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SYNTHESIS OF THE PRINCIPAL CHAIN OF THE O-ANTIGENIC POLYSACCHARIDES OF *Shigella Flexneri*. COMMUNICATON 5.* SYNTHESIS OF O-(4,6-DI-O-BENZOYL-2-DESOXY-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-RHAMNOPYRANSOYL)-(1 → 3)-4-O-BENZOYL-1,2-O-[1-(EXOCYANO)ETHYLIDENE]-β-L-RHAMNOPYRANOSE, A MONOMER PRECURSOR FOR POLYCONDENSATION

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UDC 542.91:547.458

In previous communications [1-4], we have described the synthesis of monosaccharide units A, B, C, and D, and the disaccharide assemblies BA and DC of the polysaccharide of *Sh. flexneri*. We here report the synthesis of the immediate precursor of the monomer for polycondensation, namely, the tetrasaccharide (XII), by two routes: 1) by successive assembly of the oligosaccharide chain from the reducing terminus ((A + B) + C) + D (the "1 + 3" route), and 2) by preparation of the disaccharide assemblies BA and DC, followed by their linkage together (the block route).

The principal feature of the strategy for the construction of the monomer (XX) is the alternation of deacetylation and glycosylation of the cyanoethylidene derivatives. Although in one of these reactions (glycosylation) the cyanoethylidene group is completely stable, deacetylation (0.6 M HCl in a mixture of methanol and chloroform) is accompanied by a side reaction [2, 5] resulting from the ability of the cyano group to combine with a molecule of methanol. This results in substantial reductions in the yields of the desired hydroxy compounds. Comparison of the two routes for the construction of the monomer tetrasaccharide chain shows that the block route has the obvious advantage of requiring fewer deacetylation per unit. On the other hand, the "1 + 3" route has the advantage that the same synthon can be used to construct both units B and C of the oligosaccharide chain.

Common to both routes is the aglycone component, namely, the hydroxylated disaccharide (III), which was obtained by acidic methanolysis of the monoacetate (I) in 35-40% yield (cf.

*For Communication 4, see [1].

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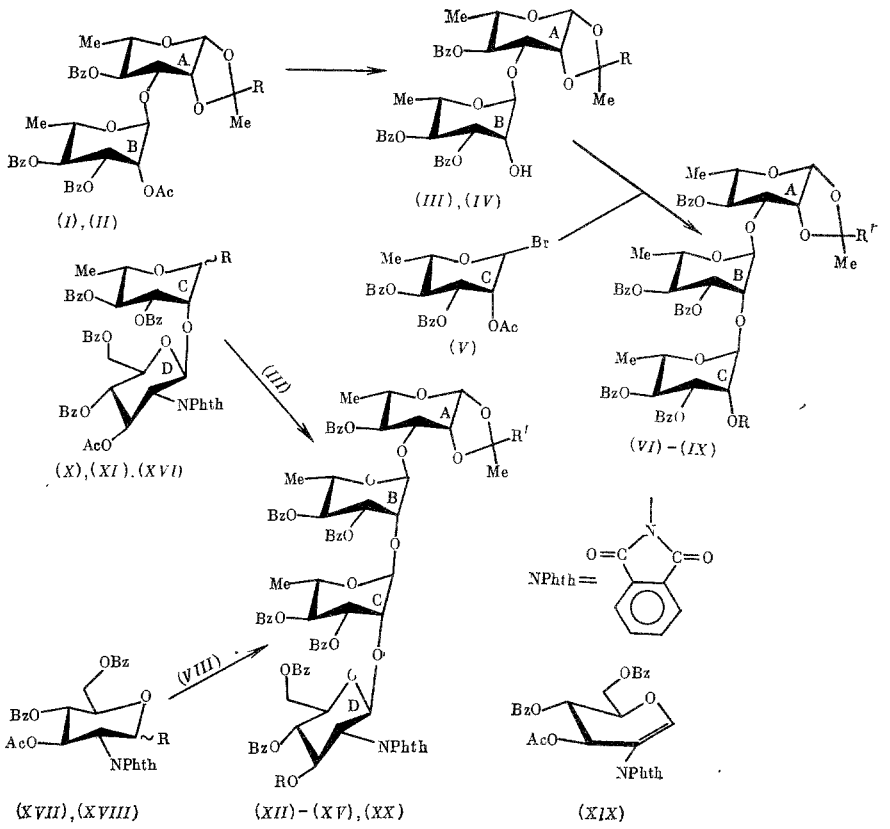
Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 5, pp. 1145-1150, May, 1985. Original article submitted January 9, 1985.

