SYNTHESIS OF 3-O-α-L-RHAMNOPYRANOSYL-D-GALACTOPYRANOSE

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In the recently described synthesis [1] of the repeating unit of the antigenic polysaccharide of Salmonella anatum bacteria one of the problems that had to be solved was building the 1 → 3 glycoside linkage with the galactopyranose moiety. At the present time this problem has apparently been solved by the glycosylation of 1,2:5,6-di-O-isopropylidene-D-galactofuranose [2]. However, when the present study was started the problem to be solved was the glycosylation of galactopyranose derivatives with either one or two unsubstituted OH groups. The known galactopyranose derivatives [3] with a free hydroxyl at C_3 are either difficulty accessible or else they give unsatisfactory results when they are glycosylated. The galactopyranose derivatives with OH groups at C_3 and C_4 are more accessible, and their glycosylation in harmony with [4, 5] proceeds in the 3 position.

In the present paper we report the synthesis of 3-O-α-L-rhamnopyranosyl-D-galactopyranose (VII) and its full acetate (VIII), with a β-configuration at C_1 of the galactose moiety. Disaccharide (VII) is a fragment of the repeating units of the antigenic polysaccharides of the Salmonella species of bacteria,, which belong to the serological groups A, B, D, and E [6].

The starting compound was methyl-1-thio-1-desoxy-β-D-galactopyranoside (I), which was obtained in high yield by a modification of the method given in [7]. The acetonation of (I) with 2,2'-dimethoxypropane in acetone, in the presence of p-toluenesulfonic acid, gives the monoisopropylidene derivatives (IIa) and (IIIa) in respective yields of 65% and 10%, the structure of which ensued from the NMR spectral data for their acetates, (IIb) and (IIIb) [8]. Acetate (IIb) has a structure of the cis-hydrindan type, in which the gem-methyl groups of the dioxolane ring are sterically nonequivalent and give signals with sharply different chemical shifts (δ 1.23 and 1.45 ppm). Acetate (IIIb) has a structure of the cis-decalin type, in which the gem-methyl groups of the m-dioxane ring are sterically more equivalent (δ 1.31 and 1.35 ppm). Acetonide (IIb) on hydrolysis by treatment with CF_3COOH in a mixture of $CHCl_3$ and acetone gives the crystalline acetate (IV) with two free OH groups at C_3 and C_4. Acetate (IV) satisfied the following two requirements: first, the glycosylation of (IV) with rhamnopyranosyl bromide should lead to the formation of the 1 → 3 glycoside linkage in harmony with the data given in [4, 5], and second, the thioglycoside group is a convenient function for inserting an acetoxy group with a β-configuration. The preparation of acetate (VIII) represented interest for studying the phosphorylation of oligosaccharides with labile linkages.

Thioglycoside (IV) was glycosylated with tri-O-acetyl-α-L-rhamnopyranosyl bromide in a dioxane—benzene mixture in the presence of $AgClO_4$ and Ag_2CO_3 as described in [9], and led to a mixture of products, which were acetylated without separation. When the mixture of acetates was chromatographed on a SiO_2 column the main reaction product (Va) was isolated in 16% yield. Since the glycosylation proceeded in a complex manner (in particular, methylthiorhamnopyranoside acetate was detected), to prove the structure of disaccharide (Va) it was necessary to determine not only the position of the glycoside linkage,* but also to confirm the presence of the thioglycoside function. For this (Va) was treated with Raney Ni in alcohol to give rhamnosyl-anhydrodulcitol hexaacetate (VI), the structure of which followed from the mass

*It is known that the α-rhamnoside linkage is always formed when glycosylation is with tri-O-acetyl-rhamnopyranosyl bromide, and consequently the configuration of the glycoside linkage was not specially proved in our case.

