SYNTHESIS OF THE PRINCIPAL CHAIN OF THE O-ANTIGENIC POLYSACCHARIDES OF *Shigella Flexneri*. COMMUNICATION 1. SYNTHESIS of 2,4- AND 3,4-DI-O-BENZOYL-α-L-RHAMNOPYRANOSIDES BY A COMBINATION OF SELECTIVE ACYLATION AND DEACETYLATION, AND THE SYNTHESIS OF 1,2-DI-O-ACETYL-3,4-DI-O-BENZOYL-L-RHAMNOPYRANOSE VIA 1,2-O-BENZYLIDENE-3,4-DI-O-BENZOYL-β-L-RHAMNOPYRANOSE

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UDC 542.91:547.458

In the course of a program aimed at synthesizing the principal chain of the O-antigenic polysaccharides of the Gram-negative bacterium *Sh. flexneri*, we developed a method for the selective removal of acetyl groups from carbohydrates in the presence of benzoyl groups by acidic methanolysis [1]. Use of this method has enabled a synthetic strategy to be devised using a combination of benzoyl and acetyl protection for the hydroxyl groups. Selective deacetylation, supplemented by selective acylation, has provided a route for the preparation of the key monosaccharide units for the construction of the tetrasaccharide repeating unit, with the subsequent polycondensation of this unit (see the following communications in this series). We have also employed selective acylation—deacetylation for the synthesis of fragments of the repeating units of the O-antigenic polysaccharides of some serotypes of *Sh. flexneri* [2].

The principal straight chain of the O-antigenic polysaccharides of all serotypes of *Sh. flexneri* contains L-rhamnose residues glucosylated at O^2 and O^3, together with N-acetyl-D-glucosamine substituted at O^3 [3].

We here describe the synthesis of L-rhamnose derivatives used for the modeling and construction of the repeating unit of the O-antigenic polysaccharide of *Sh. flexneri*.

The possibility of selective deacetylation was examined using as models methyl- and benzyl-3,4-di-O-benzoyl-2-O-acetyl-α-L-rhamnopyranosides (XII) and (XIV). The key compound in the synthesis of these glycosides was 1,2-di-O-acetyl-3,4-di-O-benzoyl-L-rhamnopyranose (VII), subsequently used by us as a synthon for introduction into the oligosaccharide chain of the rhamnose residue with removal of the protection at O^2.

1,2-O-Benzylidene-3,4-di-O-benzoyl-β-L-rhamnopyranose (V), which was readily obtained by reducing the benzobromopyranose (IV) with $NaBH_4$ [4], was debenzylated with aqueous CF_3COOH to give the crystalline diol (V). Acetylation of this diol gave the diacetate (VII) in 76% yield calculated on the precursor of the bromide (IV), namely rhamnose tetrabenzoate (III).

The Helferich reaction of the bromide (VIII), obtained from the diacetate (VII), with methanol gave the crystalline methylrhamnoside (XII) in 44% yield, together with its O-deacetylation product (XIII) (13% yield). The formation of (XIII) apparently results from the methanolysis of the acetyl group in the presence of HBr *in statu nascendi*, or of $HgBr_2$ in an excess of methanol. Condensation of the bromide (VIII) with $PhCH_2OH$ under Helferich conditions gave the benzylrhamnoside (XIV) in 77% yield. The rhamnoside (XII) was also synthesized from the orthoester (X) by benzoylation to (XI) followed by isomerization, catalyzed by isomerization, catalyzed by $HgBr_2$ [5].

Deacetylation of the rhamnosides (XII) and (XIV) by treatment with 0.6 M HCl in methanol (20°C, 16 h) gave the corresponding 2-hydroxy derivatives (XIII) and (XV) in high yield (Scheme 1).

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Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 5, pp. 1122-1128, May, 1985. Original article submitted January 9, 1985.