 0568-5230/85/3405-104609.50

Scheme 1



R = CN (I), (III); COOMe (II), (IV); R = Ac, R′ = CN (VI), (XII); R = Ac, R′ = COOMe (VII), (XIII); R = H, R′ = CN (VIII), (XIV); R = H, R′ = COOMe (IX), (XV); R = OAc (X), (XVII); R = Br (XI), (XVIII); R = β-CN (XVI); R = Tr, R′ = CN (XX).

[5]). Complete removal of the acetyl group from the O^2 position of rhamanose requires 12-16 h, but appreciable amounts of products (II) and (IV) begin to accumulate after 2-3 h treatment under the methanolysis conditions. The reaction was therefore stopped after 3-3.5 h when, according to TLC, the reaction mixture contained (I), (II), (III), and (IV) in the approximate proportions 4:1:4:1, and the mixture was fractionated by column chromatography (CC) to give 30-40% of the original acetal (I), which was again subjected to methanolysis. It is noteworthy that despite the complexity of the mixture, the products were readily separable by CC.

Glycosylation of the alcohol (III) with rhamnosyl bromide (V) (2 equiv.) under Helferich conditions gave the trisaccharide (VI) in 66% yield, 25% of unreacted (III) being recovered. Deacetylation of (VI) (4-5 h) gave the trisaccharide alcohol (VIII) in 30-50% yield, 15-50% of starting material was recovered, and the remainder consisted of (VII) and (IX) (Scheme 1).

Glycosylation of the trisaccharide alcohol (VIII) with the bromide (XVIII) (1.8 equiv) in acetonitrile in the presence of $Hg(CN)_2$ and $HgBr_2$ (1.8 equiv. + 1.4 equiv.) afforded, following CC and crystallization, the tetrasacchaide (XII) in 48% yield. The success of glycosylation in this instance is totally dependent on the maintenance of stricly anhydrous conditions, achieved by the use of vacuum techniques [1]; otherwise, only trace amounts of the tetrasaccharide are obtained. When (VIII) is glycosylated with the bromide (XVIII) (2 equiv.) in the presence of CF_3SO_3Ag and 2,4,6-collidine in dichloromethane, the tetrasaccharide (XII) is formed in only 14% yield, the principal product (44%) being the glycal (XIX), the structure of which was confirmed by its ^1H and ^{13}C NMR spectra; 74% of the starting material was recovered.

The disaccharide glycosyl bromide (XI), required for the synthesis of the tetrasaccharide (XII) by the block route, was readily obtained in a chromatographically pure state by treating the acetate (X) with HBr in chloroform. Reaction of the bromide (XI) (1.2 equiv.) with the aglycone component (III) was effected in acetonitrile in the presence of $Hg(CN)_2$ and $HgBr_2$ (1.2 equiv. + 0.6 equiv.). Direct crystallization of the reaction products gave the tetrasaccharide (XII) in 40-45% yield. The mother liquors on CC gave as by-product the bio-

syl cyanide (XVI), (20-25%), starting alcohol (III) (15-20%), and a product with the same chromatographic mobility as the tetrasaccharide (XII) (15-20%) which appeared to be a mixture of (XII) and its β-anomer. It is noteworthy that when this reaction was carried out in the presence of $Hg(CN)_2$ only, the tetrasaccharide was obtained in a yield of only 32% after CC, but increasing the amount of $HgBr_2$ (to more than 0.5 mole per mole of $Hg(CN)_2$) did not result in any increase in the yield of the tetrasaccharide.

