0.35 g (8.6%) of (XIII), 1.17 g (30%) of (XIV), 0.3 g of a mixture of (XIV) and (XV), and 0.24 g (6%) of (XV). The alcohol (XIV) had mp 158-161°C (chloroform–methanol), $[\alpha]_D$ +95.4° (C, 1). ^{13}C NMR spectrum (δ, ppm): 17.5, 17.7, 17.9 (C_A^6, C_B^6, C_C^6), 26.6, 101.8, 117.0 (MeCCN), 57.2 (C_D^2), 62.7 (C_D^6), 67.6, 67.9 (C_B^5, C_C^5), 70.2 × 2, 70.6, 70.8, 71.3, 71.9, 72.0, 72.1, 72.2, 73.4, 76.8 (C_B^2, C_C^2, C_B^3, C_C^3, C_D^3, C_A^4, C_B^4, C_C^4, C_D^4, C_A^5, C_D^5), 77.8 (C_A^3), 80.4 (C_A^2), 97.1 (C_A^1), 99.2 (C_D^1), 101.1 (C_C^1), 101.8 (C_B^1). ^{13}C NMR spectrum in $(CD_3)_2CO$ (δ, ppm): 17.9, 18.1, 18.2 (C_A^6, C_B^6, C_C^6), 27.1, 102.7, 118.2 (MeCCN), 58.3 (C_D^2) 63.8 (C_D^6), 68.5 × 2 (C_B^5, C_C^5), 69.9, 70.7, 71.8, 72.3, 72.9, 73.0, 73.2, 73.3, 73.8 (C_B^3, C_C^3, C_D^3, C_A^4, C_B^4, C_C^4, C_D^4, C_A^5, C_D^5), 78.0, 78.2, 78.3 (C_B^2, C_C^2, C_A^3), 82.0 (C_A^2) 98.2, 100.5, 101.8, 102.3 (C_A^1, C_B^1, C_C^1, C_D^1).

CONCLUSIONS

Conventional derivatives of L-rhamnose and D-glucosamine have been employed in the stepwise and block synthesis of a functionalized tetrasaccharide repeating unit of the O-antigenic polysaccharide of *Sh. flexneri*. This is a precursor of the monomer for polycondensation.

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SYNTHESIS OF THE PRINCIPAL CHAIN OF THE O-ANTIGENIC POLYSACCHARIDES OF *Shigella Flexneri*. COMMUNICATION 6.* SYNTHESIS OF THE MONOMER, ITS POLYCONDENSATION, AND PROPERTIES OF THE POLYSACCHARIDE

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UDC 542.91:547.458

We have previously reported [1] the synthesis of the tetrasaccharide (I), which is the precursor of the monomer (II) required for polycondensation. The preparation of the monomer (II) required a single step, namely, tritylation of the free hydroxyl group in (I). Previous syntheses of monomers used successfully for polycondensation have always involved tritylation of derivatives already containing the cyanoethylidene group. In those cases in which tritylation of a primary hydroxyl was required, this was effected with triphenylchloromethane in pyridine, and it proceeded smoothly. For the tritylation of secondary hydroxyl groups, a special method was developed, namely, treatment with $TrClO_4$ in the presence of 2,4-6-tri-tert-butylpyridine, 2,6-di-tert-butyl-4-methylpyridine, 2,6-lutidine, or 2,4,6-collidine [2]. It was shown in many cases that monosaccharide cyanoethylidene deriviatives containing secondary hydroxyl groups can be converted into their trityl ethers in yields of 20 to 90% without the formation of byproducts [3].

*For Communication 5, see [1].