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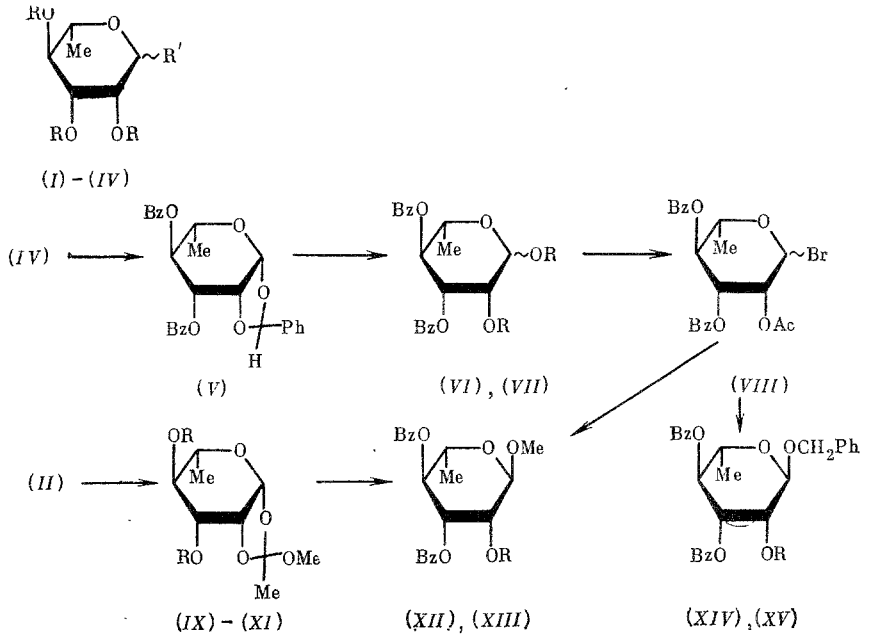
Scheme 1



R = Ac, R′ = OAc (I); R = Ac, R′ = Br (II); R = Bz, R′ = OBz (III); R = Bz, R′ = Br (IV); R = H (VI), (X), (XIII), (XV); R = Ac (VII), (IX), (XII), (XIV); R = Bz (XI)

When the possibility of selective deacetylation had been confirmed, we examined the selective acetylation and benzoylation of the diol (XIX). The latter was obtained in high yield from methyl-α-L-rhamnopyranoside (XVI) by successive acetonylation as described in [6], benzoylation, and deacetylation without isolation of the products at each stage. Acetylation of the diol (XIX) with 1.3 equiv. of AcCl in the presence of pyridine afforded the 3-acetate (XXI) (∿40%) and the 2,3-diacetate (XX) (∿20%). Also formed was the isomeric 2-acetate (XXII) (TLC), which was apparently rapidly consumed to form the diacetate (XX) and/or by isomerization to the 3-acetate (XXI). It is interesting that the selective deacetylation of the diacetate (XX) by acidic methanolysis (5°C, 16 h) gave only one monodeacetylation product, namely, the 2-acetate (XXII), isolated in 19% yield together with the diol (XIX) (73%) and the diacetate (XX) (4%).

Monobenzoylation of the diol (XIX) with 1.04 equiv. of benzoyl chloride in the presence of pyridine gave, as in the case of acetylation, principally the 3-O derivative to give the 3,4-dibenzoate (XIII) (66% yield), together with the 2,4-dibenzoate (XXIII) (6%) and the tribenzoate (XXIV) (7%) as minor products. This result is in contrast to that obtained in the monoacetylation and monobenzoylation of methyl-4-O-benzoyl-α-L-rhamnopyranoside [7], when the principal monoacylation products were the 2-O-acyl derivatives.