The tetrasaccharides obtained by the two routes were identical, as shown by the stereoselectivity of glycosylation with the bromide (XI). The yields of the tetrasaccharide, calculated on (III), were 2-3 times greater using the block route than the "1 + 3" route.

Deacetylation of the tetrasaccharide (XII) (3-4 h, cf. [1]) gave the required alcohol (XIV) in 30% yield, accompanied by two by-products, (XIII) and (XV), which are derivatives of (XII) and (XIV). Recovery of starting material was 40-45%.

The structures of the products of deacetylation followed by glycosylation were confirmed by their ^1H and ^{13}C NMR spectra. Conversion of CCHOAc into CCHOH resulted in a high-field shift in the signal for the methine H and a low-field shift in the signals for the neighboring C atoms. In the case of reactions (I) → (III) and (VI) → (VIII), there was a characteristic shift in the readily identified signals for C_B^1 and C_C^1, respectively, and in the case of the reaction (XII) → (XIV), the signal for C_D^2. The preservation of the MeCCN grouping was confirmed by the characteristic ^{13}C signals. The α-configuration of the rhamnoside bonds in the glycosylation products of (VI) and (XII) followed from the values of the chemical shifts for C_B^5 and C_C^5 of ∿68 ppm (cf. [6]).

In conclusion, it is pointed out that the by-products from the deacetylation of the disaccharide (I), the trisaccharide (VI), and the tetrasaccharide (XII), namely, the methyl esters (II) and (IV), (VII) and (IX), and (XIII) and (XV), respectively, are formed by hydrolysis of the imidates, which were isolated and characterized by their melting points and $[\alpha]_D$ values. Their structures were assigned on the basis of the results of deacetylating 3,4-di-O-acetyl-1,2-O-[1-(exocyano)ethylidene]-β-L-rhamnopyranose and the isolation of the 1,2-O-(1-methoxycarbonyl)ethylidene derivative, the structure of which has been proved conclusively [2]. Further properties of these derivatives will, in view of their potential synthetic uses, be published later.

The tritylation of the tetrasaccharide (XIV), the polycondensation of the trityl ether of the cyanoethylidene derivative (XX), and the properties of the polysaccharide will be reported in the following communication.

EXPERIMENTAL

The methods and apparatus employed have been described previously [4].