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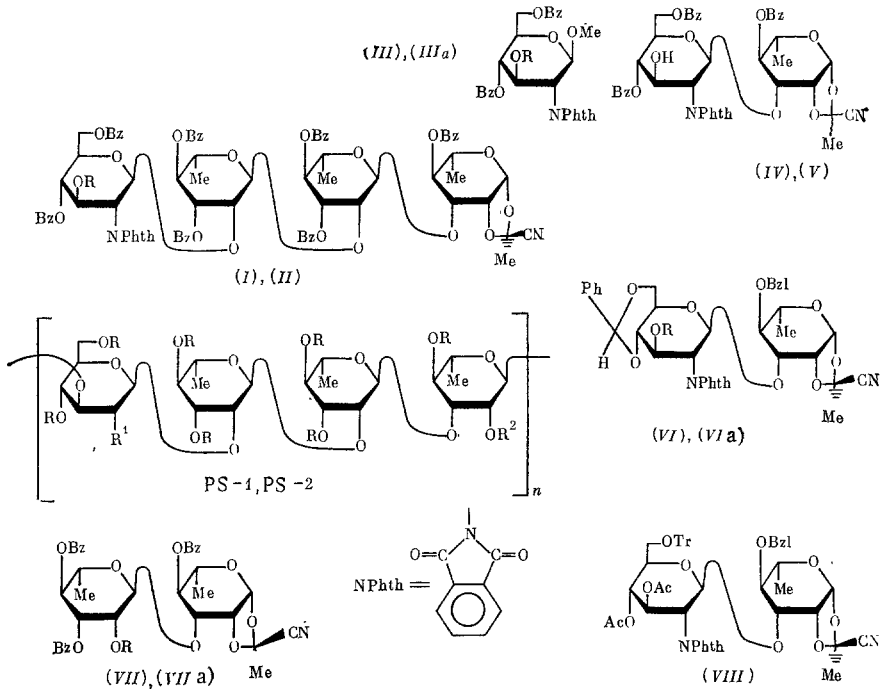
Scheme 1



R = H (I), (III), (VI), (VII); Tr (II), (IIIa), (VIa), (VIIa); exo-CN (IV), endo-CN (V);
R = Bz, R' = NPhth, R^2 = Ac (IIC-1); R = R^2 = H, R^1 = NHAc (PS-2).

The successful tritylation of secondary hydroxyl groups in glucosamine derivatives has been well shown in the cases of benzyl-2-acetamido-3,6-di-O-acetyl-2-desoxy-α-D-glucopyranoside [2] (62% yield) and methyl-6-O-benzoyl-2-desoxy-2-phthalimido-β-D-glucopryanoside [4] to give a mixture of the 3- and 4-O-trityl ethers (overall yield 80%).

We first examined the tritylation of the model compounds methyl 4,6-di-O-benzoyl-2-desoxy-2-phthalimido-β-D-glucopyranoside (III) [5] (unit D, the disaccharide (VII) (assembly BA) [1, 6], and the three trisaccharides (IV)-(VI), which are simplified models of the tetrasaccharide (II) without its two "internal" rhamnose units. It was found that introduction of the trityl group into the O^3 position in (III) required around 4 h, the tritylether (IIIa) being obtained in 81% yield, and its structure was confirmed by its ^1H and ^{13}C NMR spectra. In the cases of (IV) and (V), none of the desired products were obtained after 4 h, and in both instances a product was obtained which contained, according to the ^{13}C NMR spectrum, neither a trityl nor a cyanoethylidene group. In the case of the model compound (VI), which differs from (IV) and (VI) only in the substituents at O^4 and O^6 of the glucosamine residue and O^4 of the rhamnose residue, the trityl ether (VIa) was isolated in 57% yield together with unknown productswhich also did not contain the cyanoethylidene group. However, tritylation of the model compound (VII) proceeded without complications to give after 0.5 h an 82% yield of the trityl ether (VIIa).*

Knowing, therefore, that when a glucosamine residue and a cyanoethylidene group are both present in a molecule, tritylation with triphenylmethylium perchlorate is accompanied by unknown side reactions resulting in loss of the cyanoethylidene group, we attempted the tritylation of the tetrasaccharide (I) (Scheme 1).

Treatment of the alcohol (I) with 1.1 equiv. of $TrClO_4$ in the presence of 1.13 equiv. of 2,4,6-collidine in dichloromethane resulted in a side reaction, with the result that, in addition to the starting material (TLC, ethyl acetate–benzene, 2:8, R_f 0.39) and its trityl ether (R_f 0.70), new compounds were obtained with R_f 0.47 and 0.78. These four products were found in the reaction mixture after as little as 15-20 min following addition of $TrClO_4$. TLC examination showed that the product with R_f 0.78 subsequently increased at the expense of the others. According to ^{13}C NMR spectroscopy, theproduct with R_f 0.47 did not contain the

*The syntheses of the model compounds (IV)-(VI) and their tritylation, together with the tritylation of (VII), will be reported elsewhere.

