PARTIAL METHYLATION OF 1,2 ISOPROPYLIDENE-α-D-XYLOFURANOSE

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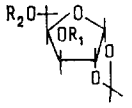
Convenient methods for obtaining methylated sugars are based on the partial methylation of methyl glycosides followed by chromatography of the resulting mixtures of methyl ethers [1]. The partial methylation of methyl glycopyranosides does not, as a rule, lead to an appreciable selectivity in the replacement of the secondary hydroxy groups [2]. In view of this, it was of interest to compare the reactivities of the primary and secondary hydroxy groups in



I. $R_1 = R_2 = H$
II. $R_1 = CH_3$, $R_2 = H$
III. $R_1 = H$, $R_2 = CH_3$
IV. $R_1 = R_2 = CH_3$

methylation reactions. As a model we selected 1,2-O-isopropylidene-α-D-xylofuranose (I) [3]. The results of partial methylation are given below.

Reagent	Amount in the mixture, %			
	I	*II*	*III*	*IV*
$CH_3I + Ag_2O$*	1.3	10.8	85.7	2.2
$(CH_3)_2SO_4 + NaOH$†	24.4	22.2	17.7	35.7
$CH_2N_2 + SnCl_2$‡	—	13.9	83.6	2.5

As can be seen from these results, methylation with diazomethane led predominantly to the substitution of the C-5 hydroxyl. Methylation with methyl iodide in the presence of silver oxide also took place praetically selectively with the participation of the hydroxyl at C-5; $k_5:k_3$ = 7.9.

On methylation under alkaline conditions, reactivity was determined mainly not by spatial factors but by the nucleophilicity of the two types of hydroxyls at C-3 and C-5, which led to the predominant substitution of the C-3 hydroxyl. The ratio $k_5:k_3$ = 0.6 (determined as the ratio of the methyl ethers in the early stages of substitution).

Liquid chromatography on silica gel L (0.1-0.16 mn, Chemapol) of the product of partial methylation of compound (I) by dimethyl sulfate in alkali was used for the separation of the methyl ethers of (I). The load on the column (3 × 40 cm) was 4.5 g of a mixture of the methyl ethers of (I). Elution was performed by a gradient of acetone in hexane. The separation was monitored by TLC in the hexane—acetone in hexane. The separation was monitored by TLC in the hexane—acetone (12:8) system and by GLC on a Tsvet-106 instrument. Columns were glass (0.3 × 200 cm) containing 1.5% of NPGS on Chromaton NAW-HMDS (0.125-0.160 mm, Chemapol). Rate of flow of argon 60 ml/min Temperature of the thermostat 170°C. Retention time of (III) 5.1 min.

As a result, (IV) was obtained with a yield of 1.6 g; syrup, $[\alpha]_D^{20}$ −34.3° (c 1.8; methanol), R_f 0.71. R_T 0.35 [4].

The yield of (III) was 0.7 g, mp 81-82°C, $[\alpha]_D^{20}$ −23.6° (c 1.0; methanol). R_f 0.53. R_T 1.00 [5].

*Compound (I) (0.1 g) in methanol (1 ml) was stirred with methyl iodide (0.3 ml) and silver oxide (0.6 g) in the dark for 1 h.
†Compound (I) (0.1 g) in water (1 ml) was stirred with dimethyl sulfate (0.3 ml) and a 30% solution of caustic soda (0.6 ml) for 1 h.
‡Compound (I) (0.1 g) in dioxane (1 ml) was stirred with stannous chloride (7 mg) and a 1 N solution of diazomethane in methylene chloride (10 ml) for 1 h.

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The yield of (II) was 0.9 g, syrup; $[\alpha]_D^{20}$ −57.8° (c 1.1; methanol). R_f 0.48. R_T 1.18 [5].

The yield of (I) was 1.0 g, mp 39-41°C, $[\alpha]_D^{20}$ −18.8° (c 1.8; methanol). R_f 0.30. R_T 3.76 [3].

The methyl ethers of (I) were identified by ^{13}C NMR spectroscopy in D_2O with allowance for the effects described previously [6]. The assignment of the ^{13}C signals in I was made in [7].

Compound	C-1	C-2	C-3	C-4	C-5	Quaternary C's	Acetonide CH_3	CH_3
I	105.1	85.4	74.6	81.8	60.0	113.2	25.8; 26.3	
II	105.2	84.2	81.9	81.4	59.7	113.2	25.9; 26.3	58.2
III	105.1	85.3	74.8	80.4	70.7	113.2	25.8; 26.3	59.2
IV	105.2	84.4	81.8	79.6	70.4	113.2	25.9; 26.3	58.2; 59.3

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STABILIZATION OF CARBOHYDRATES IN THE ALKALINE DIGESTION OF WOOD WITH ANTHRAQUINONE AND POLYSULFIDES

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The experimentally established facts of the stabilization of carbohydrates and an increase in the yield of cellulose in alkaline cooks of wood with additions of anthraquinone and polysulfide and an increase in the amount of carboxy groups in the cellulosic materials in these cooks are explained by the selective oxidation of the terminal carbonyl groups to carboxy groups, the formation of which "stabilizes" the breakdown of the polysaccharide [1, 2]. The influence of reducing agents (NH_2—NH_2, $NaBH_4$, Na_2S) causes the stabilization of the carbohydrate fraction and an increase in its yield [3], and, therefore, in alkaline cooks a considerable contribution to the degradation of the polysaccharides is also provided by their oxidative breakdown.

If the opinion is held that the "peeling" mechanism, as a depolymerization process, is determinative in the breakdown of carbohydrates, then in alkaline treatments no appreciable fall in the degree of polymerization (DP) of celluloses should be observed. However, a number of authors, including in particular, Yu. V. Brestkin, have convincingly shown that in a sulfate cook a statistical degradation of cellulose takes place [4].

We have performed investigation by the chemiluminescence method with the aim of elucidating the mechanism of the stabilizing action of anthraquinone-2-sulfonic acid (AMS) and polysulfide on the degradation of carbohydrates. It has been established that when glucose is oxidized the addition of anthraquinone-2-sulfonic acid at concentrations of 10^{-5}-10^{-4} M intensively quenches luminescence (Fig. 1). Thus, the oxidized form of AMS is itself an inhibitor of the oxidation of carbohydrates, which does not fall within the framework of the explanation of the mechanism of the stabilization of carbohydrates through the selective oxidation of ter-

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