BRIEF COMMUNICATIONS

SYNTHESIS OF THE SULFOPROPYL AND 3-CHLORO-2-HYDROXYPROPYL ETHERS OF DEXTRAN

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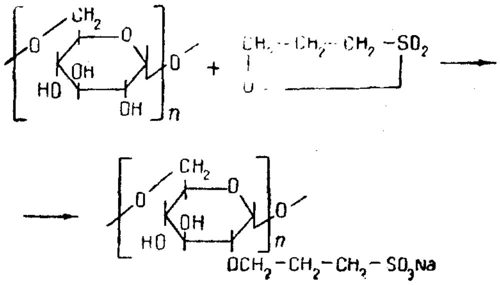
In recent years, many dextran derivatives have been obtained. Some of them have been proposed for use for the synthesis of physiologically active compounds [1–3]. Consequently, the development of methods for obtaining new dextran derivatives containing various reactive functional groups is of great interest.

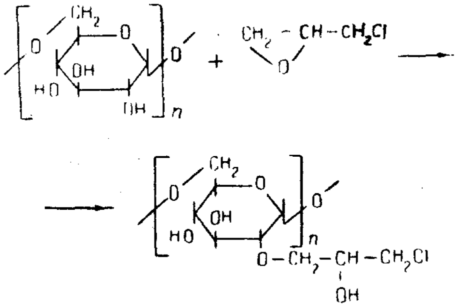
We have carried out the synthesis of the sulfopropyl and the 3-chloro-2-hydroxypropyl ethers of dextran. The sulfo group of the sulfopropyl ether of dextran and the chlorohydrin group of the 3-chloro-2-hydroxypropyl ether of dextran can be used for the addition of molecules of physiologically active substances to the macromolecule of the polymer.

For the synthesis of the sulfopropyl ester of dextran, 1 g of dextran was dissolved in 2 ml of 18% caustic soda solution, after which 1 g of the sultone of hydroxypropanesulfonic acid was added to the solution (1.3 mole of the sultone and 1.3 mole of caustic soda was used per elementary unit of the dextran). The reaction, which was carried out in a homogeneous medium at 40° C with continuous stirring for 5–8 min took place in accordance with the following scheme:



The reaction product was precipitated with acetone, washed with acetone and methanol, and then dried. The sulfur content of the product was 9.3%, which corresponded to a value of γ of 90.4. Under the conditions selected, 84% of the sultone of hydroxypropanesulfonic acid reacted with the dextran. When the amount of sultone used in the reaction was increased to 2.6 moles per elementary unit of dextran, a product was obtained which had 11.17% of sulfur (γ = 126). By means of a second treatment of the product containing 9.3% of sulfur with the sultone of hydroxypropanesulfonic acid under similar conditions, an ether with a value of γ = 160 (12.29% S) was synthesized.

For the synthesis of the 2-hydroxy-3-chloropropyl ether of dextran in accordance with the following scheme



1 g of dextran was dissolved in 1 ml of a 2.5% aqueous solution of the catalyst [$Zn(BF_4)_2$]. The solution was treated with 5 ml of epichlorohydrin. The reaction mixture was stirred for 4 hr at 100° C and cooled, and the liquid phase was decanted off. The product obtained was washed free from epichlorohydrin and its homopolymer with acetone and was dried. The chlorine content was 6.36%, which corresponded to a value of γ of 34. Both ethers had unlimited solubility in water.

Valuable information on the method of synthesis of the sulfopropyl ether was given by Prof. N. N. Shorygina and student scientific worker Z. I. Kuznetsova.

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PTERYXIN FROM THE ROOTS OF *LIBANOTIS CONDENSATA*

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From the roots of *Libanotis condensata* (L.) Crantz., collected by M. G. Pimenov on the island of Sakhalin, we have isolated 6.81% of a mixture of lactones of the coumarin group consisting, according to the results of paper chromatography, of six substances.

From an alcoholic extract of the roots of this plant we have isolated a substance with the composition $C_{21}H_{22}O_7$ having mp 78°–80° C (ether–petroleum ether), $[\alpha]_D^{24.3}$ + 12.9° (c 0.58; ethanol), which, from its chemical properties and UV spectrum λ_{max} : 246, 256, 323 mμ (log ε 3.54; 3.46; 3.96), is related to the coumarins. Its IR spectrum contained the following bands characteristic for the coumarins: 1748 (carbonyl of an α-pyrone ring), 1615 (skeletal vibrations of an α-pyrone ring), 1579 (aromatic C=C bonds), and 1321, 1234, and 1107 cm^{-1} (C–O of an α, β-unsaturated ester). A broad carbonyl band at 1748 cm^{-1} permits the assumption of the presence of one or more ester groups.

The alkaline hydrolysis of this coumarin gave a monohydroxycoumarin $C_{15}H_{16}O_5$ with mp 159°–160° C which was identified on the basis of the melting point, IR spectra, and the absence of a depression of the melting point of a mixture as methylkhellactone, which we have isolated by the hydrolysis of dihydrosamidin [1, 2], together with acetic acid and angelic acid (trans-1, 2-dimethylacrylic) acid.

The acetylation of the methylkhellactone gave an acetate $C_{17}H_{18}O_6$ with mp 147°–148° C (from methanol).

Thus, through a comparison of the constants of the coumarin isolated and its saponification products with published data, and also a comparison of their IR spectra [4], it has been identified as pteryxin (2', 2'-dimethyl-3'-acetyl-4'-angeloyl-5', 6': 8, 7-pyranocoumarin), which has been isolated from the roots of *Pteryxia terebinthina* (Hook.) [4]. Pteryxin possesses a definite spasmolytic effect [3].

By column chromatography on acidic alumina (Brockman activity grade II), we have also isolated from the roots of this plant a substance with the composition $C_{29}H_{50}O$ having mp 133°–135° C which has been identified on the basis of IR spectra, the absence of a depression of the melting point of a mixture, and by the production of an acetate, as β-sitosterol.

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