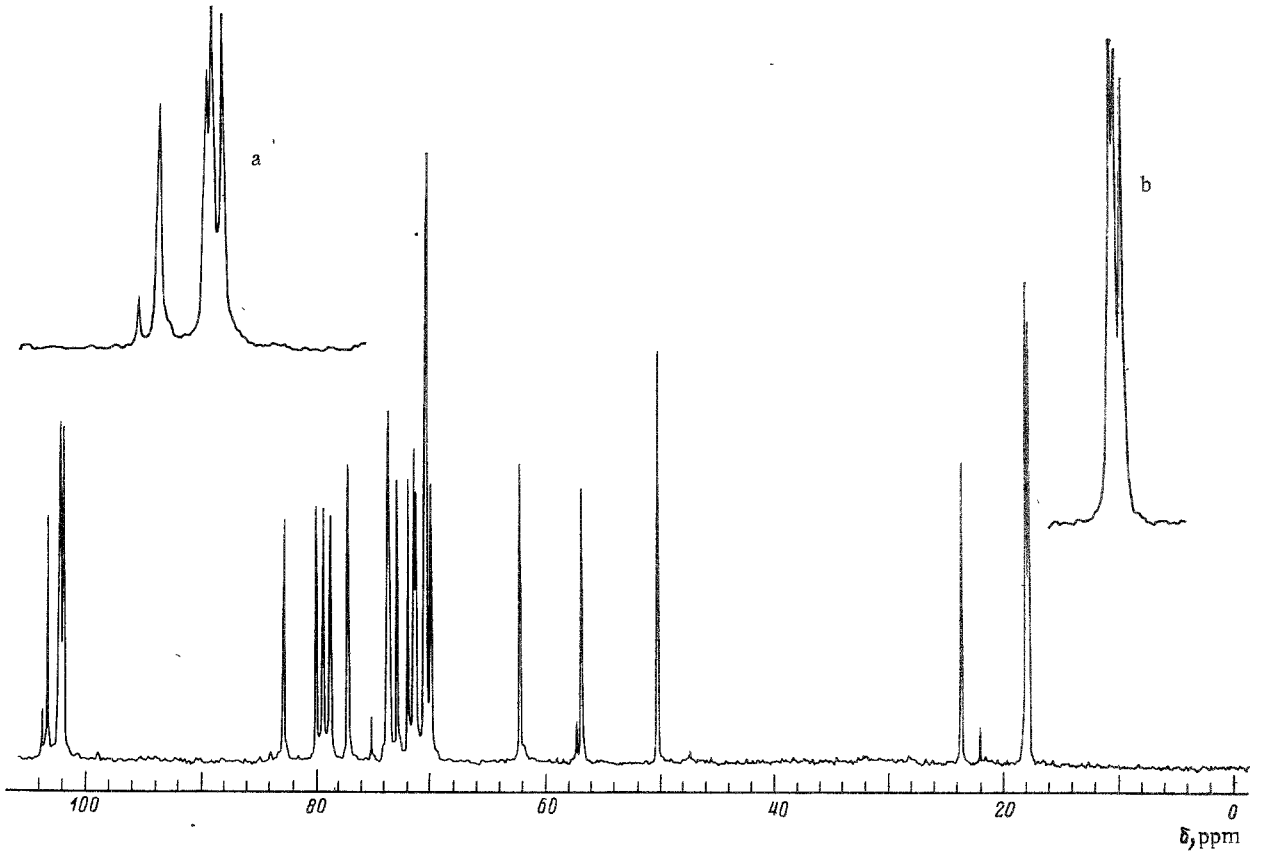


Fig. 1. ^{13}C NMR spectrum of the synthetic polysaccharide (D_2O, internal standard MeOH, δ 50.15 ppm). Extended regions: a) anomeric C atom region; b) rhamnose C^6 region.

cyanoethylidene group. Furthermore, treatment of the compound with R_f 0.47 with acetic anhydride in pyridine resulted in its complete conversion into a new product with greater chromatographic mobility. The product with R_f 0.78, which gives a characteristic yellow color on spraying the chromatogram with sulfuric acid followed by heating, is apparently the trityl ether of the compound with R_f 0.47.

