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PREPARATION OF *TRANS* DIEQUATORIAL 2,3-PYRUVATE ACETALS IN A DI- AND A TRISACCHARIDE RELATED TO THE K-ANTIGEN FROM E. COLI 0101:K103:H⁻

Anup Kumar Misra , Saibal Kumar Das and Nirmolendu Roy*

Department of Biological Chemistry
Indian Association for the Cultivation of Science
Jadavpur ; Calcutta 700 032

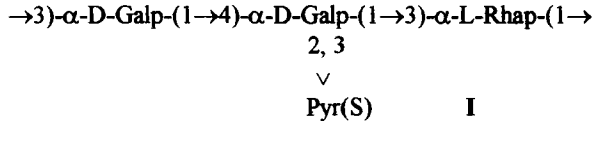
ABSTRACT: Using methyl 2,2-bis(ethylthio)propionate as acetalating agent and triflic acid-sulfuryl chloride as catalyst, synthesis of 2,3-*trans* diequatorial pyruvate ketal was achieved. Starting from D-galactose and L-rhamnose derivatives, methyl 2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl-(1→4)-6-*O*-benzyl-2,3-*O*-(1-methoxycarbonyl)ethylidene- α-D-galactopyranosyl-(1→3)-2,4-di-*O*-benzyl-α-L-rhamnopyranoside and methyl 4,6-di-*O*-benzyl-2,3-*O*-(1-methoxycarbonyl)ethylidene-α-D-galactopyranosyl-(1→3)-2,4-di-*O*-benzyl-α-L-rhamnopyranoside were synthesized. Removal of the protecting groups from the former, afforded the trisaccharide repeating unit of the K-antigen from *E.coli* O101 : K103 : H⁻ in the form of its methyl glycoside methyl ester.

INTRODUCTION

Bacterial surface structures play an important role in their recognition and elimination. Capsules protect pathogenic bacteria against the nonspecific host defense which is exerted in the preimmune phase of infection by serum complement and phagocytes. Investigations on the *E.coli* capsular polysaccharides have led to a coherent picture of their general chemical features and to a classification on a biochemical, genetic and microbiological basis[1]. The investigations have also

*To whom correspondence should be addressed.

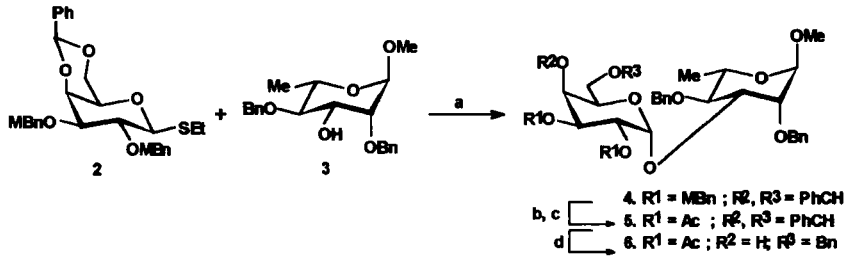
allowed the definitive structural formulation of most of the *E. coli* capsular polysaccharides known today, as well as the chemical description of intergenic structure - function relations. *E. coli* O101:K103:H⁻ is the only member of the *E. coli* O101 series, which produces capsules[2]. Coexpression with O-antigen O101 places the K 103 capsular antigen among the Group I polysaccharide[1]. Unlike the other polysaccharides of this group, it has a low molecular weight and is heat labile. The polysaccharide is acidic and its structure is *Klebsiella* - like, both characteristics of Group I polysaccharides. *E. coli* K103 has been implicated in human appendicitis. The polysaccharide from *E. coli* O101:K103:H⁻ has a trisaccharide repeating unit (**I**)[3] and contains a highly labile 2′,3′-pyruvic acid ketal. It is therefore of interest to synthesise the trisaccharide related to the K-antigen which can be coupled to a protein for studying its antigenic activity. It is also of interest to construct pyruvate acetal of 2,3-hydroxyl groups of D-galactose.



