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Practical synthesis of valuable D-rhamnoside building blocks for oligosaccharide synthesis

Régis Fauré, Tze Chieh Shiao, Sonia Damerval and René Roy*

Department of Chemistry, Université du Québec à Montréal, PO Box 8888, Succ. Centre-Ville, Montréal, Quebec, Canada H3C 3P8

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Abstract—The efficient synthesis of D-rhamnoside and the corresponding methods for its regioselective protections and deprotections have been developed in order to provide key building blocks for complex oligosaccharide syntheses toward vaccines against bacterial infections.

It is now widely recognized that bacterial cell surface carbohydrate antigens play essential roles in host defense immunity against infections. Lipopolysaccharides (LPSs) are ubiquitous components of the outer cell membranes of Gram-negative bacteria and are thought to be involved in host–pathogen cross-talk, notably through their O-specific chains, which are exposed toward the external environment.[1–3] Exopolysaccharides (EPSs) are also implicated in virulence and persistence of bacterial infections.[4] However, simple isolation and characterization of these carbohydrate antigens are insufficient to allow full elucidation of their contribution to the molecular mechanism of phatogenesis.

Increasingly, 6-deoxy-D-hexoses are receiving attention, notably concerning their significance toward infectious diseases. This is because these relatively rare sugars are frequently found on cell surface glycoconjugates of pathogenic bacteria. In particular, D-rhamnose and its 4-formamido or 4-azido-4-deoxy derivatives are common components of LPSs and EPSs from human and plant-pathogenic species, such as *Burkholderia cepacia* complex,[5,6] *Pseudomonas aeruginosa*,[7,8] and other pseudomonads,[9–11] *Helicobacter pylori*,[12] *Citrobacter freundii*,[13] *Campylobacter fetus*,[14] *Stenotrophomonas maltophilia*,[15] *Xanthomonas campestris*,[16] and *Brucella*.[17]

Given the fact that D-rhamnose is only encountered in microorganisms and not in humans, animals or plants, this rare monosaccharide is a promising target for the development of new anti-infective agents, including vaccines. Indeed, rhamnose-containing motifs should provide the basis for development of synthetic bacterial *O*-polysaccharide conjugate vaccines.[18]

Very few syntheses of D-rhamnose oligosaccharides have been hitherto reported,[17,19–22] mainly because of the lack of direct access to D-rhamnose in large quantities as precursor and as key building blocks. In addition, to our knowledge, there is no commercial supply for D-rhamnose and its known chemical synthesis only affords an already partially protected derivative.[22] A fast procedure for the preparation of this rare sugar has been described. This involves mild hydrolysis of bacterial LPS.[23] Unfortunately, this method is not particularly adapted for the production of therapeutic agents. The present work focuses on an efficient synthesis of D-rhamnoside **3**, and reports the well defined selection of regioselective protection and deprotection pathways required to provide easy access to building blocks **4**, **9**–**11**, **14**, **19**, and **23** in high yields, for complex oligosaccharide synthesis.

D-Rhamnoside **3** was synthesized from D-mannose in 87% overall yield (Scheme 1). Triflic acid-promoted glycosydation of the per-O-acetylated mannose with *p*-methoxyphenol, followed by de-O-acetylation using Zemplén conditions (NaOMe, MeOH) led to *p*-methoxyphenyl mannoside **1**.[24] Regioselective iodination of the primary hydroxyl group of **1** was achieved in 93% yield using triphenylphosphine, imidazole, and iodine

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* Corresponding author. Tel.: +1 514 987 3000x2546; fax: +1 514 987 4054; e-mail: roy.rene@uqam.ca

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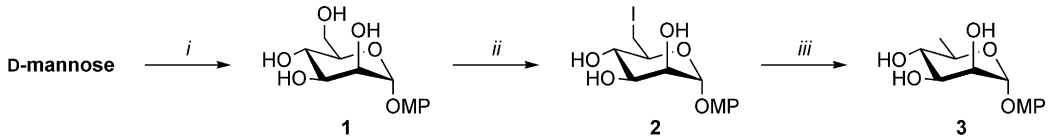
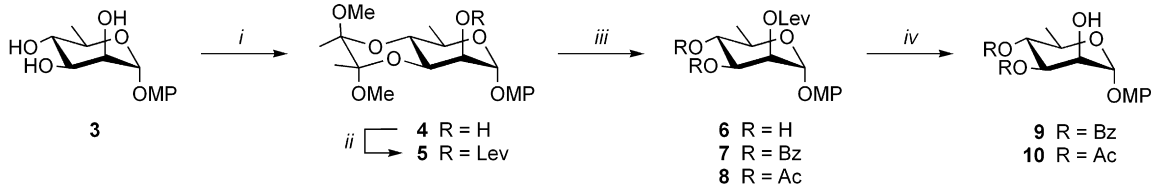