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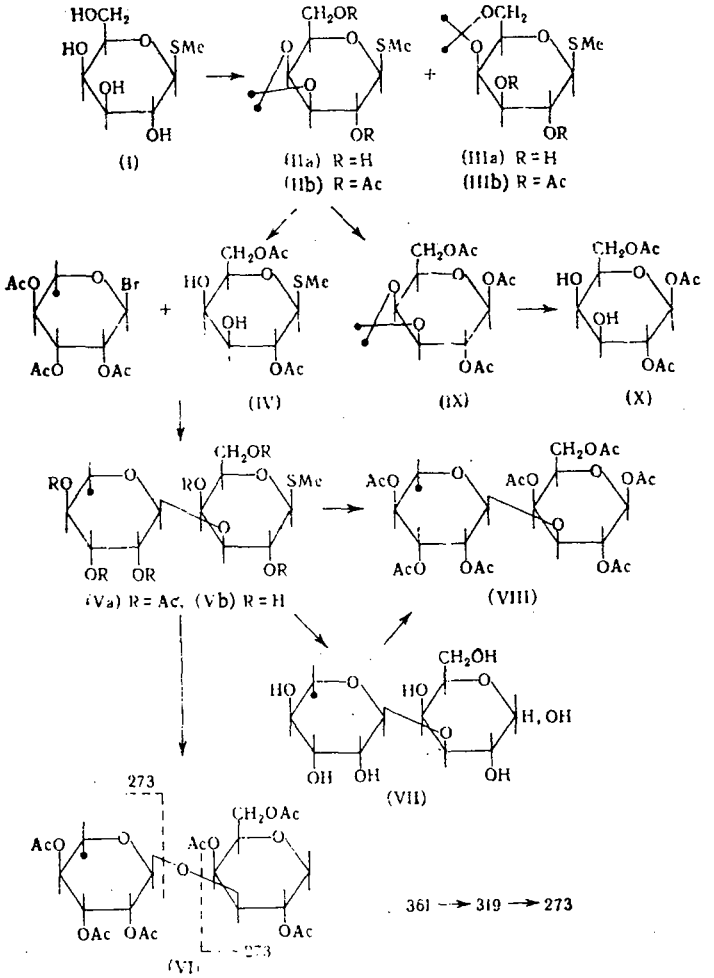
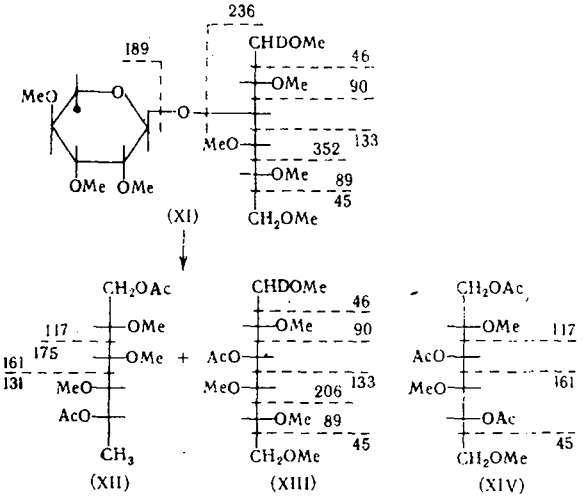


spectral data. The fragmentation of (VI) proceeded in harmony with the data for the acetates of glycosyl-anhydrohexitols [10], and led to a series of ions with m/e 361, 319, and 273. The deacetylation of derivative (Va) with CH_3ONa in methanol, and subsequent treatment with $HgCl_2$, gave disaccharide (VII), which, based on the paper chromatography data, using acid aniline phthalate for detection, was homogeneous, and gave galactose and rhamnose in a 1 : 1 ratio on acid hydrolysis. The presence of the glycoside 1 → 3 linkage in (VII), and consequently also in (Va), was proved in the following manner. The reduction of (VII) by treatment with $NaBD_4$ led to rhamnosyl-dulcitol-1-^{2}H, which after methylation in the presence of methylsulfinyl anion [11] gave, when based on the GLC data, two products in a 10 : 1 ratio. The mass spectrum of the main product (XI) fully agreed with the data given in [12] for the methyl ethers of glycosyl 1 → 3 polyols (the fragmentation is shown in Scheme 1).



