishes, protective coatings, photographic film base, etc.[41]

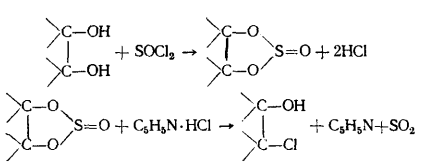
Aminocellulose exhibits increased affinity for acid dyes[6,7] and it is capable of being formed into threads from solution in acetic acid in an alkaline bath[42]. Aminocellulose and aminostarch are mentioned as basic polysaccharides which can be used for finishing fibres[35].

III. HALOGEN DERIVATIVES OF CELLULOSE

The introduction of halogen into cellulose has two aims: modification of the cellulose and the production of reactive derivatives for further syntheses[43].

1. Reactions Used for Introducing a Halogen into Cellulose

a. The reaction of cellulose with thionyl chloride. As long ago as 1931, Carré[44] obtained a substance of composition $C_6H_9O_4Cl$ by the action of thionyl chloride in pyridine on cotton linter. Recently a more detailed study was made both of the reaction itself and of the products obtained. The influence of time and temperature on the degree of substitution of chlorodeoxycellulose[45] was investigated and it was shown that replacement of pyridine by a more polar solvent, for example, dimethylformamide, accelerates the reaction[8]. Chlorodeoxycellulose obtained in pyridine or dimethylformamide at elevated temperatures is dark cinnamon-brown. Carrying out the reaction in carbon tetrachloride or chloroform at the boiling point of the solvent allows a colourless chlorodeoxycellulose to be obtained[46]. The presence of iron accelerates the reaction, especially in carbon tetrachloride. During the preparation of chlorodeoxycellulose in pyridine, hydrolysis of the cellulose takes place, which becomes apparent in a drop in its tensile strength[44]. Chlorodeoxycellulose obtained in pyridine contains sulphur, possibly as sulphate esters. The sulphur concentration depends on how the chlorodeoxycellulose is treated at the end of the reaction: with dilute alkali, sodium chlorite, sodium hydrogen carbonate, or methanol[45]. The possibility of the formation of elementary units with anhydro-rings on carrying out the reaction either in pyridine[45] or in dimethylformamide[8] is not ruled out. Chlorodeoxycellulose obtained in a medium of chloroform or carbon tetrachloride did not contain sulphur and anhydro-rings; hydrolysis of cellulose did not take place during its preparation[46]. Two mechanisms for the formation of chloro-substituted cellulose using thionyl chloride in pyridine have been suggested. In the first of these it is assumed that there are intermediate cyclic sulphate esters which are formed by the reaction of thionyl with the hydroxyl groups of the cellulose in positions 2,3 or 3,6:



The second mechanism presupposes the formation of an intermediate unstable ester of chlorosulphurous acid:

$$ROH + SOCl_2 \rightarrow ROSOCl + HCl$$
$$ROSOCl \rightarrow RCl + SO_2.$$

The first mechanism is supported by the fact that chlorodeoxycellulose is obtained under the conditions for the tosylation of cellulose where the chlorinating agent can only be pyridinium chloride:

$$C_6H_7O_2(OH)_2(OSO_2C_7H_7) + C_5H_5N\cdot HCl \rightarrow$$
$$\rightarrow C_6H_7O_2(OH)_2(OSO_2C_7H_7)_{1-x}Cl_x + C_5H_5NHSO_2C_7H_7,$$

and also by the fact of the formation of cyclic sulphites from polyhydroxy-compounds[47-49] and by the presence of stably-bound sulphur in chlorodeoxycellulose.

The second mechanism finds support from the results of a detailed investigation of the reaction of simple alcohols with thionyl chloride[50-52].

b. Nucleophilic substitution in the reaction of cellulose sulphonates and nitrates with salts of hydrohalogen acids. An exhaustive review[53] on the reactivity of cellulose sulphonates (particularly in reacting with alkali metal halides) has been published.

The specificity of this reaction, namely, the replacement first of all of the tosyl group at the primary carbon atom, was first shown with galactose[54].

A polysaccharide containing a halogen at $C_{(6)}$, 6-deoxy-6-iodo-2,3-ditosylstarch, was first obtained by the action of sodium iodide on tritosylstarch in acetone at 100°C for 3 days[55-57].