I

RESULTS AND DISCUSSION

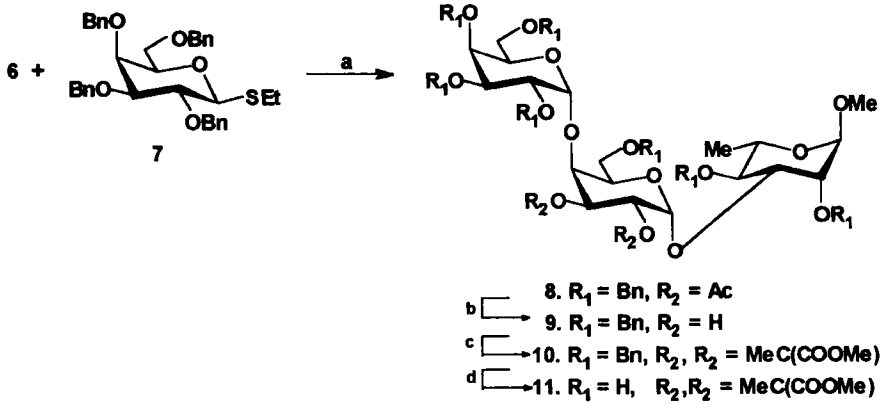
Ethyl 4,6-*O*-benzylidene-1-thio-β-D-galactopyranoside[4] (**1**) was treated with 4-methoxybenzyl chloride and sodium hydride in *N,N*-dimethylformamide. The resulting 4-methoxybenzyl derivative **2** was allowed to react with methyl 2,4-di-*O*-benzyl-α-L-rhamnopyranoside[5] (**3**) in the presence of copper(II) bromide and tetrabutylammonium bromide[6] to afford the disaccharide derivative **4** in 80% yield. Opening of the benzylidene acetal in **4** with $NaCNBH_3$ and Hcl-ether could not be achieved without removal of the 4-methoxybenzyl group. The 4-methoxybenzyl groups were therefore removed from **4** with DDQ.[7] The diol thus formed was acetylated with pyridine and acetic anhydride to give the diacetate **5**. Regioselective ring opening[8] of the benzylidene acetal in **5** with $NaCNBH_3$ now gave methyl 2,3-di-*O*-acetyl-6-*O*-benzyl-α-D-galacto-pyranosyl-(1→3)-2,4-di-*O*-benzyl-α-L-rhamnopyranoside (**6**) (Scheme 1).



Reagents: (a) $CuBr_2$ / Bu_4NBr / 5:1 $(CH_2Cl)_2$ DMF / 72 h / RT; (b) DDQ / CH_2Cl_2 / 12 h / RT; (c) Ac_2O / Pyridine / 6 h / RT; (d) $NaBH_3CN$ / HCl Et_2O / 45 min. / 0 °C

Scheme 1

Ethyl 2,3,4,6-tetra-*O*-benzyl-1-thio-galactopyranoside[9] (**7**) was allowed to react with the disaccharide acceptor **6** in the presence of copper(II) bromide and tetrabutylammonium bromide. But the result was a mixture of α- and β-linked products. The reaction was therefore repeated by using methyl triflate as promoter[10] affording a better yield (79%) of the desired α-linked trisaccharide derivative **8**. Compound **8** was deacetylated in the usual way to give 2′,3′ diol **9.** Attempted preparation of the 2′,3′-pyruvate ketal of **9** by allowing it to react with methyl pyruvate[11] had failed probably because of the mild reaction condition and the *trans* diequatorial configuration of the hydroxyl groups. The ketalation was therefore, carried out with methyl 2,2-bis(ethylthio)propionate using 1:1 triflic acid-sulfuryl chloride[12] as catalyst affording the trisaccharide pyruvate ketal **10** in 51% yield. Hydrogenolysis of **10** with H_2 / Pd-C in ethanol afforded the trisaccharide related to the K-antigen from from *E.coli* O101 : K103 : H⁻ as its methyl ester methyl glycoside, namely methyl α-D-galactopyranosyl-(1→4)-2,3-*O*-{1-(methoxycarbonyl)ethylidene}-α-D-galactopyranosyl-(1→3)-α-L-rhamno-pyranoside (**11**). ^{1}H NMR [δ 1.58 (CH_3), 3.31(OCH_3), 3.74 (s, 3H, $COOCH_3$), 4.59 (H-1), 4.90 (H-1′), 5.34 (H-1″)] and ^{13}C NMR [δ 21.64 (CH_3), 53.37 ($COOCH_3$), 55.82 (OCH_3), 95.30 (C-1′), 100.05 (C-1″), 103.10 (C-1),