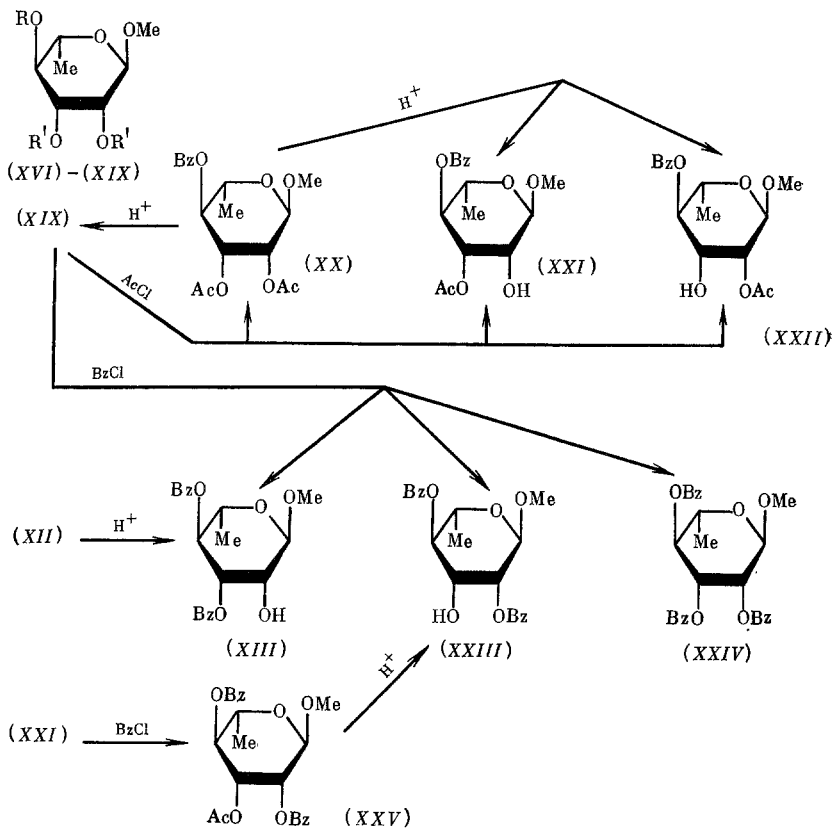
The dibenzoate (XIII) was identical to the dibenzoate obtained by deacetylating the monoacetate (XII). Benzoylation of the 3-acetate (XXI) gave methyl-3-O-acetyl-2,4-di-O-benzoyl-α-L-rhamnopyranoside (XXV), an isomer of (XII). Selective deacetylation of the acetate (XXV) gave the rhamnoside (XXIII) containing a free hydroxyl group at O^3, identical to the minor product of the monobenzoylation of the diol (XIX).

The structures of the products were confirmed by their chemical reactions (Scheme 2) and PMR spectra (Table 1).

It is noteworthy that in the PMR spectra of the 3,4-di-O-acyl derivatives (XIII), (XV), and (XXI), the signals for H^3 and H^4, seen in the remaining compounds as a doublet of doublets and a triplet, respectively, were present as multiplets with small coupling constants, indicating that the conformations of these compounds were different from $^1C_4$ (L).

A synthesis has recently been described of the 2,4-dibenzoate (XXIII) from methyl-α-L-rhamnopyranoside (XVI) via the 2,3-orthobenzoate followed by benzoylation at O^4 and regioselective opening of the orthobenzoate ring in 59% yield calculated on the methylrhamnoside (XVI) [8]. Our proposed synthetic route to (XXIII), viz, (XIX) → (XXI) → (XXV) → (XXIII), in an overall yield of 30-40% using simple reagents and with potential for optimization of the selective acetylation stage provides a good alternative for the preparation of 2,4-di-O-acylated rhamnose derivatives. The yields in the selective acetylation of the diol (XIX) and the selec-

Scheme 2



R = R′ = H (XVI); R = H, R′, R′ = Me_2C (XVII); R = Bz, R′, R′ = Me_2C (XVIII);. R = Bz, R′ = H (XIX).

tive deacetylation of the diacetate (XX) are low. However, the side products formed can be reintroduced into the synthesis following exhaustive acetylation or deacetylation.

A combination of selective benzoylation and acetylation with selective deacetylation therefore provides a route to either 2-hydroxy- or 3-hydroxyrhamnopyranoses.

EXPERIMENTAL

Acetonitrile was boiled with $KMnO_4$ in the presence of K_2CO_3, then twice distilled over P_2O_5 and once more over CaH_2. Nitromethane was redistilled over urea at 100 torr, then over CaH_2. 2,4,6-Collidine was redistilled over P_2O_5, then over CaH_2. Melting points were determined on a Kofler block, and optical rotations on a Perkin–Elmer-141 polarimeter at 20 ± 2°C in chloroform. NMR spectra were obtained on a Bruker WM-250 (250 MHz) in $CDCl_3$, internal standard TMS. Column chromatography (CC) was carried out on L 40/100 μm silica gel (Czechoslovakia), using a benzene → ethyl acetate gradient. TLC was carried out on L 5/40 μm silica gel (Czechoslovakia), developed with 70% sulfuric acid followed by heating at ∿150°C. Solvents were dried by passing through a layer of cotton wool, and evaporated *in vacuo* at 40°C.

