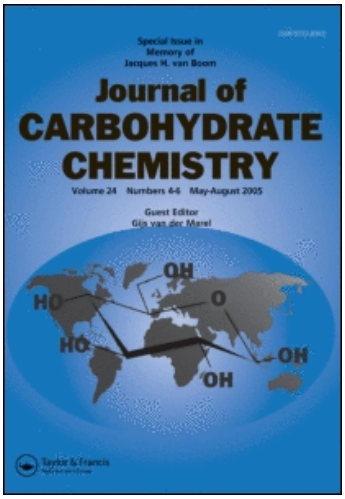

Journal of Carbohydrate Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713617200

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To cite this Article Das, Saibal Kumar , Ghosh, Rina and Roy, Nirmolendu(1993) 'Synthesis of the Tetrasaccharide Repeating Unit of the Antigen from *Klebsiella* TYPE 83', Journal of Carbohydrate Chemistry, 12: 6, 693 — 701
To link to this Article: DOI: 10.1080/07328309308019000
URL: http://dx.doi.org/10.1080/07328309308019000

J. CARBOHYDRATE CHEMISTRY, 12(6), 693-701 (1993)

SYNTHESIS OF THE TETRASACCHARIDE REPEATING UNIT OF THE ANTIGEN FROM *KLEBSIELLA* TYPE 83

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Received September 10, 1992 - Final Form March 2, 1993

ABSTRACT

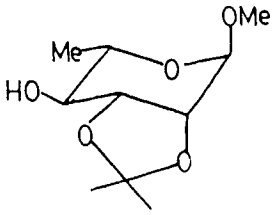
Starting from D-galactose, D-glucose and L-rhamnose, methyl 2-*O*-benzyl-3-*O*-(3-*O*-allyl-2,4,6-tri-*O*-benzyl-α-D-galactopyranosyl)-4-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranosyl)-α-L-rhamnopyranoside **(9)** and methyl 2-*O*-benzyl-3-*O*-[2,4,6-tri-*O*-benzyl-3-*O*-(methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranosyluronate)-α-D-galactopyranosyl]-4-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranosyl)-α-L-rhamnopyranoside **(13A)** have been synthesised. Removal of protecting groups from **9** and **13A** gave the trisaccharide **(11)** and the tetrasaccharide repeating unit of the antigen from *Klebsiella* type 83 in the form of its methyl ester methyl glycoside **(14A)** respectively.

INTRODUCTION

The structure of the repeating unit of the capsular polysaccharide of *Klebsiella* type 83 has been reported.[1] In support of our continuing programme to determine the structure / immunological specificity[2] relationship of carbohydrate moieties, it is necessary to synthesize oligosaccharides related to a specific antigen. The synthesis of the tetrasaccharide repeating unit of the antigen from *Klebsiella* type 83 is described here.