In order to obtain preparative amounts of the trityl ether (II), the reaction was terminated after 30-50 min, when, according to TLC, the ratio of products with R_f values 0.39, 0.47, 0.70, and 0.78 was ∿6:1:2:1. Chromatographic separation of the mixture gave 20 ± 10% of the required product (II) and 60 ± 10% of starting material (I). The unreacted starting material was again tritylated, followed by fractionation. After six cycles of tritylation, the trityl ether (II) was obtained in 40% overall yield. Its structure was confirmed by its ^{13}C NMR spectrum which, unlike that of (I), contained a signal characteristic of Ph_3CO at 88.85 ppm. The presence of signals in the spectrum of (II) at 26.5, 101.7, and 117 ppm, corresponding respectively to the carbon atoms of the MeCCN grouping, and the value of the constant $^1J_{C_1,H_1}$ for unit A (173.9 Hz) indicates the presence of the 1,2-O-(1-cyanoethylidene) group in (II). The values of the other $^1J_{C_1,H_1}$ constants (172.0, 172.0, and 162.8 Hz for units B, C, and D, respectively) confirm the presence in (II) of two α-L-rhamnopyranosyl and one β-D-glycosaminyl residues.

The monomer (II) was then subjected to $TrClO_4$-catalyzed polycondensation. We have previously shown that the monomer (VII) [7], which is a simplified model of the monomer (II), undergoes polycondensation to give a macromolecular polysaccharide containing 40-45 disaccharide units [8]. Polycondensation of the monomer (II), like (VIII), occurred under the same conditions as for the polycondensation of neutral sugar derivatives [3], namely, in the presence of 0.1 equiv. of $TrClO_4$ in dichloromethane at ∿20°C. After 16 h, TLC (ethyl acetate–benzene, 2:8) showed that the monomer had disappeared completely, and that the main product (R_f 0.00-0.10), which did not contain trityl groups, as shown by the absence of a yellow coloration on spraying the chromatogram with sulfuric acid), noncarbohydrate compounds (TrOH and TrCN), and trace amounts of two carbohydrate products (which likewise did not contain trityl groups), were present. The polymer obtained had high chromatographic mobility and, unlike the polymer obtained by the polycondensation of (VIII) [8], was readily soluble in di-

chloromethane. Two samples of the monomer were subjected to polycondensation, namely, an amorphous sample (purified by double column chromatograpy (CC)), and a crystalline sample. Following treatment of the reaction mixture with a mixture of methanol and pyridine to decompose the catalyst, it was diluted with chloroform, washed with water, and subjected to CC. From the experiments with the first and second samples of the monomer, the purified polysaccharide (PS-1) was isolated in yields of 70 and 90%, respectively. The ^{13}C NMR spectra of both samples of the purified polysaccharide were identical, containing the following characteristic signals: 17.00, 17.41, 17.53 (C^6 of the three rhamnose residues), 20.50 (MeCO), 56.36, 62.71 (C^2 and C^6 of the glucosamine residue), 67.49, 67.60, 67.80 (C^5 of the three α-L-rhamnopyranose residues, cf. [9]), 98.19, 99.28, 100.33, and 100.67 (anomeric C atoms). The spectrum contained no signals for CN (110-120 ppm). The polysaccharide thus obtained contained only the protecting acyl groups, which were removed in a single step by hydrazinolysis [10]. The free polysaccharide N-acetylated with acetic anhydride in aqueous methanol, followed by gel chromatography on Biogel P-4 to give a 90 yield of the polysaccharide PS-2 after lyophilization. The ^{13}C NMR spectrum of the polysaccharide PS-2 contained signals at 102.21, 101.88, 102.10, and 103.24 ppm ($^1J_{C,H}$ = 170.2, 172.0, 171.1, and 162.2 Hz), corresponding to the anomeric C atoms of units A, B, C, and D, respectively). The $^1J_{C,H}$ values show that all the rhamnose bonds, including the newly-formed ones, have the α configuration, and hence the polycondensation follows a stereospecific course. The low-field position of the signal for C^3 of the glucosamine residue (82.68 ppm) shows that this residue is glycosylated in the O^3 position, and that the polycondensation is therefore regiospecific. The spectrum also contains minor signals at 57.2, 75.0, and 103.7 ppm, assigned to C^2, C^3, and C^1 of the unsubstituted glucosamine residue at the nonreducing end of the polysaccharide chain.