Preparation of Acylrhamnopyranosyl Bromides. To a solution of 10 mmoles of the acylrhamnopyranose in 30 ml of chloroform and 5-10 ml of acetic acid was added 50-55 mmoles of AcBr, followed by the dropwise addition of a solution of 50-55 mmoles of water in 5-10 ml of acetic acid. The mixture was kept for 0.5-2 h at ∿20°C (the glycosyl bromides formed have greater TLC chromatographic mobility than the original acyl compounds), diluted with 120-150 ml of chloroform, poured into 200-250 ml of ice water, 20-25 ml of $CHCl_3$ were extracted from the water layer, the combined extracts and chloroform layer washed with 200 ml of ice water and cold sat. $NaHCO_3$ (2 × 20 ml), filtered through cotton wool, evaporated, and drie in vacuo. The bromides, which were obtained in near-quantitative yields and were homogeneous (TLC), were used in the subsequent steps.

3,4-Di-O-benzoyl-L-rhamnopyranose (VI). To a solution of the crystalline tri-O-benzoyl-L-rhamnopyranosyl bromide (IV), obtained from 100 mmoles of the tetrabenzoate (III) in 200ml of dry acetonitrile, was added 6 g (150 mmoles) of $NaBH_4$, and the mixture stirred at 20°C.

TABLE 1. PMR Spectral Data for 2-O-R^1-3-O-R^2-4-O-Benzoyl-α-L-rhamnopyranosides

Compound	R^1	R^2	Chemical shifts (δ, ppm) and coupling constants (J, Hz)										
			H^1	H^2	H^3	H^4	H^5 d.q.	H^6 d ($J=6$)	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	MeO	MeCOO
(XX)	Ac	Ac	4,71 d.	5,31 d.d.	5,52 d.d.	5,36 t	4,02	1,30	1,5	3,5	10	3,43	1,89, 2,17
(XXII)	Ac	H	4,72 d	5,13 d.d.	4,18 m		5,16 t	3,94	1,28	1,5	3,5	10	3,39	2,16
(XXI)	H	Ac	4,77 d	4,15 br.s.	5,45–5,40 m			4,02 m	1,30	1,5	–	–	3,45	2,00
(XVI)	H	H	4,63 s	4,10–3,67 m			5,10 t	4,10–3,67	1,17	–	–	10	3,27	–
(XXV)	Bz	Ac	4,86d	5,59 d.d.	5,68 br.d.		5,54 t	4,12	1,37	1,5	3,5	10	3,47	1,85
(XXIII)	Bz	H	4,82 d	5,38 d.d.	4,30 br.d.		5,32 t	4,00	1,30	1,5	3,5	10	3,40	–
(XII)	Ac	Bz	4,67 d	5,34 d.d.	5,65 d.d.		5,44 t	4,05	1,28	1,5	3	10	3,38	2,04
(XIII)	H	Bz	4,80 d	4,31 t	5,68–5,56 m			4,10 m	1,33	1,5	2	–	3,46	–
(XIV)	Ac	Bz	4,88 d	5,46 d.d.	5,73 d.d.		5,50 t	4,11	1,26	2	3	9	*	2,00
(XV)	H	Bz	4,95 s	4,36 br.s	5,83–5,63 m			4,14 m	1,27	–	–	–	*	–

*PCH_2 group signals, 4.56 and 4.76 ppm (two doublets, AB system).

Since the R_f values of the bromide (IV) and the benzylidene derivative (V) were identical, completion of the reaction was determined as follows: An aliquot (0.1-0.2 ml) of the liquid over the solid was evaporated, 0.2 ml of dry methanol and 0.1 ml of 1 M MeONa in MeOH added, the mixture kept for 10-20 min at ∿20°C, and analyzed by TLC (methanol—chloroform, 2:8) using authentic samples of 1,2-di-O-benzylidene-β-L-rhamnopyranose [5] (R_f 0.7) and methyl-α-L-rhamnopyranoside (R_f 0.5). The rhamnoside (XVI) was formed from the unreacted bromide (IV). Reaction was complete when treatment with MeONa gave only the product with R_f 0.7 (16-24 h). According to TLC (ethyl acetate—hexane, 1:1), when the reaction was complete the mixture contained two products with very similar R_f values (the exo and endo isomers of (V), ratio ∿10:1). The reaction mixture was treated carefully with stirring with a solution of 12 ml of acetic acid in 20 ml of water, and the clear reaction mixture was concentrated *in vacuo* (the greater part of the acetonitrile being removed), and the residue partitioned between water and chloroform (350 ml of each). The organic layer was washed with water (3 × 250 ml), treated with 40 ml of 90% CF_3COOH, and kept at ∿20°C. According to TLC (methanol—chloroform, 1:9), reaction was complete within 10-15 min. The solution was washed with water (3 × 250 ml), saturated sodium bicarbonate (3 × 250 ml), dried, and evaporated. The residue was shaken vigorously and triturated with 250 ml of heptane, and the solvent decanted off. This operation was repeated three or four times (to remove as much benzaldehyde as possible), the residue dissolved in 80 ml of dichloromethane or chloroform, 250-300 ml of hexane added, the mixture gently warmed, and the crystalline solid separated, washed with hexane (5 × 50 ml), and air-dried to give 29.8 g (80%) of the diol (VI), mp 137-145°C, $[\alpha]_D$ + 78.4 → +88°C (C 1.58, 16 h).* Found: C 64.39; H 5.62%. $C_{20}H_{20}O_7$. Calculated: C 64.50; H 5.41%.