RESULTS AND DISCUSSION

Condensation of methyl 2,3-*O*-isopropylidene-α-L-rhamnopyranoside[3] **(1)** with 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide[4] **(2)** in the presence of mercury(II) cyanide[5] gave methyl 4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-2,3-*O*-isopropylidene-α-L-rhamnopyranoside **(4)** in 82% yield. Zémplen deacetylation[6] of **4** followed by benzylation[7] gave methyl 4-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranosyl)-2,3-*O*-isopropylidene-α-L-rhamnopyranoside **(6)**. Removal of the isopropylidene group from **6** followed by selective benzylation of the product **(7)** using phase transfer method[8] yielded methyl 2-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranosyl)-α-L-rhamnopyranoside **(8)**. This glycosyl acceptor was condensed with ethyl 3-*O*-allyl-2,4,6-tri-*O*-benzyl-1-thio-β-D-galactopyranoside **(3)**, using methyl triflate[9] as promoter, to give methyl 2-*O*-benzyl-3-*O*-(3-*O*-allyl-2,4,6-tri-*O*-benzyl-α-D-galactopyranosyl)-4-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranosyl)-α-L-rhamnopyranoside **(9)** in 74% yield. Subsequent removal of the allyl group from **9** using palladium chloride[10] gave methyl 2-*O*-benzyl-3-*O*-(2,4,6-tri-*O*-benzyl-α-D-galactopyranosyl)-4-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranosyl)-α-L-rhamnopyranoside **(10)**. Debenzylation of **10** by hydrogenolysis gave methyl 3-*O*-(α-D-galactopyranosyl)-4-*O*-(β-D-galactopyranosyl)-α-L-rhamnopyranoside **(11)**. The ^{13}C NMR of this compound had signals for 19 carbon atoms in the expected regions. Methyl (2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl chloride) uronate[12] **(12)** prepared from methyl α-D-glucopyranoside,[11] was treated with **10** in the presence of mercury(II) bromide[5] to give methyl 2-*O*-benzyl-3-*O*-[2,4,6-tri-*O*-benzyl-3-*O*-(methyl 2,3,4-tri-*O*-benzyl-α and β-D-glucopyranosyl uronate)-α-D-galactopyranosyl]-4-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranosyl)-α-L-rhamnopyranoside **(13A** and **13B)** in 83% combined yield. Data from the ^{1}H NMR spectrum of this material suggested an approximately 70:30 mixture of α and β-anomers. The mixture components could not be separated by column chromatography. The mixture was therefore subjected to hydrogenolysis to give **14A** and **14B** which were then separated by column chromatography. Both **14A** and **14B** had signals for 26 carbon atoms in their ^{13}C NMR spectra. The α-anomeric configuration of the tetrasaccharide **14A** was confimed by its signals at δ 5.14 (H-1$'''$) and 3.81 ($COOCH_3$) in the ^{1}H NMR spectrum and δ 96.72 (C-1$'''$) and 173.2 ($\underline{C}OOCH_3$) in the ^{13}C NMR spectrum. Similarly β-ano-



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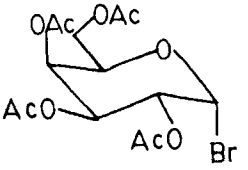

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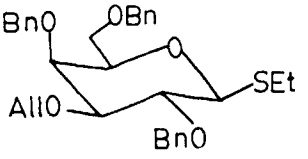

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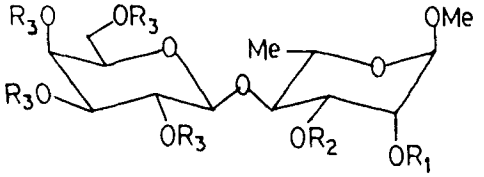
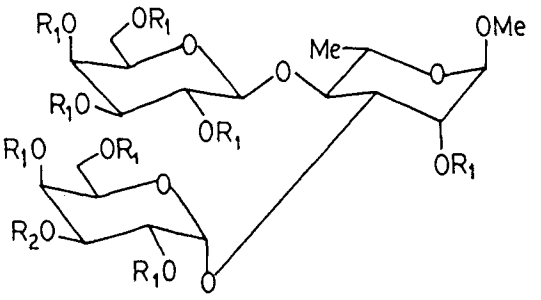
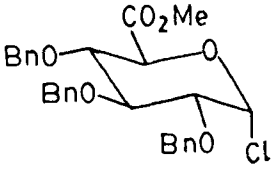


4. $R_1,R_2 = Me_2C$, $R_3 = Ac$
5. $R_1, R_2 = Me_2C$, $R_3 = H$
6. $R_1, R_2 = Me_2C$, $R_3 = Bn$
7. $R_1 = R_2 = H$, $R_3 = Bn$
8. $R_1 = R_3 = Bn$ $R_3 = H$