Scheme 1. Reagents and conditions: (i) (a) Ac_2O/pyridine, cat. DMAP, rt, 12 h, quantitative (α only); (b) 2 equiv *p*-MPOH, 0.15 equiv TfOH, CH_2Cl_2, 0 °C then rt, 7 h, 95%; (c) MeONa/MeOH, rt, 3 h, quantitative; (ii) 1.5 equiv I_2, 1.5 equiv Ph_3P, 2 equiv imidazole, THF, 65 °C, 2 h, 93%; (iii) 1.5 equiv Bu_3SnH, 0.1 equiv AIBN, toluene, 110 °C, 1 h, 98%.

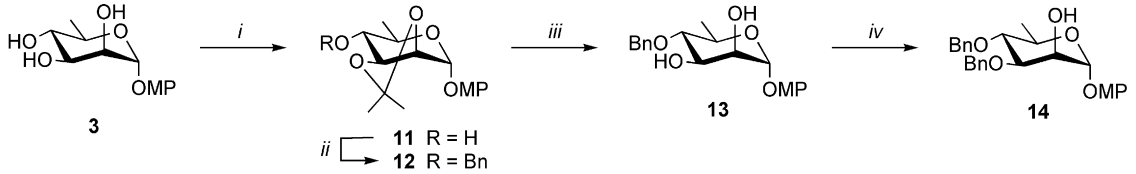
in refluxing THF.[22,25] The ^{13}C NMR of **2** showed the shielding of the C-6 signal from 61.3 to 6.2 ppm. Reduction of iodide **2** using tributyltin hydride in the presence of AIBN gave the expected D-rhamnoside **3**[26] in 98% yield.[27] The most indicative NMR data were the shielding for the H-6 signal from 3.60–3.27 to 1.23 ppm and the deshielding of the C-6 from 6.2 to 17.2 ppm. This efficient procedure for preparing D-rhamnopyranoside **3**, derived from D-mannose, was well suited to large scale synthesis given the high yields and easy isolation of intermediates at each steps.

The single step protection of the 3,4-*trans*-diol in the presence of the 2,3-*cis*-diol using α-diketone, via tetramethoxyacetal formation, was particularly powerful for the selective protection of our vicinal diequatorial diol **3** (Scheme 2). Thus, reaction of butane-2,3-dione with *p*-methoxyphenyl α-D-rhamnoside **3** in the presence of Lewis acid catalysis ($BF_3{\cdot}Et_2O$) and trimethyl orthoformate gave butane diacetal (BDA) **4** in near quantitative yield.[28,29] The ^1H and ^{13}C NMR data of **4** confirmed the BDA structure with the typical signals at δ 3.34, 3.26 (2s, 6H, OCH_3), 1.34, 1.33 (2s, 6H, CH_3), and 100.3, 99.9 (C-q), 48.1, 47.7 (OCH_3), 17.8, 17.7 (CH_3). The fully protected rhamnoside **5** was obtained in quasi-quantitative yield by the reaction of **4** with levulinic acid in the presence of *N*,*N*′-diisopropylcarbodiimide (DIPC) and 4-dimethylamino-pyridine (DMAP).[19] The low-field shifted signal of H-2 from 4.12 to 5.23 ppm and the presence of new signals corresponding to the methylene groups at 2.84–2.70 (m, 4H) and to the methyl group at 2.22 ppm of the levulinic ester confirmed the structure of derivative **5**. The BDA protecting group was then removed by aqueous acid hydrolysis[30] and then the resulting diol **6** was benzoylated or acetylated to provide intermediates **7** and **8** in 82% and 84% yields over two steps, respectively. Diol **6** might be selectively protected as function of the difference of reactivity between both hydroxyl groups (HO-3 > HO-4). The selective and mild levulinyl group removal was achieved by treatment with hydrazine hydrate in pyridine/acetic acid mixture for 10 min to afford **9** and **10** in very good yields.[31] Upfield displacements for the H-2 signals in the ^1H NMR spectra confirmed the levulynyl group cleavage.