Scheme 1

The greater intensity of the peaks of the ions with m/e 133, 89, and 45 when compared with the peaks of the ions with m/e 134, 90, and 46, and also the presence of the ion with m/e 352, indicated the presence of the 1 → 3 linkage. However, this method of choosing between the 1 → 3 and 1 → 4 linkages is not the best, since the difference in the mass spectra of the corresponding hexosyl-hexitols-1-^{2}H is caused by one ion, which differs by one mass unit (the ions with m/e 133 and 134) [12]. Consequently, derivative (XI) was subjected to combined formolysis and hydrolysis, followed by reduction with KBH_4 and acetylation, and gave a mixture of 2,3,4-tri-O-methyl-1,5-di-O-acetyl-rhamnitol (XII) and 1,2,4,5,6-penta-O-methyl-3-O-acetyldulcitol-1-^{2}H (XIII), the chromato-mass spectrometry data for which are given in the Scheme. However, in the mass spectrum of (XIII) the intensity of the peaks of the ions with m/e 90 and 60 (90—CH_2O) is observed to be greater than the intensity of the peaks of the ions with m/e 89 and 59, although according to the data on the fragmentation of the partially methylated polyols [13] the reverse relation could be expected. The presence of the 1 → 3 linkage in disaccharide (VII) was conclusively proved via the chromato-mass spectrometry of polyol (XII) and 2,4,6-tri-O-methyl-1,3,5-tri-O-acetyl-dulcitol (XIV), which were obtained from thiobioside (Vb) by successive methylation, combined formolysis-hydrolysis, reduction with KBH_4, and acetylation.

The conversion of the acetylated thiobioside (Va) to the full rhamnosyl-galactose acetate (VIII) was accomplished in high yield by the action of Cl_2 in $CHCl_3$, with subsequent treatment of the formed glycosyl chloride acetate with $Hg(OCOCH_3)_2$ in CH_3COOH as described in [14]. The β-configuration at C_1 of the galactose moiety in (VIII), which, based on the GLC data, contained up to 10% of the α-anomer, followed from the data of the NMR spectrum, which contained a signal with δ 5.65 ppm, and $J_{1,2}$ = 9 Hz, corresponding to the proton at C_1. Acetate (VIII) was also obtained by the direct acetylation of disaccharide (VII), but in this case the acetylation product contained ~25% of the α-anomer.

Since the glycosylation of the thiogalactoside derivative (IV) proceeded in a complex manner, thiogalactoside (IIb) was converted by treatment with Cl_2, and then with $Hg(OCOCH_3)_2$, to triacetate (IX), the β-configuration of which followed from the NMR spectral data. The removal of the isopropylidene protection from triacetate (IX) by treatment with CF_3COOH led to the crystalline triacetate (X), with free OH groups at C_3 and C_4. However, the obtained acetate (X) proved to be labile, and attempts to glycosylate it in the presence of $Hg(CN)_2$ and $HgBr_2$ proved unsuccessful.

EXPERIMENTAL METHOD

The melting points were determined on a Kofler block. The NMR spectra were taken on a Varian DA-60-IL instrument relative to HMDS, while the mass spectra were taken on a Varian CH_6 instrument, with direct insertion of the sample into the ion source at 70 eV. The chromato-mass spectrometry was run on a Varian MAT-111 instrument, using SE-30 and ECNSS-M as the phases, while the GLC was run on a Pye Unicam Series 104 instrument equipped with a flame-ionization detector, and using nitrogen as the carrier gas. The TLC was run on plates covered with a loose layer of SiO_2, and the compounds were detected with H_2SO_4. The paper chromatography was run in the solvent system: 6:4:3 butanol—pyridine—water (system A). The compounds were detected on the paper using alkaline $AgNO_3$ and acid aniline phthalate. The solvents were evaporated in vacuo at a temperature not exceeding 40°C.