9. $R_1 = Bn$, $R_2 = Allyl$
10. $R_1 = Bn$, $R_2 = H$
11. $R_1 = R_2 = H$



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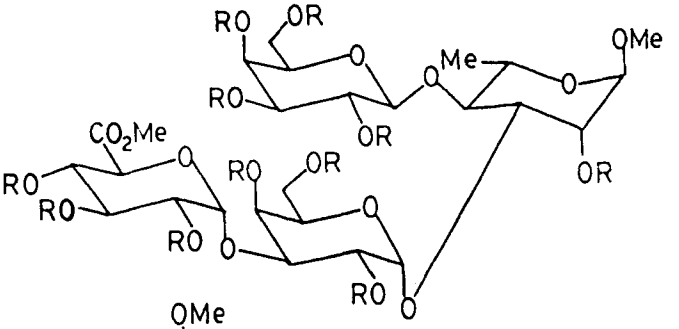
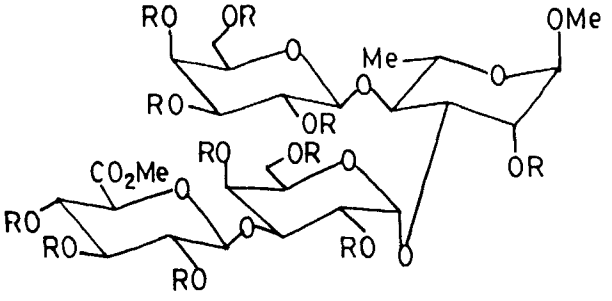


13A. R = Bn
14A. R = H
15. R = Ac



13B. R = Bn
14B. R = H.

meric configuration of **14B** was confirmed by its signal at δ 4.73 (H-1''') and 3.82 ($COOCH_3$) in the ^1H NMR spectrum and δ 104.76 (C-1''') and 171.9 ($\underline{C}OOCH_3$) in the ^{13}C NMR spectrum. Compound **14A** was further characterised *via* its crystalline per-*O*-acetyl derivative **15**.

EXPERIMENTAL

General – Reactions were monitored by TLC on silica gel G (Merck). Column chromatography was performed using silica gel (SRL, India), and all concentrations were conducted below 50 °C unless stated otherwise. Optical rotations were measured with a Perkin-Elmer 241MC polarimeter. ^1H NMR spectra were recorded with a Jeol FX-100 or Varian XL-300 spectrometer. Melting points were determined on a paraffin oil bath and are reported uncorrected. Paper chromatography was performed on Whatman No. 1 paper with 9:2:2 EtOAc-acetic acid-water as solvent and alkaline silver nitrate as the spray reagent for component visualisation.

Methyl 4-*O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-2,3-*O*-isopropylidene-α-L-rhamnopyranoside (4). To a solution of methyl 2,3-*O*-isopropylidene-α-L-rhamnopyranoside[3] **(1)** (3.3 g, 15.2 mmol) and mercury(II) cyanide (4.8 g, 18.9 mmol) in acetonitrile (36 mL) containing 4Å molecular sieve (6 g) under argon, was added a solution of 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide[4] **(2)** (7.1 g, 17.1 mmol) in acetonitrile (10 mL). The mixture was stirred at room temperature for 24 h, the contents diluted with dichloromethane and filtered through a celite bed. The organic layer was washed successively with water, aqueous 5% KI solution, and water, and then dried (Na_2SO_4) and concentrated. The residue was chromatographed (3:1 toluene-Et_2O) giving **4** (7.76 g, 82%). The product was crystallised from dichloromethane: mp 182-184 °C; $[\alpha]_D^{25}$ -24.3° (*c* 0.75, CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 1.19 (d, 3H, J=6.0 Hz, H-6), 1.35 and 1.54 (2s, 6H, Me_2C), 2.00, 2.05, 2.09 and 2.16 (4s, 12H, 4Ac), 3.38 (s, 3H, OMe), 4.92 (d, 1H, J=7.5 Hz, H-1'), 4.83 (broad s, 1H, H-1).

Anal. Calcd for $C_{24}H_{36}O_{14}$: C, 52.55; H, 6.62. Found: C, 52.37; H, 6.78.

Methyl 4-*O*-(2,3,4,6-Tetra-*O*-benzyl-β-D-galactopyranosyl)-2,3-*O*-isopropylidene-α-L-rhamnopyranoside (6). Compound **4** (2.3 g, 4.2 mmol) was stirred with methanolic 0.05 M sodium methoxide (20 mL) for