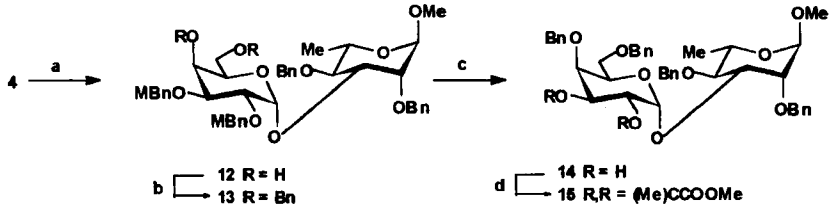
Reagents: (a) MeOTf / Et_2O / MS 4Å / 96h / RT; (b) 0.05 M MeONa / 3h / RT; (c) Methyl 2,2-di(ethylthio)propionate / 1:1 TfOH-SO_2Cl_2 / CH_2Cl_2 / 25°C (d) H_2 / Pd–C / EtOH / 48h / RT

Scheme 2

106.17 (ketalic carbon), 170.81 ($COOCH_3$)]. Signals of the compound **11** showed the presence of two α-D-galactopyranosyl, one α-L-rhamnopyranosyl moieties and the methyl pyruvate ketal (Scheme 2).

In another series of experiments, a disaccharide related to the K103 antigen and containing the 2,3-pyruvate ketal was synthesized. Compound **4** was treated with 85% acetic acid at 90 °C to give the 4,6-diol **12** which was benzylated [13] to give the perbenzyl derivative (**13**). The 4-methoxybenzyl groups of **13** were removed by treatment with DDQ to afford the 2′,3′-diol **14** in almost quantitative yield. Compound **14** was converted to its pyruvate ketal **15** using the same technique as described for the preparation of **10** (Scheme 3). Compound **15** was characterized by its NMR spectral analysis as above.

In summary, synthesis of the repeating unit of the K-antigen from *E.coli* K103 and related disaccharide containing the pyruvate ketal of 2,3-*trans* diequatorial hydroxyl groups in their D-galactose moieties have been achieved.



Reagents : (a) 85% AcOH / 90°C / 2h; (b) BnBr / NaH / RT / 6h; (c) DDQ / CH_2Cl_2 / RT ; (d) Methyl 2,2-di(ethylthio)propionate / TfOH - SO_2Cl_2 / CH_2Cl_2 / 25 °C

Scheme 3

EXPERIMENTAL

General methods.- All reactions were monitored by TLC on Silica Gel G (E. Merck). Column chromatography was performed on 100-200 mesh silica gel (SRL, India). Solvents were dried and distilled before use. All solvents were removed under reduced pressure at 40 °C unless otherwise stated. Optical rotations were measured with a Perkin-Elmer 141 MC polarimeter. Melting points were determined on a paraffin oil bath and are uncorrected. The NMR spectra were recorded with Jeol FX-100 or Bruker 200 MHz instrument using chloroform-d as solvent and Me_4Si as the internal standard, unless stated otherwise.

Ethyl 4,6-*O*-benzylidene-2,3-di-*O*-(4-methoxybenzyl)-1-thio-β-D-galactopyranoside (2). - To a soln of ethyl 4,6-*O*-benzylidene-1-thio-β-D-galactopyranoside (**1**, 1.7 g, 5.44 mmol) in DMF (10 mL) at 0 °C, was added NaH (0.53 g, 11 mmol, 50% oil coated) was stirring. To the cold soln, 4-methoxybenzyl chloride (1.5 mL, 11 mmol) was introduced dropwise and stirring was continued for 3 h. The reaction was quenched with MeOH (1 mL) and the reaction mixture was diluted with CH_2Cl_2. The organic layer was washed with water, dried (Na_2SO_4) and evaporated to give a syrupy mass. Column chromatography, using 8:1 toluene-Et_2O then afforded pure **2** (2.73 g, 91%) which was crystallised from EtOH; mp 155-156 °C; $[\alpha]_D^{24}$ + 11.3° (*c* 1.5, $CHCl_3$). ^1H NMR : δ 1.33 (t, 3 H, SCH_2CH_3), 2.78 (q, 2 H, SCH_2CH_3), 3.78 and 3.80 (2 s, 6

H, 2 $C_6H_4OCH_3$), 4.53 (d, $J_{1,2}$ 8.5 Hz, 1 H, H-1), 4.73 (dd, 4 H, 2 $CH_2C_6H_4OCH_3$), 5.46 (s, 1 H, PhC*H*), 6.76-6.97 and 7.23-7.59 (m, 13 H, 2 $C_6H_4OCH_3$ and Ph).