The identity of the structures of our PS-2 polysaccharide with the principal chain of the O-antigenic polysaccharides of *Shigella flexneri* is shown by the identity of the ^{13}C NMR spectra of PS-2 (Fig. 1) and of the naturally occurring polysaccharide of *Sh. flexneri*, variant Y [11].

The molecular weight of PS-2 was measured by gel permeation chromatography on a SynChro-Pack GPC-100 column, using as standards T-10, T-20, and T-40. It was found to be ∿6000, corresponding to a degree of polymerization of ∿10.

This synthesis, in conjunction with the previously reported synthesis of the O-antigenic polysaccharide of *Salmonella newington* [12], demonstrate the extensive possibilities of the method involving the polycondensation of tritylated cyanoethylidene derivatives of carbohydrates for the preparation of regular heteropolysaccharides of complex structure.

EXPERIMENTAL

$TrClO_4$ was obtained as described in [13], and purified by reprecipitation from dry nitromethane with dry ether [12]. The general methods and apparatus used have been described previously [14].

Tritylation of Methyl-4,6-di-O-benzoyl-2-desoxy-2-phthalimido-β-D-glucopyranoside (III). To a solution of 270 mg (0.51 mmole) of the alcohol (III) in 5 ml of dichloromethane was added 0.1 ml (0.76 mmole) of 2,4,6-collindine, followed by the portionwise addition with stirring of 210 mg (0.61 mmole) of $TrClO_4$. The mixture was stirred for 4 h, after which time TLC showed the presence of the starting material (R_f 0.26, benzene—ethyl acetate, 85:15) and a product with R_f 0.51. The mixture was treated with 0.5 ml of pyridine followed by 50 ml of chloroform, washed with water (3 × 50 ml), and subjected to CC to give 320 mg (81%) of the trityl ether (IIIa) as a foam, $[\alpha]_d$ +90° (C, 2.7). PMR spectrum (δ, ppm; J, Hz): 3.30 s (3H, MeO), 3.85 d.d.d. (1H, H^5), 4.40 d.d. (1H, H^6, $J_{6,5}$ = 5.5, $J_{6,6'}$ = 12), (1H, $H^{6'}$, $J_{6',5}$ = 3.5), 4.63 d.d. (1H, H^2, $J_{2,3}$ = 10), 4.76 d.d. (1H, H^3, $J_{3,4}$ = 8), 5.00 d (1H, H^1, $J_{1,2}$ = 8), 5.62 d.d. (1H, H^4, $H_{4,5}$ = 9.5), 6.90-7.95 m (29 H, H_{arom}). ^{13}C NMR spectrum (δ, ppm): 56.5 (C^2), 56.7 (MeO), 64.1 (C^6), 71.8, 72.2, 73.8 (C^3, C^4, C^5), 89.0 (Ph_3CO), 99.3 (C^1), 165.2, 166.1, 167.5, (CO).

Tritylation of (I) — Preparation of O-(4,6-Di-O-benzoyl-2-desoxy-3-O-trityl-2-phthalimido-β-D-glucopyranosyl)-(1 → 2)-O-(3,4)di-O-benzoyl-α-L-rhamnopyranosyl)-(1 → 2)-O-(3,4-di-O-benzoyl-α-L-rhamnopyranosyl)-(1 → 3)-4-O-benzoyl-1,2-O-[1-(exocyano)ethylidene]-β-L-rhamnopyranose (II). To a solution of 1.73 g (1.13 mmoles) of (I) in 20 ml of dichloromethane was added 0.17 ml (1.29 mmoles) of 2,4,6-collidine, followed by the portionwise addition over 20-30 min of 420 mg (1.22 mmoles) of $TrClO_4$. The mixture was stirred for a further 10-15 min, after which time the mixture contained (TLC, ethyl acetate—benzene, 2:8) four products with