5 h. The solution was treated with Dowex-50W X8(H^+) resin, filtered and concentrated to dryness to give **5**. To a cold solution of **5** in *N*,*N*-dimethylformamide (14 mL) was added sodium hydride (1.2 g, 25.2 mmol, 50% oil coated) and benzyl bromide (2.4 mL, 20.2 mmol), and the mixture was stirred at room temperature for 11 h. Methanol (1 mL) was then added, to decompose excess of the reagents, the mixture was then diluted with dichloromethane (100 mL), the organic layer was washed with water (3x50 mL), dried (Na_2SO_4), and concentrated. The crude product was chromatographed and crystallised from Et_2O-petroleum ether (40-60 °C), to give **6** (1.88 g, 60%): mp 94-95 °C; $[\alpha]_D^{33}$ -22.8° (*c* 1.4, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.3 (d, 3H, J=6.0 Hz, H-6), 1.32 and 1.44 (2s, 6H, Me_2C), 3.39 (s, 3H, OMe), 4.7 (d, 1H, J=8.0 Hz, H-1'), 4.84 (broad s, 1H, H-1), 7.28-7.4 (m, 20H, 4Ph).

Anal. Calcd for $C_{44}H_{52}O_{10}$: C, 71.33; H, 7.07. Found: C, 70.98; H, 7.15.

Methyl 2-*O*-Benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranosyl)-α-L-rhamnopyranosude (8). Compound **6** (1.2 g, 1.6 mmol) was stirred with 85% aqueous acetic acid (5 mL) at 90 °C for 2 h. Acetic acid was then removed by co-evaporation with water and then with toluene to give compound **7**, $[\alpha]_D^{26}$ -21.1° (*c* 2.2, $CHCl_3$). This material was dissolved in dichloromethane (19.5 mL) and then vigorously stirred at room temperature for 60 h with 10% sodium hydroxide (2.3 mL), benzyl bromide (0.29 mL, 2.0 mmol) and tetrabutylammonium bromide (0.13 g, 0.7 mmol). The organic layer was washed with water, dried (Na_2SO_4) and concentrated to a syrup. Column chromatography with 5:1 toluene-Et_2O gave **8** (698 mg, 55%): $[\alpha]_D^{32}$ -17.2° (*c* 1.05, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.36 (d, 3H, J=6.0 Hz, H-6), 3.33 (s, 3H, OMe), 4.62 (d, 1H, J=7.8 Hz, H-1'), 4.46-4.9 (2s, 10H, $5PhCH_2$), 4.84 (s, 1H, H-1), 7.32-7.36 (m, 25H, 5Ph).

Anal. Calcd for $C_{48}H_{54}O_{10}$: C, 72.89; H, 6.88. Found: C, 72.66; H, 6.98.

Ethyl 3-*O*-Allyl-2,4,6-tri-*O*-benzyl-1-thio-β-D-galactopyranoside (3). A mixture of ethyl 1-thio-β-D-galactopyranoside[13] (5 g, 22.3 mmol) and dibutyltin oxide[14] (5.7 g, 22.9 mmol) was stirred under reflux in benzene with azeotropic removal of water for 17 h. Allyl bromide (2.8 mL) and tetrabutylammonium bromide (8.36 g) were then added and the mixture was stirred at 63 °C for 6 h. The solvent was evaporated and the unwanted solid precipitated from cold methanol was filtered off.

The filtrate was concentrated and chromatographed with ethyl acetate as eluent, to give ethyl 3-*O*-allyl-1-thio-β-D-galactopyranoside (3.6 g, 60%). The product was crystallised from ethyl acetate: mp 122-123 °C; $[\alpha]_D^{24}$ -14.38° (*c* 0.6, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.32 (t, 3H, J=8.0 Hz, $SCH_2\underline{CH}_3$), 2.76 (q, 2H, J=7.5 Hz, $S\underline{CH}_2CH_3$), 4.22-4.3 (m, 2H, allyl H), 4.36 (d, 1H, J=10 Hz, H-1), 5.2-5.44 (m, 2H, vinyl H), 5.82-6.24 (m, 1H, vinyl H).

Anal. Calcd for $C_{11}H_{20}O_5S$: C, 49.98; H, 7.63. Found: C, 49.8; H, 7.71.