Cramer and Purves[58] were the first to replace a primary tosyl group in cellulose by iodine; they used a preparation of partially saponified triacetylcellulose[58]. Then a series of papers were devoted to the use of this reaction for studying the distribution of tosyl groups between the primary and secondary carbon atoms of the elementary unit of cellulose[59-61]. Despite the fact that tosyl groups at secondary carbon atoms are also replaced by halogen[60,62], as was noted above, this reaction has also repeatedly been used for studying the structure of various derivatives of cellulose[63-69] and other polysaccharides[70]. It was shown recently that on carrying out the reaction in a polar solvent not only tosyl groups at the primary but also those at secondary carbon atoms are replaced by halogen[71]. Halogenocellulose free from sulphur was obtained on replacing a methanesulphonate group in a mixed cellulose ester containing acetyl and mesyl groups by iodine (the cellulose ester was treated with sodium iodide). The product contained 0.4 atom of iodine per elementary unit of the cellulose. The initial content of mesyl groups was 0.9.[13]

A method for the introduction of I, Br, Cl, and F into cellulose by the reaction of alkali metal salts and hydrohalogen acids with mesylcellulose in aqueous medium, not in organic solvents, has been developed[72].

In the nucleophilic replacement of a nitrate group by iodine, on treating partially nitrated cotton cellulose with sodium iodide in ethyl methyl ketone for 12 h at 115°C iodine-containing cellulose nitrate was obtained (33% iodine and 0.7–2.5% nitrogen; initial nitrogen content 2.5–9.0%).

By analogy with the monosaccharides it is thought that the iodine replaces only the primary nitrate groups[73]. This reaction is used for studying the distribution of substituents in the elementary unit of cellulose derivatives[74,75]. An insignificant drop in temperature significantly retards the reaction. On using zinc, calcium, or barium iodide under the same conditions only 0.2–2.8% iodine could be introduced into cellulose[73].

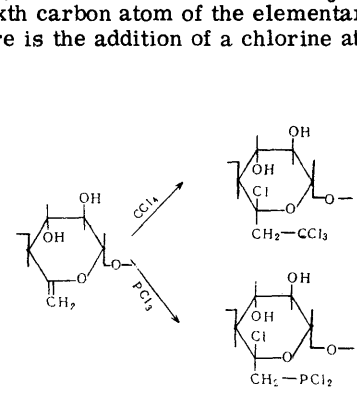
In comparing the reactivity of tosyl, nitrate, and sulphate esters of cellulose in reactions with halides it was found that with lithium chloride or potassium bromide the tosyl ester is most reactive and cellulose sulphate does not react. In reactions with sodium iodide the difference in the reactivity of cellulose *p*-toluenesulphonate and nitrate is less noticeable[76]. It was shown that as a result of side-reactions the ester groups are removed without the introduction of halogen[73,76].

c. Reaction of cellulose phosphinates with alkyl halides:

$$C_6H_7O_2(OH)_3 \xrightarrow{(C_6H_5)_2NP(C_2H_5)_2} C_6H_7O_2(OH)_{3-x}[OP(C_2H_5)_2]_x \xrightarrow{C_6H_5CH_2Cl}$$
$$\rightarrow C_6H_7O_2(OH)_{3-x}Cl_x.$$

A new method of obtaining deoxyhalogenocelluloses by the reaction of cellulose diethylphosphanate with benzyl chloride was recently developed. As a result of a fivefold treatment of a cellulose ester with 4% phosphorus ($\gamma = 30$), with benzyl chloride for 4 h at 120–130°C a chlorodeoxycellulose with 4% chlorine was obtained[77].

d. Addition of CCl_4 and PCl_3 at a double bond. There is a report of the preparation of 5-chloro-6-deoxycellulose starting from cellulose-5,6.[78] Here simultaneously with the addition of the CCl_3 and PCl_2 radicals to the sixth carbon atom of the elementary unit of cellulose there is the addition of a chlorine atom to the fifth carbon atom:



2. Properties of Deoxyhalogenocelluloses

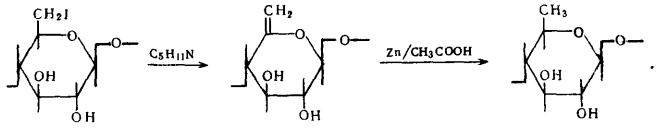
a. Structure and properties. An attempt was made with the aid of paper chromatography of the hydrolysis products to determine the position of chlorine in chlorodeoxycellulose obtained by the action of thionyl chloride in pyridine on cellulose. A specimen of chlorodeoxycellulose containing 6% chlorine was investigated. It was shown that 22% of the chlorine is at $C_{(6)}$. 6-Chloro-6-deoxyglucopyranose was isolated and characterised in this way, but the composition of the other four fractions was not studied. It is suggested that they can contain 2- or 3-monosubstituted glucose, mannose, and allose, and also 2,3- and 3,6-anhydro-derivatives of the same monosaccharides. It was noted that the chlorine in the chlorodeoxycellulose is resistant to saponification under conditions of complete hydrolysis of the latter at the glucoside bonds by 72% sulphuric acid. The introduction of halogen into the cellulose also raises the resistance of the glucoside

bonds to hydrolysis: with increase in the degree of substitution there is an increase in the amount of the unhydrolysable part[45].

On treating the chlorodeoxycellulose with concentrated aqueous solution of ammonia, in addition to the replacement of halogen by an amino-group 50% of the chlorine is saponified. When treated with an alcoholic solution of ammonia, saponification does not take place[8].

Iodine- and bromine-containing mesylcelluloses show enhanced resistance to combustion compared with the initial mesitylcellulose. The introduction of chlorine has no effect on the stability of mesylcellulose to combustion, but the introduction of fluorine impairs it[72].

b. Reactions of deoxyhalogenocelluloses. When pyridine acts on 6-deoxy-6-iodo cellulose (γ = 70), HI is lost and the cellulos-5,6-ene formed. By reduction of an unsaturated derivative of cellulose with zinc in acetic acid, a completely saturated compound is obtained, 6-deoxycellulose[79]:



Cyanodeoxycellulose was obtained by the reaction of chlorodeoxycellulose with potassium cyanide in dimethylformamide or methanol at elevated temperatures. Under the conditions used not more than 65% of the chlorine atoms are replaced. When even a little water (1–1.5%) is present in the reaction mixture, gradual saponification of the nitrile groups takes place[8].

$$C_6H_7O_2(OH)_{2.37}Cl_{0.63} \xrightarrow{KCN} C_6H_7O_2(OH)_{2.59}(CN)_{0.41}.$$

A solution of sodium hydrazide in absolute hydrazine or liquid ammonia (in nitrogen atmosphere) acts on chlorodeoxycellulose to give deoxyhydrazinocellulose. It is possible that there is the parallel formation of anhydrides, since there was some disagreement between the proportion of chlorine atoms removed and the content of hydrazino-groups:

$$C_6H_7O_2(OH)_{2.37}Cl_{0.63} \rightarrow C_6H_7O_2(OH)_{2.37+(0.63-x)}(NHNH_2)_x.$$

IV. HYDRAZINO-, THIOCYANATO-, NITRO-, MERCAPTO-, AND OTHER DEOXY-DERIVATIVES OF CELLULOSE; PREPARATION AND PROPERTIES

Deoxyhydrazinocellulose with a 0.16–0.88 substitution was obtained on the reaction of a solution of sodium hydrazide in absolute hydrazine with tosyl or mesyl esters of cellulose containing 0.44–1.71 sulphonate groups per elementary unit of the cellulose. The reaction was carried out at 20° and –33°C for 15–72 h [80]. Whistler and Shasha[81] obtained 6-deoxy-6-hydrazinocellulose from 6-*O*-tosylcellulose with a degree of replacement of 0.64 by treatment with hydrazine for 30 min at 100°C. Viscosimetric measurements showed that hydrazinolysis took place to an insignificant extent under the conditions of the experiment.

Note that not all the tosyl groups are replaced by hydrazine residues. Since the deoxyhydrazinocellulose did not contain sulphur, evidently part of the tosyl or mesyl groups are saponified under the conditions of the experiment.

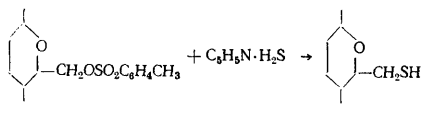
Highly substituted deoxyhydrazinocelluloses (γ = 70–80) are soluble in water and dilute acids, but do not dissolve in alcohol or acetone[80]. The hydrochloride of 6-deoxy-6-hydrazinocellulose is stable and dissolves in water to form a transparent, stable solution. Oxygen, hydrogen peroxide, nitrous acid, iodine, and potassium iodide oxidise the free base[81]. Fabric based on deoxyhydrazinocellulose is readily dyed by acid dyes and absorbs from 1.5 to 1.7 moles hydrochloric acid per hydrazino-group[80]. A deoxy(phenylhydrazino)cellulose with degree of substitution 1–1.35 was obtained on the basis of ditosylcellulose. This preparation also contained from 0.61 to 0.96 tosyl groups per elementary unit of the cellulose. Deoxy(phenylhydrazino)cellulose is soluble in dimethylformamide and does not dissolve in acetone, chloroform, or methanol[80].