Methyl 4,6-*O*-benzylidene-2,3-di-*O*-(4-methoxybenzyl)-α-D-galacto-pyranosyl-(1→3)-2,4-di-*O*-benzyl-α-L-rhamnopyranoside (4). -To a flask containing $CuBr_2$ (1.5 g, 6.73 mmol), Bu_4NBr (290 mg, 0.89 mmol) and MS 4Å (10 g), was added a soln of **2** (2.48 g, 4.49 mmol) and methyl 2,4-di-*O*-benzyl-α-L-rhamnopyranoside (**3**; 1.34 g, 3.74 mmol) in 1,2-dichloroethane-DMF (120 mL; 5:1 v/v) and the mixture was stirred vigourously under argon at 24 °C for 72 h. The contents were filtered through a celite bed and diluted with CH_2Cl_2. The organic layer was washed successively with water, aq $NaHCO_3$, and water, dried (Na_2SO_4) and concd. The residue was chromatographed using 20:1 toluene-Et_2O to give pure **4** (2.53 g, 80%); $[\alpha]_D^{24}$ + 52.7° (*c* 0.7, $CHCl_3$). ^1H NMR ($CDCl_3$) : δ 1.32 (d, *J* 5.6Hz, 3 H, CCH_3), 3.28 (s, 3 H, OCH_3), 3.68 and 3.73 (2 s, 6 H, 2 $C_6H_4OCH_3$), 4.89 (bs, 1 H, H-1), 5.14 (d, $J_{1',2'}$ 3.1 Hz, 1 H, H-1'), 5.28 (s, 1 H, PhC*H*), 6.70-6.83 and 7.22-7.47 (m, 23 H, 3 Ph and 2 $C_6H_4OCH_3$). Anal. Calcd. for $C_{50}H_{56}O_{12}$: C, 70.73; H, 6.65. Found: C, 70.61; H, 6.84.

Methyl 2,3-di-*O*-acetyl-6-*O*-benzyl-α-D-galactopyranosyl-(1→3)-2,4-di-*O*-benzyl-α-L-rhamnopyranoside (6). - A soln of **4** (2.24 g, 2.64 mmol), and DDQ (1.31 g, 5.79 mmol) in 60 mL of CH_2Cl_2 satd with water was stirred overnight at room temperature. The reaction mixture was then washed successively with water, aq $NaHCO_3$ and water, dried (Na_2SO_4) and concd. The resulting diol was acetylated conventionally with acetic anhydride and pyridine to give compound **5** (1.73 g). To a soln of **5** (772 mg, 1.12 mmol) in dry THF (20 mL) cooled to 0 °C were introduced MS 3 Å (3 g) and $NaBH_3CN$ (1.05 g, 15.9 mmol). A satd soln of HCl in Et_2O (5 mL) was then added dropwise to this mixture with vigourous stirring until moistened pH paper gave a reading of 2-3 when dipped into soln. Stirring was continued for another 45 min. The reaction mixture was filtered

through a celite bed and washed with CH_2Cl_2. The organic layer was washed with aq $NaHCO_3$ and water, dried (Na_2SO_4) and concd to dryness. Column chromatography of the residue using 6:1 toluene- Et_2O gave pure **6** (614 mg, 79%); $[\alpha]_D^{25}$ + 92.2°(*c* 0.6, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 1.37 (d, *J* 6 Hz, 3 H, CCH_3), 1.84 and 2.12 (2 s, 6 H, 2 $COCH_3$), 3.27 (s, 3 H, OCH_3), 4.78 (bs, 1 H, H-1), 5.36 (bs, 1 H, H-1′), 7.23-7.39 (m, 15 H, 3 Ph). Anal. Calcd. for $C_{37}H_{46}O_{12}$: C, 65.08; H, 6.79. Found : C, 64.92; H, 6.95.