The 3-*O*-allyl derivative was benzylated as described for preparation of **6**. The material thus obtained was purified by column chromatography to give syrupy **3** (4.39 g, 72%): $[\alpha]_D^{31}$ +67.7° (*c* 0.9, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.3 (t, 3H, J=8.0 Hz, $SCH_2\underline{CH}_3$), 2.75 (q, 2H, J=8.0 Hz, $S\underline{CH}_2CH_3$), 4.4 (d, 1H, J=9.0 Hz, H-1), 5.1-5.5 (m, 2H, vinyl H), 5.7-6.1 (m, 1H, vinyl H), 7.3-7.4 (m, 15H, 3Ph).

Anal. Calcd for $C_{32}H_{38}O_5S$: C, 71.88; H, 7.16. Found: C, 71.76; H, 7.26.

Methyl 2-*O*-Benzyl-3-*O*-(3-*O*-allyl-2,4,6-tri-*O*-benzyl-α-D-galactopyranosyl)-4-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranosyl)-α-L-rhamnopyranoside (9). To a mixture of the disaccharide **8** (670 mg, 0.8 mmol) and the thioglycoside **3** (690 mg, 1.3 mmol) in Et_2O containing 4Å molecular sieve (3 g), methyl triflate[7] (1 mL) was added. The mixture was stirred under argon at 22 °C for 96 h. The reaction was then quenched with triethylamine, the mixture was stirred for 1 h, filtered through a Celite bed and the filtrate was concentrated. Chromatography of the crude product (3:1 hexane-Et_2O) gave **9** as a syrup (792 mg, 74%): $[\alpha]_D^{22}$ +32.3° (*c* 1.8, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.34 (d, 3H, J=6.0 Hz, H-6), 3.22 (s, 3H, OMe), 4.66 (d, 1H, J=8.0 Hz, H-1'), 4.92 (broad s, 1H, H-1), 5.16 (m, 1H, vinyl H), 5.34 (m, 2H, vinyl H, and H-1''), 5.7-6.1 (m, 1H, vinyl H), 7.2-7.3 (m, 40H, 8Ph).

Anal. Calcd for $C_{78}H_{86}O_{15}$: C, 74.15; H, 6.86. Found: C, 73.91; H, 6.98.

Methyl 2-*O*-Benzyl-3-*O*-(2,4,6-tri-*O*-benzyl-α-D-galactopyranosyl)-4-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranosyl)-α-L-rhamnopyranoside (10). A mixture of **9** (502 mg, 0.41 mmol), $PdCl_2$[10] (98.2 mg, 0.63 mmol) and sodium acetate trihydrate (222 mg) in 20:1 AcOH-H_2O (6 mL) was stirred at 24 °C for 18 h. The reaction mixture was then worked up in

the usual way. Column chromatography with 12:1 toluene-Et_2O then gave pure **10** (308 mg, 61.3%): $[\alpha]_D^{24}$ +39.4° (*c* 0.7, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.34 (d, 3H, J=6.0 Hz, H-6), 2.2 (broad s, 1H, OH), 3.28 (s, 3H, OMe), 4.68 (d, 1H, J=8.0 Hz, H-1'), 4.9 (broad s, 1H, H-1), 5.4 (d, 1H, J=4.0 Hz, H-1''), 7.2-7.32 (m, 40H, 8Ph).

Anal. Calcd for $C_{75}H_{82}O_{15}$: C, 73.64; H, 6.71. Found: C, 73.51; H, 6.88.

Methyl 3-*O*-(α-D-Galactopyranosyl)-4-*O*-(β-D-galactopyranosyl)-α-L-rhamnopyranosude (11). A solution of compound **10** (177 mg, 0.15 mmol) in ethanol (7.0 mL) was hydrogenolyzed for 12 h in the presence of 10% Pd-C (60 mg) at 24 °C. The reaction mixture was filtered (Celite), concentrated, membrane filtered and concentrated to give **11** (68.8 mg, 94.5%). Paper chromatography of this compound for 60 h showed a single spot (R_{gal} 0.7): $[\alpha]_D^{33}$ +42.6° (*c* 1.2, H_2O); ^1H NMR (D_2O) δ 1.33 (d, 3H, J=6.5 Hz, H-6), 3.36 (s, 3H, OMe), 4.61 (d, 1H, J=7.8 Hz, H-1'), 4.72 (broad s, 1H, H-1), 5.18 (d, 1H, J=3.66 Hz, H-1''); ^{13}C NMR (D_2O) δ 17.97 (C-$\underline{C}H_3$), 55.77 (O-$\underline{C}H_3$), 61.85, 62.22, 65.9, 67.44, 68.51, 69.02, 69.58, 70.28, 71.87, 71.91, 73.85, 74.05, 75.76, 76.40, 94.10 (C-1''), 101.39 (C-1), 103.68 (C-1').