Deoxynitrocellulose was obtained by the nucleophilic replacement of tosyl groups in tosylcellulose. The tosylcellulose (γ = 100–180) was treated with sodium nitrite in water and in dimethylformamide for different periods at temperatures from 20° to 140°C. All the tosyl groups could not be replaced. The cellulose derivatives obtained contained both tosyl and nitro-groups. The maximal degree of substitution was 0.4 for nitro-groups[82]:

$$[C_6H_7O_2(CH)_{1.96}(OSO_2C_6H_4CH_3)_{0.62}(NO_2)_{0.42}]_n.$$

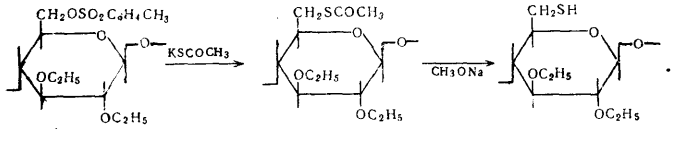
Thiocyanatocellulose (γ = 100) was obtained by the action of sodium or potassium thiocyanate on ditosylcellulose for 8–10 h [59,71]. Partially substituted deoxythiocyanatocellulose was obtained from cellulose nitrate. The maximal degree of substitution of ester groups by thiocyanato-groups under these conditions was 42%.[83]

Deoxymercaptocellulose was obtained by the action of hydrogen sulphide in pyridine on a mixed ester of cellulose containing acetyl (2.44 per elementary unit) and tosyl (0.35 per elementary unit) groups. 80% of the tosyl groups were replaced by mercapto-groups in 8 hours at 35–40°C. When the reaction product,



which is soluble in acetone, was held in air or treated with iodine, it lost its solubility, owing to the formation of disulphide bridges between the cellulose macromolecules[84].

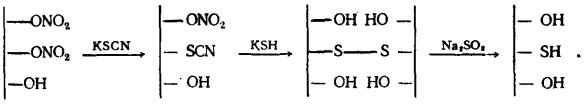
A small number of mercapto groups (0.16 per elementary unit) was introduced into cellulose by the action of potassium thioacetate on a mixed cellulose ester containing ethoxy- and tosyl groups with subsequent deacetylation. The product is soluble in acetone, but in air it oxidises readily, being converted into an insoluble cross-linked polymer[85]:



A cotton cellulose with mercapto-groups was obtained similarly[86].

By passing hydrogen sulphide through a solution of ditosylcellulose in dimethylformamide from 0.5 to 1.79 mercapto-groups could be introduced into the cellulose (calculated per elementary unit)[71].

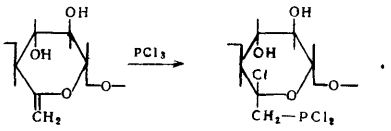
A cellulose derivative containing mercapto-groups was also obtained by the denitration of deoxythiocyanatocellulose nitrate with subsequent reduction[83]:



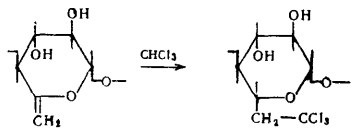
Phosphorus-containing deoxycellulose is formed by the reaction of tosylcellulose with sodium diethyl phosphite[87]:

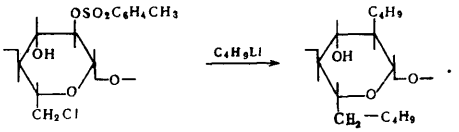
$$\text{cell}{-}OSO_2C_6H_4CH_3 + NaPO(OC_2H_5)_2 \rightarrow \text{cell}{-}PO(OC_2H_5)_2 .$$

An original reaction of radical addition of phosphorus trichloride to a cellulose-5,6-ene has been described[78]:

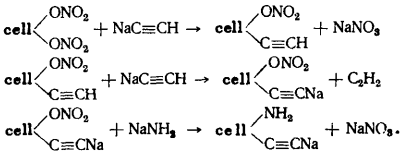


Alkyldeoxycellulose. Papers appeared recently on two methods of introducing alkyl radicals into the glucopyranose unit of cellulose[78,88]:



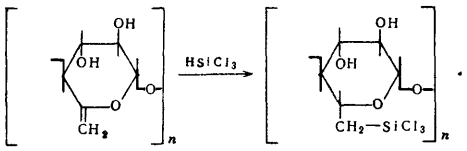


Ethynyldeoxycellulose. As a result of the reaction of cellulose nitrate (11.9% nitrogen) with sodium acetylide in liquid ammonia, a product is obtained with one acetylene and one amino-group for each elementary unit of cellulose:



The acetylene derivative of cellulose in the preparation is readily soluble in liquid ammonia and is not precipitated by water and alcohol. However, after evaporating off the ammonia the product loses its solubility, both in ammonia and in organic solvents, probably because of polymerisation at the acetylene groups[89].

Silicon-containing deoxycellulose is obtained as a result of the following reaction[78]:



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Despite the fact that the chemistry of the *C*-derivatives of cellulose began to develop a long time ago and that interest in it has intensified recently, it is noteworthy that even the most serious investigations have not been pursued to the end. Many authors considered it sufficient to show just the possibility in principle of some particular reaction.

There is a need for further development of the investigations in the field of *C*-derivatives of cellulose, both to seek for new reactions and to find conditions under which these reactions would proceed as completely as possible and not be accompanied, if possible, by various side-processes and by the change in the configuration of the elementary unit of cellulose.

There is special interest in specific reactions which would ensure the production of cellulose derivatives with a definite position of a substituent in its elementary unit. New reactions, for example, the condensation of 2,3-dialdehydo-6-*O*-tritylcellulose with *p*-tolylhydrazine[21,22] and the radical addition of a series of compounds to cellulose-5,6-ene[78], show that possibilities in this direction are far from exhausted.

The study of the properties of *C*-derivatives of cellulose can be considered an almost untouched field of investigation.

1. D.M.Jones, Adv.Carbohydrate Chem., 19, 219 (1964).
2. E.M.Fettes, "High Polymers. Vol.XIX. Chemical Reactions of Polymers" (Edited by K.Ward, Jnr., and A.J.Morak), Interscience, New York, 1964, p.321.
3. Z.A.Rogovin and N.N.Shorygin, "Khimiya Tsellyulozy i Eë Sputnikov" (Chemistry of Cellulose and Its Satellites), Goskhimizdat, 1953.
4. E.Ott, "Cellulose and Cellulose Derivatives", Interscience, New York, 1954.
5. L.Vignon, Compt.rend., 112, 487 (1891).
6. R.Karrer, B.P. 249 842 (1925); Chem.Abs., 21, 1019 (1927).
7. H.Dreyfus, U.S.P. 2 233 475; Chem.Abs., 35, 3814[8] (1941).
8. A.I.Polyakov and Z.A.Rogovin, Vysokomol.Soed., 5, 11 (1963).
9. M.L.Wolfrom, M.I.Tana, and D.Horton, J.Org.Chem., 28, 3553 (1963).
10. R.Karrer and W.Wehrli, Helv.Chim.Acta, 9, 591 (1926).
11. I.Sakurada, J.Soc.Chem.Ind., Japan, 32, 11B (1929).
12. I.Sakurada, Bull.Inst.Phys.Chem.Res., Tokyo, 8, 265 (1929).
13. J.S.Gardner, J.Polymer Sci., 1, 121 (1946).