Methyl 2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl-(1→4)-2,3-di-*O*-acetyl-6-*O*-benzyl-α-D-galactopyranosyl-(1→3)-2,4-di-*O*-benzyl-α-L-rhamnopyranoside (8). A mixture of ethyl 2,3,4,6-tetra-*O*-benzyl-1-thio-β-D-galactopyranoside (**7**, 968 mg, 1.66 mmol), **6** (575.7 mg, 0.83 mmol) and MS 4 Å (4 g) in Et_2O (28 mL) was stirred under Ar for 1 h at 25 °C. Methyl triflate (0.93 mL) was then added and stirring was continued for 20 h. The reaction was quenched with Et_3N (~0.5 mL), stirred for 1h, filtered through a celite bed. The filtrate was concentrated to a syrup which, on column chromatography of the crude syrup using 25:1 toluene-ether, gave pure **8** (800 mg, 79%); $[\alpha]_D^{24}$ + 68.22°(*c* 0.82, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 1.35 (d, *J* 6 Hz, 3 H, CCH_3), 1.84 and 1.96 (2 s, 6 H, 2 $COCH_3$), 3.24 (s, 3 H, OCH_3), 4.90 (bs, 1 H, H-1), 5.32 (d, $J_{1'',2''}$ 3.3 Hz, 1 H, H-1″), 5.38 (d, $J_{1',2'}$ 3.5 Hz, 1 H, H-1′), 7.22-7.36 (m, 35 H, 7 Ph). ^{13}C NMR ($CDCl_3$) : δ 17.97 (CCH_3), 20.55, 20.67 (2 C, 2 $COCH_3$), 54.60 (OCH_3), 67.82, 69.04, 69.28, 69.57, 69.98, 70.60, 70.97, 72.20, 72.44, 72.98, 73.55, 74.48, 74.66, 74.83, 74.95, 75.77, 76.41, 78.28, 78.75, 79.75, 80.98, 94.67 (C-1′), 98.47 (C-1″), 100.23 (C-1), 127.01-138.37 (aromatic carbons).

Methyl 2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl-(1→4)-6-*O*-benzyl-2,3-*O*-(1-methoxycarbonyl)ethylidene-α-D-galactopyranosyl-(1→3)-2,4-di-*O*-benzyl-α-L-rham-nopyranoside (10). - A soln of **8** (800 mg, 0.66 mmol) in 0.05 M MeONa in MeOH (20 mL) was stirred at room temperature for 3 h. The reaction mixture was decationised with Dowex 50W-X8 (H^+) resin, cotton filtered

and concd to give **9** as a yellowish syrup in quantitative yield. A mixture of **9** (209.3 mg, 0.184 mmol), methyl 2,2-bis(ethylthio)propionate (43 mg) and MS 4 Å (1 g) in CH_2Cl_2 (5 mL) was stirred under argon at -20 °C for 1 h. TfOH-SO_2Cl_2 (1:1; 0.53 mL; 1 M in toluene-ether) was then injected into it and the mixture was stirred at room temperature for 24 h. The reaction mixture was filtered, diluted with CH_2Cl_2 and the organic layer was washed with water, aq $NaHCO_3$ and water, dried (Na_2SO_4) and concd to a syrup. The syrupy mass was chromatographed using 20:1 toluene-Et_2O to give pure **10** (114.7 mg, 51%); $[\alpha]_D^{24}$+ 49.4° (*c* 0.9, $CHCl_3$). ^{1}H NMR ($CDCl_3$) : δ 1.28 (d, 3 H, CC*H*$_3$), 1.36 (s, 3 H, C*H*$_3$), 3.52 (s, 3 H, OC*H*$_3$), 3.58 (s, 3 H, COOC*H*$_3$), 4.78 (bs, 1 H, H-1), 4.88 (bs, 1 H, H-1″), 5.50 (d, $J_{1'',2''}$ 3.5 Hz, 1 H, H-1″), 7.28-7.48 (m, 35 H, 7 Ph). ^{13}C NMR ($CDCl_3$) : δ 14.3 (*C*CH$_3$), 21.6 (*C*H$_3$), 52.8 (COO*C*H$_3$), 54.5 (O*C*H$_3$), 66.7, 67.3 (2 C-6), 68.5, 68.7, 68.9, 71.3, 71.8, 72.0, 72.6, 73.1, 73.4, 74.1, 74.4, 74.5, 75.7, 76.8, 78.3, 79.2, 80.0, 80.9, 81.8, 82.1, 83.7, 84.8, 91.6 (C-1′), 97.8 (C-1″), 98.4 (*C*-COOCH$_3$), 100.9 (C-1), 127.1-127.9 (aromatic carbons), 176.55 (*C*OOCH$_3$). Anal. Calcd. for $C_{72}H_{80}O_{17}$: C, 71.03; H, 6.62. Found : C, 70.85; H, 6.81.