4-O-Benzoyl-3-O-(3,4-di-O-benzoyl-α-L-rhamnopyranosyl)-1,2-O-[1-(exocyano)ethylidene]-β-L-rhamnopyranose (III). To a solution of 1.2 g (1.68 mmoles) of (I) in 10 ml of chloroform containing 0.2 ml of acetyl chloride was added a solution of HCl in methanol (1 ml of acetyl chloride in 10 ml of methanol), and the mixture kept for 4 h at 20°C. TLC (ethyl acetate–benzene, 1:2) showed the presence of four compounds, with R_f values 0.59 (starting material), 0.57, 0.45, and 0.40. The solution was diluted with 150 ml of chloroform, neutralized with an excess of an aqueous solution of $KHCO_3$, evaporated, the residue partitioned between water and chloroform (30 ml of each), the chloroform layer washed with water (2 × 15 m), dried, and evaporated. The residue when subjected to CC gave 470 mg (39%) of starting material (I) (R_f 0.59); 120 mg (9.5%) of (II), R_f 0.57; 420 mg (37%) of (III), R_f 0.45; and 120 mg (10%) of (IV), R_f 0.40. (III), mp 207-209°C (MeOH), $[\alpha]_D$ +107° (C 0.9). Found: C 63.98; H 5.24; N 2.27%. $C_{36}H_{35}NO_{12}$. Calculated: C 64.18; H 5.24; N 2.08%. In other experiments, there were obtained (amounts of (I) taken and (I) and (III) isolated, %): 710 mg, 31 and 49; 1.07 g, 27 and 44; 5.71 g, 44 and 46; 10.27 g, 39 and 33; 6.77 g, 45 and 43 g; 8 g, 48.5 and 38. PMR spectrum (δ, ppm; J, Hz): 1.29 and 1.36, two d (3H each, C_A^6, C_B^6, $J_{6,5}$ = 6), 2.00 s (3H, MeCCN), 2.83 s (1H, OH), 3.69 d.q. (1H, H_A^5), 4.04 br. s (1H, H_B^2), 4.20 d.d. (1H, H_A^3, $J_{3,4}$ = 9.5), 4.38 m (1H, H_B^5, $J_{5,4}$ = 2.5), 4.72 d.d. (1H, H_A^2, $J_{2,3}$ = 4), 5.09 s (1H, H_B^1), 5.38 t (1H, H_A^4, $J_{4,5}$ = 9.5), 5.46 d (1H, H_A^1, $J_{1,2}$ = 2), 5.57-5.67 m (2H, H_B^3, H_B^4). ^{13}C NMR spectrum (δ, ppm): 17.5, 17.7 (C_A^6, C_B^6), 26.6, 101.8 117.0 (MeCCN), 69.7 (C_A^5), 71.4, 71.9 (C_A^4, C_B^4), 70.3 (C_B^2), 72.2 (C_B^3), 78.1 (C_A^3), 80.5 (C_A^2), 97.0 (C_A^1), 102.8 (C_B^1).

O-(2-O-Acetyl-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 (VI).

To a solution of 337 mg (0.5 mmole) of (III) and 150 mg (0.6 mmole) of $Hg(CN)_2$ in 2 ml of acetonitrile was added with stirring over 10-15 min a solution of the bromide (V), obtained from 0.6 mmole of 1,2-di-O-acetyl-3,4-di-O-benzoyl-L-rhamnopyranose [4], in 3 ml of acetonitrile. The mixture was stirred for 2 h, a further 0.6 mmole of the bromide (V) and 0.6 mmole of $Hg(CN)_2$ added, stirred for 1.5 h, evaporated, the residue distributed between water and chloroform (15 ml of each), the organic layer washed with 1M KBr (3 × 15 ml) and water, dried, and evaporated. The residue was subjected to CC to give 490 mg (92%) of the trisaccharide (VI), which when rechromatographed gave 430 mg (80%) of chromatograpically homogeneous product as a colorless foam, $[\alpha]_D$ +104.8° (C 1.7). Found: C 64.85; H 5.45; N 2.02%. $C_{58}H_{55}NO_{19}$. Calculated: C 65.10, H 5.18; N 1.31%. In another experiment, starting from 3.12 g (4.6 mmoles) of (III) and 10 mmoles of the bromide (V) in the presence of 10 mmoles of $Hg(CN)_2$ (the whole of the bromide being added over 20 min), CC gave 3.06 mmoles (66%) of the trisaccharide (VI) together with 1.15 mmoles (25%) of the starting material (III). PMR spectrum (δ, ppm J, Hz): 1.03, 1.30, 1.45 three d (3H each, H_A^6, H_B^6, H_C^6, J = 6), 2.02 s (3H, MeCOO), 2.04 s (3H, MeCCN), 5.57 d.d. (1H, H_C^2, J = 1.5 and 3.5). ^{13}C NMR spectrum (δ, ppm): 17.3, 17.6 × 2 (C_A^6, C_B^6, C_C^6), 20.5 (MeCO), 26.4, 101.8, 116.9 (MeCCN), 67.6, 68.1, (C_B^5, C_C^5), 69.5, 69.8, 70.2, 70.7, 71.6 × 2, 72.0 (C_A^5, C_C^2, C_B^3, C_C^3, C_A^4, C_B^4, C_C^4), 76.8 (C_B^2), 77.9 (C_A^3), 80.3 (C_A^2), 97.0 (C_A^1), 99.4 (C_C^1), 101.9 (C_B^1), 165.1, 165.3 × 2, 165.5, 165.8 (PhCO), 169.0 (MeCO).