Until now, the synthetic manipulations proposed by Evans et al.[32] constituted the most convenient route toward an anomeric analog of the 2,3-*O*-isopropylidene D-rhamnoside **11**. However, in their procedure, this reaction involved the competition between the formation of 1,3-dioxane and dioxolane rings using kinetic or thermodynamic controls. Therefore, graded acid hydrolysis has to be employed to afford the acetonide mannoside intermediate with a 'moderate' yield of 75%. In our case, the key intermediate **3** reacted with 2,2′-dimethoxypropane and *p*-TsOH acid catalyst in acetone (Scheme 3). Temporary protection at positions 2 and 3 was accomplished by the formation of acetonide **11** in excellent



Scheme 2. Reagents and conditions: (i) 1.1 equiv butan-2,3-dione, 0.5 equiv $BF_3{\cdot}Et_2O$, 4 equiv $CH(OMe)_3$, MeOH, rt, 20 h, 99%; (ii) 5.6 equiv $CH_3C(O)CH_2CH_2CO_2H$, 6.6 equiv DIPC, cat. DMAP, CH_2Cl_2, rt, 12 h, 99%; (iii) TFA/H_2O (9:1), rt, 3 min, **6**: 62% or (a) TFA/H_2O (9:1), rt, 3 min; (b) 2.4 equiv RCl, pyridine, 0 °C then rt, 12 h, **7**: R = Bz, 82% (over two steps), **8**: R = Ac, 84% (over two steps); (iv) 1.2 equiv hydrazine hydrate, pyridine/AcOH, 20 °C, 10 min, **9**: R = Bz, 94%, **10**: R = Ac, 90%.

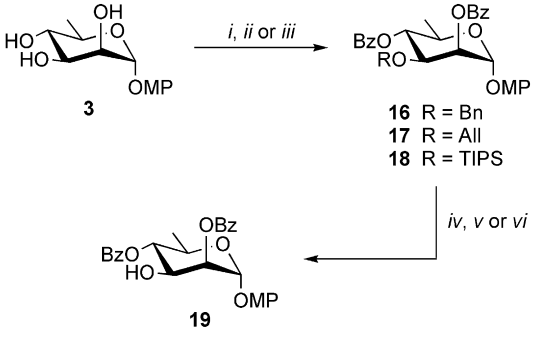


Scheme 3. Reagents and conditions: (i) 2,2′-dimethoxypropane/acetone (1:1), 0.2 equiv *p*-TsOH·H_2O, rt, 0.5 h, 98%; (ii) 3 equiv NaH, 3 equiv BnBr, cat. Bu_4NI, DMF, 0 °C then rt, 14 h, 99%; (iii) TFA/H_2O/THF (1:1:4), 0 °C then rt, 1 h, 95%; (iv) 1.1 equiv Bu_2SnO, toluene, reflux, 2 h then 1.1 equiv BnBr, 1.1 equiv Bu_4NBr, 65 °C, 14 h, 81%.

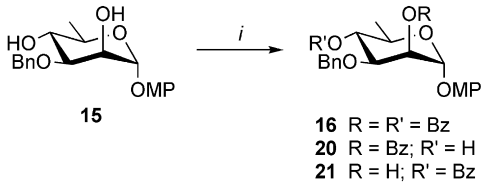
98% yield. Building block **14** was synthesized from **11** by benzylation and ketal cleavage in 94% yields over two steps, followed by dibutyl-stannylidene mediated benzylation of the *O*-3. The high yield of **14** (81%) shows the excellent regioselectivity of this method. Due to the subtle differences of chemical shifts between ether-protected and non-protected positions, the structures of compounds **11**–**14**,[33] notably characterized through the observation of signal muliplicities, were also confirmed by COSY experiments.

The selective *O*-3 protection of key rhamnoside **3** was a very useful procedure because it can substantially simplify reaction pathways in complex oligosaccharide synthesis (Scheme 4). The 'stannylation method', by which unprotected **3** was activated with dibutyltin oxide, and then alkylated in the presence of alkyl bromide and tetrabutylammonium halide, followed by benzoylation, afforded 3-O-benzylated **16** and 3-O-allylated **17** in 77% and 64% yields, respectively, over three steps.[34] Another strategy consisted of the direct high *O*-3 selective treatment of **3** with triisopropylsilyl trifluoromethanesulfonate to give only silylated compound **18** in 70% yields over two steps. Deprotection of compounds **16**–**18**, with no benzoyl migration, was accomplished in 99%, 74%, and 63% yields using the corresponding smooth procedures, that is hydrogenolysis (palladium on carbon and H_2 at atmospheric pressure), palladium-catalyzed de-O-allylation,[19] and treatment with tetrabutylammonium fluoride (TBAF), respectively. Compounds **16**–**19**[35] gave NMR signals for H-3 upfield and H-2 and H-4 downfield, clearly indicating the *O*-3 modifications compared to 2,4-di-O-benzoylation.