Methyl α-D-galactopyranosyl-(1→4)-2,3-*O*-(1-methoxycarbonyl) ethylidene-α-D-galactopyranosyl-(1→3)-α-L-rhamnopyranoside (11). Compound **10** (85 mg, 0.07 mmol) and 10% Pd-C (100 mg) in dry EtOH (3 mL) were stirred under hydrogen for 48 h at 25 °C. The mixture was filtered through Celite and concd to give **11** (35.6 mg, 87 %) as a white solid; $[\alpha]_D^{24}$ + 39.7° (*c* 0.8, H_2O). ^{1}H NMR (D_2O) : δ 1.22 (d, *J* 5.5 Hz, 3 H, CC*H*$_3$), 1.58 (s, 3 H, C*H*$_3$), 3.31 (s, 3 H, OC*H*$_3$), 3.74 (s, 3 H, COOC*H*$_3$), 4.59 (bs, 1 H, H-1), 4.90 (bs, 1 H, H-1′), 5.34 (d, $J_{1'',2''}$ 3Hz, 1 H, H-1″). ^{13}C NMR (D_2O) : δ 16.45 (*C*CH$_3$), 21.64 (*C*H$_3$), 53.37 (COO*C*H$_3$), 55.82 (O*C*H$_3$), 67.57 (C-6″), 68.89 (C-6′), 73.01, 73.38, 73.55, 73.83, 74.09, 75.12, 75.54, 76.09, 76.48, 78.52, 79.88, 81.45, 81.65, 95.30 (C-1′), 100.05 (C-1″), 103.10 (C-1), 106.17 (ketalic carbon), 170.81 (*C*OOCH$_3$). Anal. Calcd. for $C_{23}H_{38}O_{17}$: C, 47.09 ; H, 6.53. Found : C, 46.96 ; H, 6.63.

Methyl 4,6-Di-*O*-benzyl-α-D-galactopyranosyl-(1→3)-2,4-di-*O*-benzyl-α-L-rhamnopyranoside (14). -A soln of **4** (600 mg) in 85% AcOH (20 mL) was stirred at 90 °C for 2h. The solvents were evaporated off to give the diol **12** (quantitative yield). To a soln of **12** (537 mg, 0.70 mmol) in DMF (5 mL) were added NaH (100 mg, 2.1 mmol, 50% oil coated) and benzyl bromide (0.25 mL, 2.1 mmol) and the mixture was stirred at room temperature for 5 h. The reaction mixture was quenched with MeOH (1 mL) and the mixture was diluted with CH_2Cl_2. The organic layer was washed with water, dried (Na_2SO_4) and concd to a syrupy mass which was chromatographed using 8:1 toluene-Et_2O to give pure **13** (598.7 mg, 91%); $[\alpha]_D^{25}$ + 66.7° (*c* 1.07, $CHCl_3$). A soln of **13** (598 mg, 0.64 mmol) and DDQ (433 mg, 1.9 mmol) in 20 mL of CH_2Cl_2 satd with water was stirred overnight at room temperature. The reaction mixture was then washed successively with aq $NaHCO_3$ and water, dried (Na_2SO_4) and concd. Column chromatography of the crude product using 6:1 toluene-Et_2O, gave pure **14** (368 mg, 83%); $[\alpha]_D^{25}$ + 57.3° (*c* 0.9, $CHCl_3$). ^{1}H NMR ($CDCl_3$) : δ 1.33 (d, *J* 6Hz, 3 H, CC*H*$_3$), 3.32 (s, 3 H, OC*H*$_3$), 4.84 (d, $J_{1,2}$ 1.5 Hz, 1 H, H-1), 5.08 (d, $J_{1',2'}$ 2 Hz, 1 H, H-1'), 7.24-7.46 (m, 20 H, 4 Ph).