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 (VIII). To a solution of 560 mg (0.52 mmole) of the trisaccharide (VI) in 1 ml of chloroform and 3 ml of methanol was added 0.12 ml of acetyl chloride. The mixture was kept for 4 h at 20°C, and worked up as for (III) above. Following CC there was isolated 120 mg (2.14%) of starting material (VI), R_f 0.60 (benzene—ether, 8:2), 60 mg (10%) of (VII), R_f 0.54, 290 mg (54%) of the alcohol (VIII), R_f 0.41, and 80 mg (14%) of (IX), R_f 0.36. In other experiments there were obtained (amount of (VI) taken, and (VI) and (VIII) isolated, %): 2.25 g, 15.5 and 43; 2.73 g, 49 and 30.5 3.1 g, 33 and 29. Compound (VIII) was obtained as an amorphous powder, $[\alpha]_D$ +115° (C, 0.68). PMR spectrum (δ, ppm J, Hz): 1.04, 1.32, 1.42, three d (3H each, H_A^6, H_B^6, H_C^6, J = 6), 2.04 s (3H, MeCCN), 4.32 br. s (1H, H_C^2). ^{13}C NMR spectrum (δ, ppm): 17.4, 17.6, 17.8 (C_A^6, C_B^6, C_C^6), 26.5, 101.8, 117.0 (MeCCN), 67.7, 68.1 (C_B^5, C_C^5), 69.6, 70.4, 71.2, 71.6, 71.7, 72.1, 72.2, (C_C^2, C_B^3, C_C^3, C_A^4, C_B^4, C_C^4, C_A^5), 76.8 (C_B^2), 78.1 (C_A^3), 80.4, (C_A^2), 97.1 (C_A^1), 101.4 (C_C^1), 102.0 (C_B^1), 163.3, 165.4, 165.5, 165.8, 165.9 (PhCO).

O-(3-O-Acetyl-4,6-di-O-benzoyl-2-desoxy-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 (XII).

"1 + 3"

a) A mixture of 1.65 g (1.6 mmoles) of the trisaccharide alcohol (VIII), 810 mg (3.2 mmoles) of $Hg(CN)_2$, and 860 mg (2.4 mmoles) of $HgBr_2$ was dried in a vacuum apparatus [1] for 6-8 h. The bromide (XVIII) (obtained from 1.75 g (2.88 mmoles) of the acetate (XVII)) was lyophilized in the apparatus from 20 ml of dry benzene. In an atmosphere of dry argon, to a suspension of (VIII), $Hg(CN)_2$, and $HgBr_2$ in 6 ml of acetonitrile (distilled twice over CaH_2 in the vacuum apparatus) was added with stirring a solution of the bromide (XVIII) in 15 ml of acetonitrile (as described in [1]). The mixture was kept overnight, diluted with 100 ml of chloroform, washed with 1 M KBr (3 × 50 ml) and water, dried, evaporated, and the residue subjected to CC in the system ethyl acetate—heptane (45:55) to give 1.63 g of the tetrasaccharide (XII). This was recrystallized from a mixture of methanol and chloroform to give 1.21 g (48%) of (XII), mp 154-158°C, $[\alpha]_D$ +106° (C, 1.1).