14. M.L.Wolfrom, J.C.Sowden, and E.A.Metcalf, J.Amer. Chem.Soc., 63, 1688 (1941).
15. S.N.Danilov and I.S.Lishanskii, Zhur.Obshch.Khim., 25, 2106 (1955).
16. M.L.Wolfrom, P.Charavarty, and D.Horton, J.Org. Chem., 30, 2728 (1965).
17. R.L.Whistler and D.G.Medcalf, Arch.Biochem.Biophys., 104, 150 (1964).
18. P.C.Scherer and J.M.Feild, Rayon Textile Monthly, 22, 607 (1941).
19. Z.A.Rogovin, V.A.Derevitskaya, and L.S.Gal'braikh, Vysokomol.Soed., 3, 1561 (1961).
20. J.F.Haskins and A.U.Weinstein, J.Org.Chem., 19, 67 (1954).
21. R.G.Krylova, S.N.Ryadovskaya, and O.P.Golova, Izv. Akad.Nauk SSSR, Ser.Khim., 947 (1966).
22. R.G.Krylova, S.N.Ryadovskaya, and O.P.Golova, Vysokomol.Soed., 9, 993 (1967).
23. P.C.Scherer and A.J.Green, Rayon Textile Monthly, 25, 123 (1944).
24. A.M.Foster, E.F.Martlew, and M.Sacey, Chem.and Ind., 825 (1953).
25. P.P.Schorigin and N.N.Makarova-Semljanskaja, Ber., 68, 965 (1935).
26. A.B.Foster and I.M.Webber, Adv.Carbohydrate Chem., 15, 371 (1964).
27. S.N.Danilov and E.A.Plisko, Zhur.Obshch.Khim., 24, 1761 (1954).
28. S.N.Danilov and E.A.Plisko, Zhur.Obshch.Khim., 24, 2071 (1954).
29. S.N.Danilov and E.A.Plisko, Zhur.Obshch.Khim., 28, 2217 (1958).
30. S.N.Danilov and E.A.Plisko, Zhur.Obshch.Khim., 31, 469 (1961).
31. P.P.Schorigin and E.Hait, Ber., 67, 1712 (1934).
32. P.P.Schorigin and N.N.Makarova-Semljanskaja, Ber., 68, 969 (1935).
33. P.P.Schorigin and E.Hait, Ber., 68, 971 (1935).
34. S.N.Danilov, E.A.Plisko, and E.A.Pyaivinen, Izv.Akad. Nauk SSSR, Otd.Khim.Nauk, 1500 (1961).
35. K.Reinartz, W.Graulich, W.Lehmann, and H.Kleiner, German P. 908133 (1954); Chem.Abs., 52, 10600h (1958).
36. B.P. 279801 (1926); Chem.Abs., 22, 3044^{7} (1928).
37. German P. 473097 (1926); Chem.Abs., 23, 2822^{3} (1929).
38. French P. 641043 (1927); Chem.Abs., 23, 1266^{7} (1929).
39. French P. 783148 (1935); Chem.Abs., 29, 6904^{5} (1935).
40. M.Hagedorn and A.Ossenbrunner, U.S.P. 1833286 (1932); Chem.Abs., 26, 1119^{5} (1932).
41. J.W.Mench and B.Fulkerson, U.S.P. 2861069 (1958); Chem.Abs., 53, 4737h (1959).
42. D.L.Green, U.S.P. 2478265 (1949); Chem.Abs., 44, 328g (1950).
43. U.M.Maratova, M.Askarov, and A.Yuldashev, "Khimiya i Fiziko-Khimiya Prirodnykh i Sinteticheskikh Polimerov" (Chemistry and Physicochemistry of Natural and Synthetic Polymers), Akad.Nauk Uzbek.SSR, 1964, Vol.2, p.153.
44. P.Carré, Compt.rend., 192, 1567 (1931).
45. R.L.Boehm, J.Org.Chem., 23, 1716 (1958).
46. S.Fumasoni and G.Schippa, Ann.Chim.(Italy), 53, (7), 894 (1963).
47. C.C.Price, J.Amer.Chem.Soc., 76, 1211 (1954).
48. P.B.B.De la Mare, W.Klyne, D.J.Millen, J.G.Pritchard, and D.Watson, J.Chem.Soc., 1813 (1956).
49. German P. 875804 (1953); Chem.Abs., 52, 9196e (1958).
50. W.Cowdrey, E.D.Hughes, C.K.Ingold, S.Masterman, and A.D.Scott, J.Chem.Soc., 1267 (1937).
51. E.S.Lewis and C.E.Boozer, J.Amer.Chem.Soc., 74, 308 (1952).