Methyl-1-thio-1-desoxy-β-D-galactopyranoside (I). With cooling, to a solution of 48 g of 2,3,4,6-tetra-O-acetyl-α-D-galactopyranosyl bromide [15] in 50 ml of absolute DMF was added in drops a solution of CH_3SK in methanol (obtained by the addition of 4.5 g of K and 11 ml of CH_3SH to 70 ml of methanol). The mixture was kept at 20° for 1 h, the KBr precipitate was separated, the filtrate was evaporated in vacuo, and the residue was refluxed for 10 min with 200 ml of acetic anhydride and 21 g of anhydrous CH_3COONa. The cooled mixture was poured on ice, the obtained oil solidified when washed with water, and the precipitate was filtered, dissolved in 250 ml of $CHCl_3$, decolorized by treatment with carbon, evaporated, and the residue was recrystallized from alcohol. We obtained 30.1 g (70%) of 2,3,4,6-tetra-O-acetylmethyl-1-thio-1-desoxy-β-D-galactopyranoside [7], mp 109-111°. To a suspension of 30 g of the obtained tetraacetate in 150 ml of absolute methanol was added 30 ml of a 0.2 N solution of CH_3ONa in methanol and the mixture was heated on the water bath until the precipitate dissolved. The mixture was cooled, and then kept at 5° for 2 h. We obtained 14 g of (I). The mother liquor was deionized with 25 ml of cationite KU-2 (H^+ form) and then evaporated to give an additional amount of (I). Recrystallization from alcohol gave 15.8 g (95%) of (I) [7], mp 176-178°; $[\alpha]_D^{20}$ + 10.3° (C 2, water).

3,4-O-Isopropylidene-methyl-1-thio-1-desoxy-β-D-galactopyranoside (IIa). A mixture of 10 g of (I), 250 ml of absolute acetone, 10 ml of 2,2'-dimethoxypropane, and 20 mg of p-toluenesulfonic acid was stirred at 20°. After 12 h an additional 50 ml of acetone and 2 ml of dimethoxypropane were added, the

whole was stirred for 12 h, neutralized with 10-15 g of K_2CO_3, filtered, and evaporated. Direct recrystallization of the residue from an acetone—pentane mixture gave 7.2 g (65%) of (IIa), mp 137-139°; $[\alpha]_D^{20}$ + 45° (C 1.87, $CHCl_3$). Mass spectrum (m/e): 250 (M^+), 235 (M—CH_3), 232 (M—H_2O), 203 (M—SCH_3), 145 (M—SCH_3—CH_3COCH_3), 127 (145—H_2O), 109 (145—$2H_2O$). Found: C 47.83; H 7.11; S 13.52%. $C_{13}H_{18}SO_5$. Calculated: C 47.98; H 7.25; S 13.10%.

2,6-Di-O-acetyl-3,4-O-isopropylidene-methyl-1-thio-1-desoxy-β-D-galactopyranoside (IIb). Compound (IIa) (6 g) was acetylated with a mixture of 10 ml of acetic anhydride and 20 ml of pyridine at 20° for 48 h. The mixture was evaporated with toluene and heptane, and the residue was recrystallized from an acetone—ether—pentane mixture. We obtained 7.4 g (92.5%) of (IIb), mp 102-104°, $[\alpha]_D^{20}$ + 70.9° (C 1.86, $CHCl_3$). Found: C 50.12; H 6.47; S 10.02%. $C_{14}H_{22}SO_7$. Calculated: C 50.29; H 6.63; S 9.59%.

2,3-Di-O-acetyl-4,6-O-isopropylidene-methyl-1-thio-1-desoxy-β-D-galactopyranoside (IIIb). After separating the crystalline (IIa), the residue from the mixture of acetonation products of (I) was chromatographed on a column containing neutral Al_2O_3 (II activity), with elution using a gradient mixture of ethyl acetate and methanol, to give the sirupy acetonide (IIIa), which on acetylation gave diacetate (IIIb) as a sirup, $[\alpha]_D^{20}$ + 33.3° (C 1.95, $CHCl_3$). Mass spectrum (m/e): 309 (M—CH_3), 287 (M—SCH_3), 274 (M—CH_3-COOH), 229 (M—SCH_3—CH_3COCH_3), 227 (M—SCH_3—CH_3COOH), 169 (M—SCH_3—CH_3COCH_3—CH_3COOH), 167 (M—SCH_3—$2CH_3COOH$), 109 (M—SCH_3—CH_3COCH_3—$2CH_3COOH$).