b) A mixture of 380 mg (0.37 mmole) of the alcohol (VIII) and 190 mg (0.74 mmole) of CF_3SO_3Ag was dried in the vacuum apparatus for 5-6 h, 0.1 ml of 2,4,6-collidine added under argon, 3-5 ml of dichloromethane distilled into the flask, and a further 0.1 ml of collidine added under argon followed by a solution of the bromide (XVIII) (prepared from 450 mg (0.75 mmoleβ of the acetate (XVII) and lyophilized from 10 ml of benzene) in 10 ml of dichloromethane at −20 to −30°C. The mixture was then kept for 16 h at 20°C. TLC (ethyl acetate—benzene, 3:17) showed the presence of three main products the glycal (XIX), R_f 0.65; the tetrasaccharide (XII), R_f 0.70; and the starting material (VIII), R_f 0.60. The mixture was filtered, the solid washed on the filter with chloroform, and the combined filtrates washed with water and evaporated. The residue was subjected to CC to give 180 mg (44%) of the glycal (XIX) and 360 mg of a mixture of (XII) and (VIII). Rechromatography of the mixture in hexane—ethyl acetate (6:4) gave 80 mg (14%) of the tetrasaccharide (XII) and 280 mg (74%) of

the starting material (VIII). The glycal (XIX) was obtained as a syrup, $[\alpha]_D$ −75.2° (C, 1.3). PMR spectrum (δ, ppm; J. Hz): 1.96 s (3H, MeCOO), 4.77 d (1H, H^6, J = 1), 4.80 s (1H, $H^{6'}$), 4.93 m (1H, H^5), 5.70 t (1H, H^4, $J_{4,5}$ = 3.5), 5.76 d.d. (1H, H^3, $J_{3,4}$ = 3.5, $J_{3,5}$ = 1.5), 6.89 s (1H, H^1), 7.43-8.16 m (14H, H_{arom}). ^{13}C NMR spectrum (δ, ppm): 20.6 (MeCOO), 61.8 (C^6), 67.5, 67.8, 74.6 (C^3—C^5), 105.8 (C^2), 148.5 (C^1), 165.1, 166.0, 167.7, 170.0 (CO). The tetrasaccharide (XII) was identical with that obtained by method a) (TLC, mp, and $[\alpha]_D$).

BLOCK ROUTE

2-O-(3-O-Acetyl-4,6-di-O-benzoyl-2-desoxy-2-phthalimido-β-D-glucopyranosyl)-3,4-di-O-benzoyl-L-rhamnopyranosyl Bromide (XI). To a solution of 8.3 g (8.7 mmoles) of the acetate (X) [4] in 12 ml of chloroform was added at 0°C a solution of HBr in chloroform (obtained by adding 6.15 ml (153 mmoles) of methanol and 50 ml of chloroform to a solution of 20 ml of acetyl bromide in 50 ml of chloroform at 0°C), and the mixture was kept for 35-40 min at 0°C. TLC showed the presence of a new product with R_f 0.60 (ethyl acetate—benzene, 2:8), the starting material ((x) with R_f 0.50) being absent. The solution was poured into 300 ml of an ice-water mixture, and the organic layer washed with 150 ml of water at 0°C and saturated $NaHCO_3$ solution (3 × 150 ml), dried, and evaporated to give 8.46 g (100%) of chromatographically homogeneous, syrupy (XII). The syrup was dissolved in 15-20 ml of dry benzene, and lyophilized in the vacuum apparatus.