1,2-Di-O-acetyl-3,4-di-O-benzoyl-L-rhamnopyranose (VII). To a solution of 14.8 g (39.8 mmoles) of the diol (VI) in 120 ml of pyridine was added 50 ml of acetic anhydride, and the mixture kept for 16 h at ∿20°C. The mixture was decomposed at 0°C with 20 ml of water, poured into 500 ml of ice water, and the oil which separated was isolated, dissolved in 400 ml of chloroform, washed with 1 M HCl (2 × 400 ml) and water, dried, evaporated, and the residue dried *in vacuo* to give the diacetate (VII), yield 17.26 g (95%), yellow foam which caramelized on standing, $[\alpha]_D$ + 35.7° (C 2.35).

Methyl-2-O-acetyl-3,4-di-O-benzoyl-α-L-rhamnopyranoside (XII). a) To a solution of 9.67 g (27.3 mmoles) of the bromide (II), obtained from 9.3 g (28 mmoles) of the tetraacetate (I), in 30 ml of nitromethane, was added a mixture of 6.7 ml of 2,4,6-collidine and 6 ml of dry methanol. The mixture was kept for 72 h at ∿20°C, and 10 ml of methanol and 5 ml of 1 M MeONa in methanol added. The mixture was kept for 3 h at 20°C, evaporated, 75 ml of saturated NaCl solution added, shaken with chloroform (6 × 70 ml), and the combined extracts evaporated to give 4.4 g of a mixture of the endo and exo isomers of the orthoester (X) (72% calculated on the bromide (II)), containing traces of collidine. Crystallization from a mixture of ethyl acetate and hexane gave 1.1 g of the main exo-methoxy isomer.

To a solution of 1.1 g of the crystalline orthoester (X) in 8 ml of pyridine was added at 0°C 1.2 ml of benzoyl chloride, the mixture kept for 16 h at 20°C, and decomposed at 0°C with 1 ml of water. It was then poured into 100 ml of sat. $NaHCO_3$ solution and kept for 1 h. The solution over the oil was decanted off and extracted with chloroform (3 × 50 ml), the oil dissolved in the extract, dried, and evaporated to give 2.22 g (97%) of the dibenzoate (XI), which after recrystallization from ether and hexane gave 1.5 g mp 111-114°C, $[\alpha]_D$ + 105.5° (C, 1.8). PMR spectrum (δ, ppm; J, Hz): 1.36 d (3H, H^6, J = 6), 1.80 s (3H, MeC), 3.26 s (3H, MeO), 3.80 m (1H, H^5), 4.88 d.d. (1H, H^2, $J_{2,1}$ = 2, $J_{2,3}$ = 3.5), 5.51-5.58 m (2H, H^3, H^4), 5.61 d (1H, H^1, $J_{1,2}$ = 2). Found: C 64.46; H 5.82%. $C_{23}H_{24}O_8$. Calculated: C 64.48; H 5.65%.