52. D.J.Cram, J.Amer.Chem.Soc., 75, 332 (1953).
53. R.S.Tipson, Adv.Carbohydrate Chem., 8, 108 (1953).
54. K.Freudenberg and K.Raschig, Ber., 60, 1633 (1927).
55. K.Hess and R.Pfleger, Annalen, 507, 48 (1933).
56. K.Hess, O.Littman, and R.Pfleger, Annalen, 507, 55 (1933).
57. K.Hess and W.Sveking, Ber., 67, 1909 (1934).
58. F.B.Cramer and C.B.Purves, J.Amer.Chem.Soc., 61, 3458 (1939).
59. J.F.Carson and W.D.Maclay, J.Amer.Chem.Soc., 70, 2220 (1948).
60. C.J.Malm, L.J.Taughl, and B.C.Laird, J.Amer.Chem. Soc., 70, 2740 (1948).
61. E.Heuser, M.Heath, and W.H.Shoekley, J.Amer.Chem. Soc., 72, 670 (1950).
62. R.C.Hockett, H.G.Fletcher, Jnr., E.L.Sheffield, and R.M.Goepp, Jnr., J.Amer.Chem.Soc., 68, 927 (1946).
63. I.Honeyman, J.Chem.Soc., 168 (1947).
64. J.F.Mahoney and C.B.Purves, J.Amer.Chem.Soc., 64, 9, 15 (1942).
65. T.S.Gardner and C.B.Purves, J.Amer.Chem.Soc., 64, 1539 (1942).
66. G.W.Tasker and C.B.Purves, J.Amer.Chem.Soc., 71, 1023 (1949).
67. T.Timell, Svensk kem.Tidskr., 61, 146 (1949); Chem. Abs., 44, 325b (1950).
68. P.L.E.Faurnier, Ann.Chim.(France), [12], 7, 75 (1952).
69. N.S.Ushakov, O.M.Klimova, and E.I.Faingor, Zhur.Prikl. Khim., 27, 71 (1954).
70. W.Low and E.V.White, J.Amer.Chem.Soc., 65, 2430 (1943).
71. A.I.Polyakov, Candidate's Thesis, Moscow Technical Institute, Moscow, 1963.
72. E.Pacsu and R.F.Schwenker, Textile Res.J., 27, 173 (1957).
73. G.E.Murray and C.B.Purves, J.Amer.Chem.Soc., 62, 3194 (1940).
74. V.A.Derevitskaya, Yu.S.Kozlova, and Z.A.Rogovin, Zhur. Obshch.Khim., 26, 1466 (1956).
75. V.A.Derevitskaya, M.V.Prokof'eva, and Z.A.Rogovin, Zhur.Obshch.Khim., 28, 716 (1958).
76. L.S.Sletkina, A.I.Pol'yakov, and Z.A.Rogovin, Vysokomol. Soed., 7, 199 (1965).
77. K.A.Petrov, E.E.Nifant'ev, L.V.Khorkhoyanu, and V.F.Voblikov, Vysokomol.Soed., 5, 348 (1963).
78. D.G.Dimitrov, L.S.Gal'braikh, and Z.A.Rogovin, Vysokomol.Soed., 7, 2174 (1965).
79. E.D.Kaverzneva, V.I.Ivanov, and A.S.Salova, Izv.Akad. Nauk SSSR, Otd.Khim.Nauk, 369 (1949).
80. A.I.Polyakov and Z.A.Rogovin, in Collected Papers, "Vysokomolekulyarnye Soedineniya: Tsellyuloza i Eë Proizvodnye" (High Molecular Compounds. Cellulose and Its Derivatives), Izd.Akad.Nauk SSSR, Moscow, 1963, p.147.
81. R.L.Whistler and B.Shasha, J.Org.Chem., 29, 880 (1964).
82. N.Kholmuradov, Yu.S.Kozlova, A.I.Polyakov, and Z.A.Rogovin, Vysokomol.Soed., 7, 439 (1965).
83. M.O.Lishevskaya, A.D.Virnik, and Z.A.Rogovin, in Collected Papers, "Vysokomolekulyarnye Soedineniya: Khimicheskie Svoistva i Modifikatsiya Polimerov" (High Molecular Compounds: Chemical Properties and Modifications of Polymers), Izd.Nauka, Moscow, 1964, p.243.
84. E.F.Isard and F.W.Morgan, Ind.Eng.Chem., 41, 617 (1949).
85. G.N.Richards, J.Appl.Polymer Sci., 5, 557 (1961).
86. R.F.Schwenker, L.Lifland, and E.Pacsu, Textile Res.J., 32, 797 (1962).
87. Z.A.Rogovin, Zhur.Vses.Khim.Obshch.im.Mendeleeva,