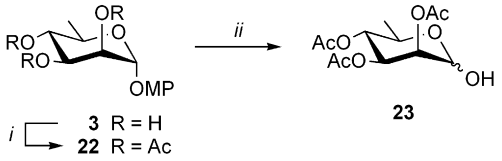
An interesting observation was the isolation of *p*-methoxyphenyl 2-*O*-benzoyl-3-*O*-triisopropylsilyl-α-D-rhamnoside in 21% yield during the preparation of **18** by treatment with benzoyl chloride instead of benzoic anhydride. In addition, the selective benzoylation of diol



Scheme 4. Reagents and conditions: (i) (a) 1.05 equiv Bu_2SnO, toluene/MeOH (10:1), reflux, Dean–Stark, 2 h; (b) 1.05 equiv BnBr, 1.05 equiv Bu_4NI, toluene, 65 °C, 20 h, 78% (over two steps); (c) 2.4 equiv BzCl, pyridine, 0 °C then rt, 12 h, 99%; (ii) (a) 1.05 equiv Bu_2SnO, toluene/THF (10:1), reflux, Dean–Stark, 2 h; (b) 1.05 equiv AllBr, 1.05 equiv Bu_4NBr, toluene, 65 °C, 12 h, 65%; (over two steps); (c) 2.4 equiv BzCl, pyridine, 0 °C then rt, 12 h, 99%; (iii) (a) 1.05 equiv TIPSOTf, 1.6 equiv 2,6-lutidine, CH_2Cl_2/DMF (9:1), 0 °C, 3 h; (b) 3 equiv Bz_2O, pyridine, cat. DMAP, reflux, 8 h, 70% (over two steps); (iv) H_2, cat. Pd–C, EtOH/CH_2Cl_2 (10:1), cat. HCl, rt, 12 h, 99%; (v) 0.3 equiv $PdCl_2$, MeOH/CH_2Cl_2 (3:2), rt, 5 h, 74%; (vi) 5 equiv TBAF, 5.5 equiv AcOH, THF, 0 °C then rt, 8 h, 63%.



Scheme 5. Reagents and conditions: (i) 1 equiv BzCl, pyridine, −50 °C to rt, 12 h, **15**: 24%, **16**: 19%, **20**: 59%, and **21**: 2%.



Scheme 6. Reagents and conditions: (i) Ac_2O/pyridine, cat. DMAP, rt, 12 h, 99%; (ii) 10 equiv CAN, toluene/CH_3CN/H_2O (1:1.4:1), rt, 2.5 h, 76%.

intermediate **15**, obtained during the synthesis of 3-O-benzylated **16**, by using 1 equiv of benzoyl chloride at −50 °C mainly leads to the 2-*O*-benzoyl rhamnoside **20** (Scheme 5). Thus, the order of reactivity for the hydroxyl groups of rhamnosides seemed to be in agreement with the reported selective acylation of mannoside, that is HO-3 > HO-2 > HO-4.[36,37]

The oxidative removal of the *p*-methoxyphenyl group of per-O-acetylated rhamnoside **22** with ceric ammonium nitrate (CAN) afforded hemiacetal **23** in 76% yield (Scheme 6), which could be easily activated as trichloroacetimidate glycosyl donor (not shown). The formation of **23** was observed in the NMR spectra and notably by the disappearence of the AB system of the phenyl group at δ 7.02–6.98, 6.85–6.82 ppm and the singlet corresponding to the methoxy group at 3.78 ppm.

In conclusion, an efficient large scale synthesis of D-rhamnoside **3**, a rare sugar, has been accomplished. The orthogonal protection–deprotection pathways were performed in very high yields, providing useful key building blocks for the synthesis of D-rhamnose oligosaccharides that are common motifs of LPSs or EPSs of pathogenic bacteria. Glycosylation reactions involving D-rhamnosides **4**, **9**, **10**, **14**, and **19** toward the preparations of complex oligosaccharidic structures are currently underway.

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