R_f 0.39 (starting material), 0.47 (trityl-negative), 0.70 (trityl-positive), and 0.78 (trityl-positive). After stirring for 10-12 min with $TrClO_4$, in addition to the characteristic yellow tritylium color, the mixture assumed a violet tint (this did not normally appear if tritylation proceeded smoothly without the formation of byproducts). The reaction was terminated by adding 1-2 ml of a 3:1 mixture of pyridine and methanol, diluted with chloroform, washed with water, dried, evaporated, and the residue chromatographed in the system benzene—ethyl acetate (up to 10-15% of ethyl acetate) to give 310 (15%) of the trityl ether (II), R_f 0.70, and 1.26 g (72.8%) of starting material (I). Repeated CC gave 240 mg of (II), which was crystallized from chloroform and methanol to give a crystalline sample of (II), mp 243-245°C, $[\alpha]_D$ +104.3° (C, 1.33). ^{13}C NMR spectrum (δ, ppm; J, Hz): 17.67 × 2, 17.84 (C_A^6, C_B^6, C_C^6), 26.52 (MeCCN), 56.81 (C_D^2), 63.44 (C_D^6), 67.67, 67.90 (C_B^5, C_C^5), 80.40 (C_A^2), 88.85 ($Ph_3\underline{C}O$), 97.05 (C_A^1, $^1J_{C,H}$ = 173.9, cf. [15]), 98.36 (C_D^1, $^1J_{C,H}$ = 162.8), 100,89 (C_C^1, $^1J_{C,H}$ = 172.0), 101.9 (C_B^1, $^1J_{C,H}$ = 172.0), 101.76 (Me$\underline{C}$CN), 117.0 (CN). Unreacted starting material (I) was again tritylated and fractionated. In this way, from 3.6 g (2.36 mmoles) of (I) there were obtained after six cycles of tritylation 1.66 g (39.8%) of (II) and 240 mg (6.7%) of (I), the average yield at each tritylation step being 15-20%, and the recovery of starting material 60%.

Polycondensation of the Monomer (II). In one arm of a γ-shaped ampul fitted with a vacuum tap and a ground glass joint for attachment ot a vacuum line was placed 440 mg (0.25 mmole) of (II) (amorphous, after double CC) in 1 ml of dry benzene, and in the other arm was placed a solution of 8.5 mg (0.025 mmole) of $TrClO_4$ in 0.5 ml of dry nitromethane. The ampul was attached to the vacuum line ($4 \cdot 10^{-3}$ torr), and the contents lyophilized. Into the arm containing the monomer was distilled 2 ml of benzene (previously twice distilled over CaH_2 in the apparatus), the monomer dissolved, and lyophilization repeated, followed by drying for 2-3 h at 20°C. Dichloromethane (1.5 ml) (previously twice distilled in the apparatus over CaH_2) was distilled into each arm of the ampul (3 ml in all), and the solutions of the monomer and catalyst mixed and kept for 16 h at 20°C. The ampul was filled with dry argon, and the solution treated with 0.1 ml of a 1:3 mixture of methanol and pyridine. Before addition of this mixture, TLC (ethyl acetate—benzene, 2:8) showed the presence of products with R_f 0.90 (TrOH and TrCN), 0.36 and 0.43 (minor carbohydrate-containing products), and 0.0-0.1 (the principal carbohydrate product). None of the carbohydrate products contained trityl groups (no yellow coloration in TLC). The mixture was diluted with 50 ml of chloroform, washed with water, dried, and evaporated. The residue (450 mg) was chromatographed on a column containing 50 g of silica gel and eluted with 25-30% ethyl acetate in benzene to give 265 mg (70%) of PS-1 as an amorphous, white powder, R_f 0.5 (benzene—ethyl acetate, 7:3) or 0.9 (benzene—ethyl acetate, 1:1). In another experiment, using 630 mg (0.36 mmole) of the cyrstalline monomer (II), 485 mg (90%) of PS-1 was obtained, $[\alpha]_D$ +117.4°.