Glycosylation of Alcohol (III) with Bromide (XI). Acetonitrile (50 ml, previously twice distilled over CaH_2 in the vacuum apparatus) was distilled into a mixture of 4.7 g (7 mmoles) of the disaccharide alcohol (III), 2.16 g (8.6 mmoles) of $Hg(CN)_2$, and 1.55 g (4.3 mmoles) of $HgBr_2$, previously dried in the vacuum apparatus. The bromide (XI) (obtained in the experiment described above), lyophilized from benzene, in a 30 mL MeCN solution, was dried as described above, and added dropwise under argon over 30-40 min to the stirred suspension of (III), $Hg(CN)_2$, and $HgBr_2$. The mixture was stirred for 16 h at 20°C, evaporated, the residue shaken with chloroform (5 × 50 ml), the solution descanted from the mercury salts filtered, the filtrate washed with 2 M KBr (3 × 150 ml), saturated $NaHCO_3$ (150 ml), and water (150 ml), dried, evaporated, and the residue (13.78 g) crystallized from a mixture of 30 ml of chloroform and 100 ml of methanol to give 5 g (45.5%) of the tetrasaccharide (XII). The mother liquors were evaporated, and the residue subjected to CC to give: 1.36 g (17%) of biosyl cyanide (XVI), R_f 0.61 (ethyl acetate—benzene, 2:8), and 1.05 g (9.5%) of a fraction with the same R_f value as the tetrasaccharide (XII), R_f 0.52. Rechromatography of the mixed fractions gave a further 400 mg (5%) of biosyl cyanide (XVI), 1.1 g (10%) of a fraction with R_f 0.52, and 870 mg (18.5%) of starting material (III), R_f 0.26. The tetrasaccharide (XII) after repeated crystallization from chloroform—methanol (4.7 g, 43%) had mp 154-157°C, $[\alpha]_D$ +105.5° (C 2.1). Found: C 65.88; H 4.92; N 2.06%. $C_{86}H_{76}N_2O_{27}$. Calculated: C 65.81; H 4.88; N 1.78%. ^{13}C NMR spectrum (δ, ppm): 17.5, 17.7, 17.9 (C_A^6, C_B^6, C_C^6), 20.2 (MeCO), 26.5, 101.8, 117.0 (MeCCN) 54.9 (C_D^2), 62.5 (C_D^6), 67.6, 68.0 (C_B^5, C_C^5), 77.7 (C_A^3), 80.4 (C_A^2), 97.1 (C_A^1), 99.0 (C_D^1), 101.0 (C_C^1), 101.8 (C_B^1), 169.8 (MeCO), 165.7-164.8 (PhCO).

Biosyl cyanide (XVI) [2-O-(3-O-acetyl-4,6-di-O-benzoyl-2-desoxy-2-phthalmido-β-D-glucopyranosyl)-3,4-di-O-benzoyl-1-desoxy-1-cyano-α-L-rhamnopyranose], mp 134-135°C (alcohol), $[\alpha]_D$ +0.57° (C 2). Found: C 66.47; H 4.64; N 3.18%. $C_{51}H_{42}N_2O_{15}$. Calculated: C 66.37; H 4.59; N 3.03%. ^{13}C NMR spectrum (δ, ppm): 17.46 (C_C^6), 20.2 (MeCO), 54.7 (C_D^2), 62.7 (C_D^2), 67.1 (C_C^5), 99.8 (C_D^1), 114.6 (CN).

In another experiment, starting with 720 mg (1.07 mmoles) of (III) and bromide (XI) (obtained from 1.36 mmoles of (X)) in the presence of 360 mg (1.43 mmoles) of $Hg(CN)_2$ (no $HgBr_2$) in MeCN, there were obtained 480 mg (38%) of the cyanide (XVI), 530 mg (32%) of the tetrasaccharide (XII), and 420 mg (58%) of starting material (III).

O-(4,6-Di-O-benzoyl-2-dexosy-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 (XIV). To a solution of 4 g (2.55 mmoles) of (XII) in a mixture of 13 ml of chloroform and 40 ml of methanol was added 2.12 ml of acetyl choride at 0°C, followed by 2.5 (by volume) acetyl chloride in chloroform until all the (XII) had dissolved (∿20 ml), and the mixture kept for 3 h 40 min at 20°C. TLC (ethyl acetate—benzene, 2:8) showed the presence of compounds (XII)-(XV), R_f values 0.52, 0.46, 0.37, and 0.29. The solution was diluted with 250 ml of chloroform, washed with 100 ml of water, the aqueous layer extracted with chlorofrom (2 × 40 ml), and the combined extracts washed with saturated $NaHCO_3$ solution (100 ml) and water, dried, and evaporated. The residue was subjected to CC to give 1.6 (40%) of (XII), 0.38 g of mixture of (XII) and (XIII),

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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Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 5, pp. 1151-1156, May, 1985. Original article submitted January 9, 1985.