Anal. Calcd for $C_{19}H_{34}O_{15}$: C, 45.42; H, 6.82. Found: C, 45.27; H, 6.90.

Methyl (2,3,4-Tri-*O*-benzyl-α-D-glucopyranosyl chloride)uronate (12). Acetyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranosiduronic acid methyl ester[11] (1.0 g, 1.92 mmol) was converted to **12** using an established method.[12] Purification by column chromatography using toluene-Et_2O (60:1) gave pure **12** (690 mg, 73%): $[\alpha]_D^{25}$ +67.5° (*c* 0.3, $CHCl_3$); Lit[11]: $[\alpha]_D^{24}$ +78.6° (*c* 1.4, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 3.64 (s, 3H, $COOCH_3$), 4.9 (d, 1H, J=8.0 Hz, C-5 H), 5.96 (d, 1H, J=2.4 Hz, H-1), 7.23-7.28 (m, 15H, 3Ph).

Methyl 2-*O*-Benzyl-3-*O*-[2,4,6-tri-*O*-benzyl-3-*O*-(methyl 2,3,4-tri-*O*-benzyl-α and β-D-glucopyranosyluronate)-α-D-galactopyranosyl]-4-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranosyl)-α-L-rhamnopyranoside (13A and 13B). To compound **12** (240 mg, 0.48 mmol) in 1,2-dichloroethane (10 mL), were added 4Å molecular sieve (2 g) and mercury(II) bromide (860 mg, 2.4 mmol) and the mixture was stirred under argon for 30 min. Compound **10** (290 mg, 0.24 mmol) in 1,2-dichloroethane (4 mL) was then injected into the above mixture and stirred at 24 °C for 96 h. The

mixture was diluted with chloroform and filtered through Celite. The filtrate was processed as described for the preparation of 4. Chromatography (25:1 toluene-Et_2O) gave a syrupy mixture (332 mg, 83%) having $[\alpha]_D^{30}$ +48.8° (*c* 0.5, $CHCl_3$). ^1H NMR ($CDCl_3$) δ 1.30 (d, 3H, J=6.0 Hz, H-6 of **13B**, intensity 37), 1.32 (d, 3H, J=6.0 Hz, H-6 of **13A**, intensity 88), 3.28 (s, 3H, OMe of **13A** and **13B** combined, intensity 128), 3.75 (s, 3H, $COOCH_3$ of **13B**, intensity 40), 3.76 (s, 3H, $COOCH_3$ of **13A**, intensity 91), 5.36 (broad s, 1H, H-1‴ for **13A**, intensity 84), 5.44 (broad s, 1H, H-1″ for **13A** and **13B** combined, intensity 118).