To a solution of 1.61 g (3.76 mmoles) of the orthoester (XI) in 10 ml of nitromethane was added 135 mg (0.37 mmoles) of $HgBr_2$, and the mixture heated for 2.5 h at 90°C. Completion of the reaction was assessed using a hydrolytic sample as described in [10], since the orthoester (XI) and the glycoside (XII) had the same mobilities on TLC. The mixture was kept for 16 h at 20°C, evaporated to dryness, 30 ml of chloroform added, and washed with 1 M KI (2 × 20 ml) and water, dried, and evaporated to give 1.45 g (90%) of the glycoside (XII), mp 94-96°C (ether—hexane), $[\alpha]_D$ + 46.5° (C, 1.95).

b) A solution of the bromide (VIII), obtained from 4 mmoles of the diacetate (VII), in 5 ml of acetonitrile was added to a mixture of 1 g of $Hg(CN)_2$ (4 mmoles) and 1 ml of methanol in 5 ml of acetonitrile, and the mixture stirred for 16 h. The mixture was then diluted with

*An $[\alpha]_D$ value of +44° was erroneously given in [9].

50 ml of chloroform, washed with 1 M KI and water, and evaporated to give 1.66 g of a mixture from which was isolated by CC 760 mg (44.4%) of the glycoside (XII), mp 94-96°C (ether–hexane), $[\alpha]_D$ + 43.7° (C, 1.4), R_f 0.75 (benzene–ethyl acetate, 8:2). Found: C 64.92; H 5.80%. $C_{23}H_{24}O_8$. Calculated: 64.48; H 5.65%. Also isolated was 210 mg (13.2%) of (XIII), $[\alpha]_D$ + 28.5° (C, 2.1), R_f 0.52, identical with a sample of (XII) obtained by deacetylating (XII) or monobenzoylation of the diol (XIX) (see below).

Benzyl-2-O-acetyl-3,4-di-O-benzoyl-α-L-rhamnopyranoside (XIV). A solution of the bromide (VIII), obtained from 6 mmoles of the diacetate (VII), in 20 ml of acetonitrile was added to a suspension of 1 ml (10 mmoles) of benzyl alcohol and 1.51 g (6 mmoles) of $Hg(CN)_2$ in 8 ml of acetonitrile. The mixture was stirred for 2 h at 20°C, then kept for 16 h at 20°C, then it was poured into 130 ml of water, the supernatant decanted from the oil and extracted with chloroform (50 ml), and the oil dissolved in the extract. This was then diluted with 50 ml of chloroform, washed with water, 1 M KI, and water, dried, and evaporated. The residue (3.4 g) was subjected to CC to give 2.35 g (77.7%) of the benzylglycoside (XIV), syrup, $[\alpha]_D$+24.5° (C, 2.4).

Methyl-3,4-di-O-benzoyl-α-L-rhamnopyranoside (XIII). The 2-acetate (XII) (430 mg; 1 mmole) was dissolved in methanolic HCl (obtained by adding 0.4 ml of acetyl chloride to 10 ml of MeOH at 0°C), and kept for 16 h at 20°C. The mixture was diluted with 70 ml of chloroform, washed with water, dried, and evaporated. The residue was subjected to CC to give 350 ml (90%) of the glycoside (XIII), which crystallized on evaporation of its methanol solution, mp 155-160°C, $[\alpha]_D$ +26° (C 0.79). Found: c 65.33; H 5.92%. $C_{21}H_{22}O_7$. Calculated: C 65.27; H 5.74%.

Benzyl-3,4-di-O-benzoyl-α-L-rhamnopyranoside (XV). The benzylrhamnoside (XIV) (700 mg) was dissolved in 15 ml of 0.6 M HCl in methanol, kept for 16 h at 20°C, neutralized with an excess of $KHCO_3$ solution, the methanol partially removed, diluted with 50 ml of chloroform, washed with water, dried, and evaporated. The residue was subjected to CC to give 480 mg (74.8%) of the alcohol (XV) as a syrup, $[\alpha]_D$ +12.8° (C, 1.57).