7, 154 (1962).
88. E.M.Akavbyan, L.S.Gal'braikh, O.Yu.Okhlobystin, and Z.A.Rogovin, Vysokomol.Soed., 8, 959 (1966).
89. R.Scherer and G.A.Saul, Rayon Textile Monthly, 72 (September 1947); 51 (October 1947).

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U. D. C. 535.34

THE ELECTRONIC ABSORPTION AND LUMINESCENCE SPECTRA OF *N*-HETERO-AROMATIC COMPOUNDS AND THEIR DERIVATIVES

R. N. Nurmukhametov

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1. GENERAL REMARKS

In recent years considerable progress has been made towards establishing the relationship between the structure and the spectroscopic-luminescent properties of polyatomic organic molecules. This progress is due to the mutual enrichment of theoretical and experimental studies. The work of a large number of experimentalists, using the results of theory, has revealed comparatively simple and general features, which reflect the relationship between spectra and structure and for which theoretical papers have given further qualititative or semi-quantitative explanations based on an examination of successfully chosen approximations and models. The *N*-hetero-aromatic compounds form one class of compound for which important results have been obtained.

N-Heteroaromatic compounds differ formally from aromatic hydrocarbons in that a =CH– group has been replaced by =N– in the aromatic ring. Since the π-system is preserved, it might be expected that the absorption spectra of *N*-heterocyclic compounds would contain bands similar to chose of the hydrocarbon analogues and due to $\pi-\pi^*$ transitions (excitation of an electron from a filled bonding π-orbital of an unoccupied antibonding π^*-orbital). Such bands are in fact observed, although the intensities and positions are slightly different, because of the inductive effect of the N atom and the decreased symmetry of the molecule. In addition to these bands, the spectra of *N*-heterocycles contain other less intense bands due to $n-\pi^*$ transitions (excitation by promotion of an electron of an unshared pair from the non-bonding orbital of the N atom to an antibonding π^*-orbital). The bands due to $n-\pi^*$ transitions are clearly distinguished in the spectrum only when they are the bands with longest wavelength. The assignment of the bands to $\pi-\pi^*$ and $n-\pi^*$ transitions and the classification of the bands of aza-heterocycles and other organic compounds, based on this assignment, were developed in a paper by Kasha[1].

Goodman made a systematic experimental and theoretical study of the electronic spectra of azines, and summarised the results in a review[2], in which he put forward a theory to explain the energies of the transitions, their intensities, and the singlet-triplet splitting. Mason[3-6] made a systematic study of the position and intensities (oscillator strengths) of the π, π^* and n, π^* absorption bands for various *N*-heterocyclic aromatic compounds. Clementi and Kasha[7] examined the problem of spin-orbital coupling in the n, π^*-state of *N*-heterocycles; this was subsequently developed by El-Sayed[8].

The n, π^*- and π, π^*-states show significantly different luminescent properties, which therefore depend on the relative arrangement of the singlet and triplet n, π^*- and π, π^*-levels. For this reason, the luminescent properties of aza-aromatic compounds differ from those of the corresponding hydrocarbon analogues. Aromatic hydrocarbons exhibit fluorescence and phosphorescence, whereas many *N*-heterocycles are non-fluorescent.

If the spectroscopic-luminescent properties of molecules depend on the relative arrangement of the n, π^*- and π, π^*- levels, this arrangement is determined by the structure of the molecules. The similarity in the π, π^*- bands of *N*-heteroaromatic compounds and their hydrocarbon analogues, demonstrated by Zanker[9], makes it possible to transfer the relationships known for the π, π^*-bands of aromatic hydrocarbons to the corresponding *N*-heterocycles.

The empirical relationships between the structure and spectra of aromatic polynuclear condensed hydrocarbons[10] are found to be applicable for the π, π^*-bands of *N*-heterocyclic compounds. These relationships facilitate the examination of the electronic spectra of these compounds. A general feature of triplet-singlet ($T-S_0$) transitions in aromatic hydrocarbons is that they exhibit polarisation perpendicular to the plane of the molecule. Dorr[11,12], who established this characteristic feature, showed that it also applies to the $T-S_0$ transitions of the π, π^* phosphorescence of *N*-heterocyclic compounds. El-Sayed and Brewer[13] showed for various *N*-heterocycles that the n, π^* phosphorescence exhibits polarisation in the plane of the molecule whereas the π, π^* phosphorescence exhibits polarisation perpendicular to the plane of the molecule. Zimmerman and Joop[14] showed that the polarisation of the π, π^*-bands for the absorption and fluorescence of *N*-heterocycles is the same as that for their hydrocarbon analogues.

The presence of an *N*-hetero-atom produces a marked change in the interaction between the molecule and the solvent, compared with the hydrocarbon analogue. This interaction is responsible for the influence of the solvent