Methyl 3-*O*-[3-*O*-(Methyl α-D-glucopyranosyluronate)-α-D-galactopyranosyl]-4-*O*-(β-D-galactopyranosyl)-α-L-rhamnopyranoside (14A). The mixture of **13A** and **13B** (300 mg, 0.18 mmol) and 10% Pd-C (110 mg) in 2:1 ethanol-toluene (10 mL) was stirred under hydrogen for 12 h at 25 °C. The mixture was filtered through Celite and concentrated. Chromatography of the mixture (10:5:1 $CHCl_3$-MeOH-H_2O) gave first the α-isomer **14A** (77 mg, 58%); $[\alpha]_D^{34}$ +72.5° (*c* 1.2, H_2O) and further elution gave the β-isomer **14B** (33 mg, 24%); $[\alpha]_D^{34}$ +27.8° (*c* 0.4, H_2O). ^1H NMR from **14A** (D_2O) δ 1.33 (d, 3H, J=6.1 Hz, C-5 Me), 3.39 (s, 3H, OMe), 3.81 (s, 3H, $COOCH_3$), 4.57 (d, 1H, J=7.9 Hz, H-1′), 4.7 (d, 1H, J=10.9 Hz, H-5‴), 4.73 (broad s, 1H, H-1), 5.14 (d, 1H, J=3.7 Hz, H-1″), 5.23 (d, 1H, J=3.4 Hz, H-1‴). ^{13}C NMR from **14A** (D_2O) δ 17.85 ($C\underline{C}H_3$), 53.87 ($O\text{-}\underline{C}H_3$), 55,72 ($COO\underline{C}H_3$), 61.86, 62.15, 65.53, 67.12, 67.33, 67.51, 68.22, 69.66, 71.49, 71.78, 71.80, 71.85, 72.49, 73.28, 73.84, 75.57, 75.88, 76.04, 93.45 (C-1″),96.72 (C-1‴), 101.42 (C-1), 103.81 (C-1′), 173.2 ($\underline{C}OOCH_3$). ^1H NMR data from **14B** (D_2O) δ 1.35 (d, 3H, J=6.1 Hz, C-5 Me), 3.39 (s, 3H, OMe), 3.82 (s, $COOCH_3$), 4.66 (d, 1H, J=7.5 Hz, H-1′), 4.73 (d, 1H, J=6.3 Hz, H-1‴), 4.74 (broad s, 1H, H-1), 4.75 (d, 1H, J=11.0 Hz, H-5‴), 5.22 (d, 1H, J=3.5 Hz, H-1″). ^{13}C NMR from **14B** (D_2O) δ 17.94 ($C\text{-}\underline{C}H_3$), 54.02 ($O\text{-}\underline{C}H_3$), 55.72 ($COO\underline{C}H_3$), 61.79, 62.08, 65.74, 67.41, 67.51, 68.02, 68.41, 69.47, 69.89, 71.61, 71.7, 72.17, 73.68, 74.33, 75.36, 75.73, 76.48, 80.58, 93.78 (C-1″), 101.40 (C-1), 103.73 (C-1′), 104.76 (C-1‴), 171.9 ($\underline{C}OOCH_3$).

Anal. Calcd for $C_{26}H_{44}O_{21}$: C, 45.09; H, 6.40. Found for **14A**: C, 44.98; H, 6.52. Found for **14B**: C, 44.91; H, 6.55.

Methyl 2-*O*-Acetyl-3-*O*-[2,4,6-tri-*O*-acetyl-3-*O*-(methyl 2,3,4-tri-*O*-acetyl-α-D-glucopyranosyluronate)-α-D-galactopyranosyl]-4-*O*-(2,3,4,6-

tetra-*O*-acetyl-β-D-galactopyranosyl)-α-L-rhamnopyranoside (15). Compound **14A** (65 mg, 0.09 mmol) was acetylated with acetic anhydride (1.1 mL0 and pyridine (1.1 mL) at room temperature for 4.5 h to give **15** (102 mg, 94%); mp 116-117 °C [from Et_2O-petroleum ether (40-60 °C)]; $[\alpha]_D^{25}$ +68.5° (*c* 0.6, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.30 (d, 3H, J=5.9 HZ, H-6), 1.97, 2.00, 2.04, 2.10, 2.15, 2.17 (s, 33H, 11Ac), 3.3 (s, 3H, OMe), 3.74 (s, 3H, $COOCH_3$), 4.59 (d, 1H, J=1.9 Hz, H-1), 4.65 (d, 1H, J=10.3 Hz, H-5"'), 4.89 (d, 1H, J=7.0 Hz, H-1'), 5.30 (d, 1H, J=3.7 Hz, H-1"), 5.36 (d, 1H, J=3.5 Hz, H-1"').

Anal. Calcd for $C_{48}H_{66}O_{32}$: C, 49.91; H, 5.76. Found: C, 49.81; H, 5.88.

ACKNOWLEDGMENTS

The authors are thankful to Prof. G. Magnusson and Dr. A. K. Ray of the Lund Institute of Technology, Sweden, for running some ^1H and ^{13}C NMR spectra. Financial assistance to S. K. D. by C.S.I.R., India, is gratefully acknowledged.

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