Methyl 4,6-di-*O*-benzyl-2,3-*O*-(1-methoxycarbonyl)ethylidene-α-D-galactopyranosyl-(1→3)-2,4-di-*O*-benzyl-α-L-rhamnopyranoside (15).- A mixture of **14** (160 mg, 0.207 mmol), methyl 2,2-bis(ethylthio)propionate (47.4 mg, 0.269 mmol) and MS 4Å (0.5 g) in CH_2Cl_2 (5 mL) was stirred under argon at -20 °C with 1:1 triflic acid-sulfuryl chloride (1:1; 0.591 mL; 1 M in toluene-ether) and the reaction mixture was worked up as described for **10**. The crude syrupy product was chromatographed, using 20:1 toluene-ether to give pure **15** (100.5 mg, 62%); $[\alpha]_D^{24}$+ 49.4°(*c* 0.9, $CHCl_3$). ^{1}H NMR ($CDCl_3$) : δ 1.26 (d, *J* 5.5 Hz, 3 H, CC*H*$_3$), 1.36 (s, 3 H, C*H*$_3$), 3.26 (s, 3 H, OC*H*$_3$), 3.68 (s, 3 H, COOC*H*$_3$), 4.81 (bs, 1 H, H-1), 5.10 (d, $J_{1',2'}$ 3.5 Hz, 1 H, H-1'), 7.28-7.48 (m, 20 H, 4 Ph). ^{13}C NMR ($CDCl_3$) : δ 17.81 (C*C*H$_3$), 22.62 (*C*H$_3$), 52.41 (COO*C*H$_3$), 54.30 (O*C*H$_3$),

67.57 (C-6'), 73.55, 73.83, 74.09, 75.11, 75.54, 76.08, 76.48, 79.88, 96.02 (C-1'), 103.86 (C-1), 106.01 (ketalic carbon), 127.22-138.61 (aromatic carbons), 173.3 ($COOCH_3$). Anal. Calcd. for $C_{45}H_{52}O_{12}$: C, 68.87; H, 6.63. Found : C, 68.71 ; H, 6.79.

REFERENCES

1. B.Jann and K. Jann, *Current topics in Microbial. Immunol.*, **1990,** *150,* 20.
2. I. Ørskov, F. Ørskov, B. Jann and K. Jann, *Bacteriol. Rev.*, **1977,***41,* 667.
3 M. R. Grue, H. Parolis and L. A. S. Parolis, *Carbohydr. Res.*,**1994**,*262*, 311.
4. Y. Nakahara, F. Iijima, S. Shibayama and T. Ogawa, *Carbohydr.Res.*, **1991**, 216, 211.
5. A. Lipták, A. Neszmély and H. Wagner, *Tetrahedron Lett.*, **1979,** *20,* 741.
6. S. Sato, M. Mori, Y. Ito and T. Ogawa, *Carbohydr. Res.*, **1986,** *155,* C6.
7. Y. Oikawa, T. Yoshioko and O. Yonemitsu, *Tetrahedron Lett.*,**1982**, *23*,885.
8. P. J. Garegg and H. Hultberg, *Carbohydr. Res.*,**1981**, *93,* C10.
A. K. Sarkar, A. K. Ray and N. Roy, *Carbohydr. Res.*, **1989**, *190*, 181.
10. H. Lönn, *J. Carbohydr. Chem.*, **1987**, *6,* 301.
11. T. Ziegler, *Carbohydr. Res.*, **1994**,*253*, 151.
12. I. Bajza, J. Kerékgyártó, J. Hajkó, L. Szilágyi and A. Lipták, *Carbohydr. Res.*, **1994,** *253*, 111.
13. J. S. Brimacombe, *Methods Carbohydr. Chem.*, **1972**, *6*, 376.

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