Methyl-4-O-benzoyl-α-L-rhamnopyranoside (XIX). A mixture of 17.8 g (100 mmoles) of crystalline methyl-α-L-rhamnopyranoside (XVI), 50 ml of 2,2-dimethoxypropane, and 200 mg of TsOH·H_2O was kept at 20°C for 1.5-2 h, until the rhamnoside had dissolved completely. After ∿2 h, approximately 7-10% of the starting material remained (TLC), and this persisted for a period of 3-4 h. The mixture was diluted with 100 ml of chloroform, washed with saturated $NaHCO_3$ solution (3 × 100 ml) and water, and the solvent evaporated. From this, 20 g of chromatographically homogeneous product (XVII) was obtained as a syrup. The product was dissolved in 50 ml of pyridine, 17.4 ml (150 mmoles) of benzoyl chloride added with cooling, and kept for 20 min at 20°C (the reaction was complete after this time (TLC)). The mixture was decomposed at 0°C by adding 10-12 ml of water, and poured into 1.5 liters of a saturated solution of $NaHCO_3$ containing ice, stirred for 0.5 h, the oil separated and dissolved in 350 ml of chloroform, washed with 1 M HCL (3 × 200 ml) and water, to the moist solution of (XVIII) obtained was added 40 ml of 90% CF_3COOH, and the mixture kept for 10-15 min at 20°C (after this time, the reaction was complete according to TLC). The solution was washed with water, saturated $NaHCO_3$ solution, and water, dried, and evaporated to give 25.4 g (90%) calculated on (XVI)) of the chromatographically homogeneous diol (XIX) as a syrup which crystallized on standing, $[\alpha]_D$ −82.3° (C, 2.9).

Methyl-4-O-benzoyl-2,3-O-isopropylidene-α-L-rhamnopyranoside (XVIII). For analytical purposes, 5-8 ml of the chloroform solution of the benzoylation product were withdrawn from the preceding experiment (prior to treatment with CF_3COOH), washed with saturated $NaHCO_3$ solution and water, dried, and evaporated to give (XVIII), mp 101-102°C (alcohol) $[\alpha]_D$ −3.1° (C, 3.3). Found: C 63.67; H 7.00%. $C_{17}H_{22}O_6$. Calculated: C 63.34; H 6.88%.

Selective Acetylation of Diol (XIX). To a solution of 4.23 g (15 mmoles) of the diol (XIX) in 20 ml of pyridine was added at 0°C a solution of 1.4 ml (19.6 mmoles) of acetyl chloride in 12 ml of dry benzene, and the mixture kept for 20 min at 0°C and 10 min at 20°C. According to TLC (ethyl acetate–benzene, 1:1), the reaction mixture contained the diacetate (XX), the 3-acetate, the original diol, and traces of the 2-acetate (R_f 0.66, 0.31, 0.15, and 0.41, respectively). The mixture was diluted with 100 ml of chloroform, poured into 150 ml of ice water, the organic layer washed with water, 1 M HCl, water, and saturated $NaHCO_3$ solution, dried, and evaporated. CC gave the diacetate (XX), yield 1.06 g (19.3%) as a syrup, $[\alpha]_D$ −17.4° (C, 2.1), and the 3-acetate (XXI), yield 1.98 g (40.7%), syrup, $[\alpha]_D$ −46.5° (C, 2.2).

Selective Benzoylation of the Diol (XIX). To a solution of 1.4 g (5 mmoles) of the diol (XIX) in 6 ml of pyridine was added at 0°C a solution of 0.6 ml (5.2 mmoles) of benzoyl chloride in 2 ml of dry benzene, and the mixture kept for 20 min at 0°C (TLC, ethyl acetate–ben-

zene, 2:8, R_f 0.87, 0.64, 0.43, and 0.10 for the tribenzoate, 2.4- and 3,4-dibenzoates, and the diol, respectively). The mixture was decomposed at 0°C with 2-3 ml of water, poured into 100 ml of saturated $NaHCO_3$ solution, the oil separated, dissolved in 70 ml of chloroform, washed with water, 1 M HCl (3 × 50 ml), water, saturated $NaHCO_3$ (2 × 50 ml), and water, dried, and evaporated. CC gave: 1) the tribenzoate (XXIV), yield 180 mg (7.2%), mp 135-136°C (alcohol), $[\alpha]_D$ +172° (C, 1). Found: C 68.49; H 5.43%. $C_{28}H_{26}O_8$. Calculated: C 68.56; H 5.34%; 2) the 2,4-dibenzoate (XXIII), yield 110 mg (5.6%) (identical with a sample obtained by deacetylating the acetate (XXV) (TLC, PMR)); 3) the 3,4-dibenzoate (XIII), yield 1.28 g (66%), identical (TLC, PMR) with a sample obtained by deacetylating the acetate (XII) as described above.

In another experiment, 14.8 mmoles of the diol (XIX) and 19.2 mmoles of benzoyl chloride gave 37.8% of the tribenzoate (XXIV), 1.3% of the 2,4-dibenzoate (XXIII), and 41.9% of the 3,4-dibenzoate (XIII). With a benzoyl chloride to diol (XIX) ratio of 15:10, the tribenzoate (XXIV) and 3,4-dibenzoate (XIII) were isolated in yields of 52 and 41%, respectively.