2,6-Di-O-acetyl-methyl-1-thio-1-desoxy-β-D-galactopyranoside (IV). To a solution of 1.65 g of (IIb) in 10 ml of $CHCl_3$ were added 20 ml of 80% CF_3COOH and 5 ml of acetone. The mixture was kept at 20° for 7-8 min, evaporated, and the residue was evaporated with toluene to remove traces of CF_3COOH. The residue was chromatographed on a SiO_2 column, with elution using a gradient mixture of $CHCl_3$ and methanol (1-3%). We isolated 70 mg of the starting (IIb) and 1.3 g (90%) of (IV), mp 116-119° (from ethyl acetate—heptane); $[\alpha]_D^{20}$ + 33.5° (C 2.09, $CHCl_3$). Mass spectrum (m/e): 247 (M—SCH_3), 234 (M—CH_3-COOH), and two series of ions that are formed from the fragment with m/e 247: 229—169—127—109 and 187—145—127. Found: C 44.76; H 6.22; S 11.13%. $C_{11}H_{18}SO_7$. Calculated: C 44.89; H 6.17; S 10.89%.

3-O-(2,3,4-Tri-O-acetyl-α-L-rhamnopyranosyl)-2,4,6-tri-O-acetylmethyl-1-thio-1-desoxy-β-D-galactopyranoside (Va). A mixture of 2 g of (IV), 130 ml of absolute benzene, and 35 ml of absolute dioxane was stirred for 2 h with 300 mg of $AgClO_4$, 2.5 g of Ag_2CO_3, and 4 g of Drierite, after which 2.5 g of acetobromorhamnose [16] and 4-5 g of Drierite were added, and the stirring was continued for 48 h without admitting moisture, air, and light. To the mixture was added a solution of 10 g of NaCl and 2 g of K_2CO_3 in 60 ml of water, the organic layer was separated, the aqueous layer was extracted with $CHCl_3$ (3 × 15 ml), and the combined extract was dried over $CaCl_2$ and evaporated. The residue (3 g) was acetylated with a mixture of 8 ml of acetic anhydride and 15 ml of pyridine at 20° for 48 h. The mixture was evaporated, and the residue was evaporated with toluene and heptane. The obtained mixture of products, which contained the monosaccharide components (Rf 0.7, 8: 2 benzene—ethyl acetate), disaccharide (Va) with Rf 0.5, and a number of less mobile compounds, was chromatographed on a SiO_2 column, using a gradient benzene—ethyl acetate (0.5-15%) mixture for elution, to give 645 mg (15.6%) of sirupy (Va), $[\alpha]_D^{20}$ —12.3° (C 2.74, $CHCl_3$). Mass spectrum (m/e): 561 (M—SCH_3), and ions 273 and 331, which correspond to the rhamnose—galactose sequence with an unreducible end.

A mixture of 5 mg of (Va) and a little Raney Ni in alcohol was refluxed for 1.5 h, after which a fresh portion of nickel was added and the refluxing was continued for another 3 h. Preparative TLC (75:25 benzene—ethyl acetate) gave hexaacetate (VI) with Rf 0.4. Mass spectrum (m/e): 562 (M^+), 502 (M—CH_3COOH), and a series of ions: 361—319—273.

3-O-(α-L-Rhamnopyranosyl)-methyl-1-thio-1-desoxy-β-D-galactopyranoside (Vb). The deacetylation of 400 mg of (Va) with 30 ml of an 0.5% solution of CH_3ONa in absolute methanol was run at 20° for 20 h. The solution was deionized with cationite KU-2 (H^+ form). Evaporation gave a crystalline residue, the recrystallization of which from an alcohol—methanol mixture gave 210 mg (90%) of (Vb) that, based on the data of chromatographing in system A, is homogeneous, R_{Gal} 1.83, mp 218-220°; $[\alpha]_D^{20}$ —65° (C 1.87, methanol). Found: C 43.71; H 6.92; S 9.17%. $C_{13}H_{24}SO_9$. Calculated: C 43.81; H 6.79; S 8.99%.