Hydrazinolysis Followed by N-Acetylation of PS-1. A suspension of 200 mg (0.13 mmole) of PS-1 in a mixture of 15 ml of alcohol and 1.5 ml(99%)hydrazine hydrate was boiled for 20-25 h(the solution became homogeneous after boiling for 5-6 h). The solution was evaporated, the hydrazine hydrate removed by repeated coevaporation with n-butanol, and the residue treated with 10 ml of methanol, 2 ml of water, and 4 ml of acetic anhydride. The mixture was kept for 16 h at 20°C, evaporated to dryness, the residue suspended in 6 ml of water, centrifuged, the supernatant separated, the solid from the first centrifugation again suspended in 6 ml of water and centrifuged, the combined supernatants evaporated, and the residue subjected to gel chromatography on a column containing Biogel P-4 (55 × 2.5 cm, 400 mesh, $V_0 \sim 110$ ml) in 0.1 N acetic acid. The eluate collected over the range 90-150 ml was evaporated, the residue lyophilized from water, the lyophilizate dried *in vacuo* over P_2O_5 (60°C, 3 h) to give 80 mg (92%) of PS-2, $[\alpha]_D$ −46° (C, 0.87, H_2O). From 450 mg (0.30 mole) of another sample of PS-1 (obtained from crystalline monomer (II)) following similar treatment there was obtained 180 mg (93.5%) of the unprotected polysacchride PS-2, $[\alpha]_D$ −55° (C 0.75, H_2O).

CONCLUSIONS

Regio- and stereospecific polycondensation has been used to synthesize the principal chain of the O-specific polysaccharides of the bacterium *Sh. flexneri*.

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SYNTHESIS OF MACROLIDE ANTIBIOTICS. COMMUNICATION 6*. SYNTHESIS OF C^{13}-EPI-C^{9}—C^{13} FRAGMENT OF ERYTHRONOLIDE A

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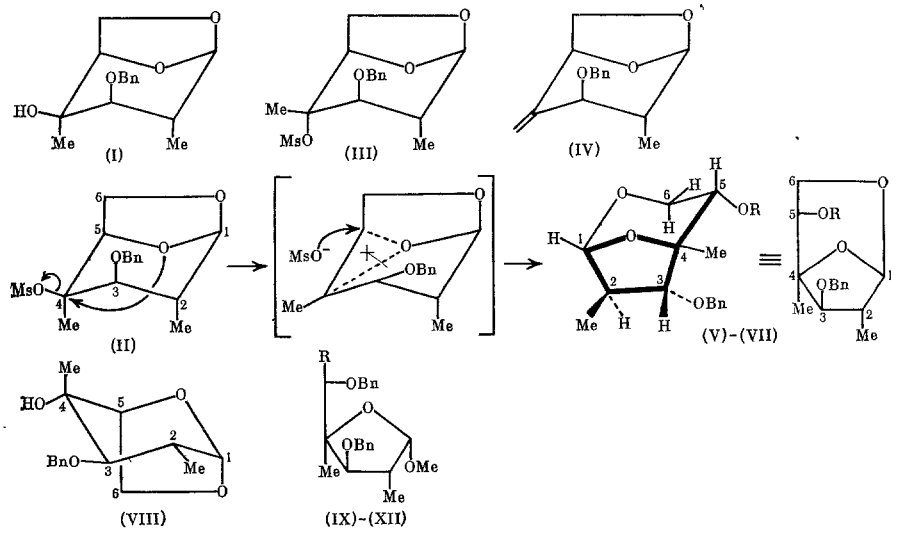
UDC 542.91:547.455:615.779.9

In the synthesis of the C^{9}—C^{13} fragment of erythronolide A, we used the isomerization product of the tertiary alcohol mesylate (II), already described in [2], as the starting material. From the data available at that time, the pyranose structure (III), epimeric at C^{4} with respect to the initial mesylate (II), was ascribed to this compound



Bn = $PhCH_2$. R = Ms (V); H (VI); $PhCH_2$ (VII); CH_2OH (IX); CHO (X); $CH{=}CH_2$ (XI); Et (XII).

*For Communication 5, see [1].

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