Selective Deacetylation of the Diacetate (XX). To a solution of 2.08 g (5.7 mmoles) of (XX) in 6 ml of chloroform and 25 ml of methanol was added at 0°C 1.2 ml of acetyl chloride, and the mixture kept for 16 h at 5°C. It was then neutralized with an excess of $KHCO_3$ solution, the methanol distilled off, and the residue partitioned between water and chloroform (60 ml of each). The aqueous layer was extracted with 20 ml of $CHCl_3$, and the combined extracts washed with water, dried, and evaporated. CC of the residue in the system methanol–chloroform (up to 2.5% of methanol) gave 80 mg (3.8%) of the diacetate starting material (XX), R_f 0.66 (ethyl acetate–benzene, 1:2), 360 mg (19.4%) of the 2-acetate (XXII), syrup, $[\alpha]_D$ −29° (C, 1.2), R_f 0.41, and 1.2 g (73%) of the diol (XIX), R_f 0.15.

Methyl-3-O-acetyl-2,4-di-O-benzoyl-α-L-rhamnopyranoside (XXV). Compound (XXI) (1.39 g, 4.29 mmoles) was benzoylated with 1.5 ml of benzoyl chloride in 5 ml of pyridine at 20°C (the reaction was complete after 10-15 min). The usual workup procedure gave the acetate (XXV), yield 1.84 g (100%), chromatographically pure syrup, $[\alpha]_D$ +71.8° (C, 1.4) (cf. [8]: mp 91°C (ethyl acetate–hexane), $[\alpha]_D$ +88.5° (CH_2Cl_2)).

Methyl-2,4-di-O-benzoyl-α-L-rhamnopyranoside (XXIII). To a solution of 4.3 g (10 mmoles) of the 3-acetate (XXV) in 12 ml of chloroform and 50 ml of methanol was added at 0°C 2.2 ml of acetyl chloride, and the mixture kept for 16 h at 5°C and 3 h at 20°C. It was then worked up as described above for the deacetylation of (XII), to give 3.82 g of a syrup from which was isolated by CC 3.08 g (79.8%) of the 2,4-dibenzoate (XXIII), syrup, $[\alpha]_D$ +63.2° (C, 1.1) (cf. [8]: $[\alpha]_D$ +57.3° (CH_2Cl_2)).

CONCLUSIONS

Some derivatives of L-rhamnopyranose have been obtained which contain easily-removed O^2 or O^3 protection. These are synthons for oligosaccharide synthesis.

LITERATURE CITED

1. N. E. Byramova (Bairamova), M. V. Ovchinnikov, L. V. Backinowsky (Bakinovskii), and N. K. Kochetkov, Carbohydr. Res., 124, C8 (1983).
2. L. V. Bakinovskii, A. R. Gomtsyan, N. É. Bairamova, and N. K. Kochetkov, Bioorg. Khim., 11, 254 (1985).
3. L. Kenne, B. Lindberg, K. Petersson, E. Katzenellenbogen, and E. Romanowska, Eur. J. Biochem., 91, 279 (1978).
4. V. I. Betaneli, M. V. Ovchinnikov, L. V. Backinowsky (Bakinovskii), and N. K. Kochetkov, Carbohydr. Res., 107, 285 (1982).
5. A. F. Bochkov, V. I. Betaneli, and N. K. Kochetkov, Bioorg. Khim., 3, 39 (1977).
6. A. Lipták, J. Imre, and P. Nánási, Carbohydr. Res., 92, 154 (1981).
7. L. B. Bakinovskii, A. R. Gomtsyan, N. É. Bairamova, and N. K. Kochetkov, Bioorg. Khim., 10, 79 (1984).
8. H.-P. Wessel and D. R. Bundle, Carbohydr. Res., 124, 301 (1983).
9. V. I. Betaneli, L. V. Backinowsky (Bakinovskii), N. E. Byramova (Bairamova), M. V. Ovchinnikov, M. M. Litvak, and N. K. Kochetkov, Carbohydr. Res., 113, C1 (1983).
10. N. K. Kochetkov and A. F. Bochkov, in: Methods for the Study of Carbohydrates [in Russian], Mir, Moscow (1975), p. 366.