Rhamnose and galactose were detected in the hydrolyzate of thioglycoside (Vb) (1 M H_2SO_4, 100°, 2.5 h in a sealed ampul) when it was subjected to paper chromatography in system A.

3-O-(α-L-Rhamnopyranosyl)-D-galactopyranose (VII). To a solution of 60 mg of (Vb) in 5 ml of water were added 10 ml of acetone, 300 mg of $HgCl_2$, and 500 mg of yellow HgO. The mixture was stirred at 45° for 4-5 h, the precipitate was filtered, the filtrate was passed through a column containing KU-2 (H^+ form) and a column containing Dowex resin (CO_3^{2-} form), and traces of mercury were removed with

H_2S. Evaporation gave 50 mg of (VII) as a colorless sirup with R_{Gal} 0.85 (system A); $[\alpha]_D^{23}$ −7.6° (equilibrium, C 2.23, methanol).

The reduction of 30 mg of (VII) with 50 mg of $NaBD_4$ in 3 ml of 50% methanol was run at 20° for 36 h. The solution was neutralized with cationite KU-2 (H^+ form), the filtrate was evaporated to dryness, and the residue was evaporated several times with methanol. We obtained 30 mg of a sirup with R_{Gal} 0.85 (system A) and $[\alpha]_D^{23}$ −45° (C 1.5, methanol). The methylation of 10 mg of the obtained rhamnosyl-dulcitol-1-^{2}H by the Hakomori method [11] gave 8.5 mg of a mixture that mainly contained a substance with R_f 0.38 (TLC, 95 : 5 $CHCl_3$—methanol), which was contaminated with less mobile components. Based on the GLC data (5% SE-30, 200-235°, with a program of 3 deg/min), the obtained mixture contains two substances in a 10 : 1 ratio, with retention times of 12 and 13.7 min. It was established by the chromato-mass spectrometry method that the main product is 3-O-(2,3,4-tri-O-methyl-6-desoxyhexosyl)-1,2,4,5,6-penta-O-methyl-hexitol-1-^{2}H (XI).

A mixture of 3 mg of (XI) and 1 ml of 85% HCOOH was heated in a sealed ampul at 100° for 2 h, evaporated, hydrolyzed with 0.3 N HCl solution at 100° for 16 h, the hydrolyzate was evaporated, traces of HCl were removed in vacuo over solid KOH, and the residue was reduced with KBH_4 in aqueous methanol and then acetylated. Based on the chromato-mass spectrometry data (ECNSS-M, 160°), the mixture contains the partially methylated polyols (XII) and (XIII), with retention times of 2.68 and 2.74 min.

Compound (Vb) (3.5 mg) was methylated by the Hakomori method, and then subjected to formolysis-hydrolysis, reduction, and acetylation. Based on the GLC data, a mixture of (XII) and (XIV) was obtained.

3-O-(2,3,4-Tri-O-acetyl-α-L-rhamnopyranosyl)-1,2,4,6-tetra-O-acetyl-β-D-galactopyranose (VIII). To a solution of 250 mg of (Va) in 3 ml of absolute $CHCl_3$ was added a 2.5-fold excess of Cl_2 in 0.3 ml of $CHCl_3$, and the same amount of Cl_2 was added after 1.5 h. Only traces of the starting (Va), with R_f 0.5 (8 : 2 benzene—ethyl acetate), remain in the mixture after 20 h, and the glycosyl chloride with R_f 0.6 appears. The mixture was evaporated, and the residue was evaporated several times with absolute $CHCl_3$ and absolute ether. The obtained glycosyl chloride was dissolved in 5 ml of glacial CH_3COOH and 70 mg of $Hg(CH_3COO)_2$ was added, after which the solution was kept at 20° for 20 h and then lyophilized. The residue was dissolved in 50 ml of $CHCl_3$, washed with aqueous KI solution (3 × 20 ml), then with water (2 × 20 ml), dried over Na_2SO_4, and evaporated. The residue was chromatographed on a SiO_2 column. Elution with a gradient benzene—ethyl acetate (1-15%) mixture gave 160 mg (63%) of sirupy (VIII); $[\alpha]_D^{19}$ + 14.6° (C 2.23, $CHCl_3$). Based on the GLC data (SE-30, 265°), the product represents a mixture of two substances in a 10 : 1 ratio, with retention times of 8.75 and 10.7 min. Mass spectrum (m/e): 273 and 331, which correspond to the rhamnose and galactose moieties, and 561 (M—CH_3COO).

1,2,6-Tri-O-acetyl-3,4-O-isopropylidene-β-D-galactopyranose (IX). To a solution of 2 g of (IIb) in 10 ml of CCl_4 was added a solution of 0.8 g of Cl_2 in 20 ml of CCl_4. The mixture was kept at 20° for 1 h, and then another 10 ml of Cl_2-containing CCl_4 was added. After 4 h the mixture was evaporated, and the residue was evaporated several times with CCl_4 and absolute ether. The obtained glycosyl chloride was dissolved in 40 ml of glacial CH_3COOH, 2.04 g of $Hg(OCOCH_3)_2$ was added, the mixture was kept at 20° for 16 h, the precipitate was separated, and the filtrate was diluted with 150 ml of $CHCl_3$, washed with 1 N KI solution (2 × 60 ml), then with water, and evaporated to dryness. Recrystallization of the residue from an acetone—ether—petroleum ether mixture gave 930 mg (42.3%) of (IX), mp 119-120°, $[\alpha]_D^{20}$ + 59.2° (C 1.91, $CHCl_2$). NMR spectrum (δ, ppm, in $CHCl_3$): 1.36 s and 1.58 s (6H, Me_2C), 2.10-2.16 2 s (9H, CH_3COO), and 5.62 d (1 H, $J_{1,2}$ = 7.5 Hz, H_1). Found: C 52.12; H 6.32%. $C_{15}H_{22}O_9$. Calculated: C 52.02, H 6.40%.

Evaporation of the mother liquor, obtained from the recrystallization of (IX), gave 750 mg of a sirupy residue, which, based on the GLC data (OV-17, 216°), contains two substances in a 8 : 10 ratio, with retention times of 5.41 and 6.38 min. As a result, the β-acetate (IX) is formed in 65% yield, while the substance with a retention time of 5.41 min is apparently the α-anomer.

1,2,6-Tri-O-acetyl-β-D-galactopyranose (X). To a solution of 0.4 g of (IX) in 5 ml of $CHCl_3$ were added 20 ml of 80% CF_3COOH and 5 ml of acetone, after 5 min the homogeneous solution was evaporated, and the residue was evaporated several times with $CHCl_3$ and toluene in order to remove traces of CF_3-COOH. The residue was chromatographed on SiO_2, using a $CHCl_3$—methanol (1-5%) gradient for elution, to give 100 mg (28%) of (X), mp 100-120°; $[\alpha]_D^{20}$ + 40° (C 3.52, $CHCl_3$). The substance is labile and becomes chromatographically inhomogeneous on attempted recrystallization. NMR spectrum (δ, ppm, in $CHCl_3$): 2.12-2.15 2 s (9H, CH_3COO), 5.65 d (1 H, $J_{1,2}$ = 8.5 Hz, H_1). Mass spectrum (m/e): 288 (M—H_2O),

247 (M—$OCOCH_3$), 229 (M—$OCOCH_3$—H_2O), 189 (229—CH_3COOH), 129 (229—$2CH_3COOH$), 187 (M—$OCOCH_3$—CH_3COOH), 127 (187—CH_3COOH), 186 (M—$2CH_3COOH$), and 126 (186—CH_3COOH).

CONCLUSIONS

The synthesis of 3-O-(α-L-rhamnopyranosyl)-D-galactopyranose, a disaccharide that is a fragment of the repeating units of a number of polysaccharides of the Salmonella species of bacteria, was described.

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