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Note

Towards the synthesis of new dideoxy δ-dicarbonyl heptoses

Venerando Pistarà *, Maria Assunta Chiacchio, Antonino Corsaro

Università di Catania, Dipartimento di Scienze Chimiche, I-95125 Catania, Italy

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ABSTRACT

The preparation of a δ-dicarbonyl sugar thorough ring-opening, by a methoxymercuration–demercuration procedure, of a 5-spirocyclopropanated D-galactose derivative, is reported. This method constitutes a new route for the transformation of a hexose into new and interesting δ-dicarbonyl sugars, synthetic precursors of cyclitols, carba- and azasugars. Moreover this is, to our best knowledge, the first reported example of an elongation to a higher sugar starting from a spirocyclopropanated saccharide.

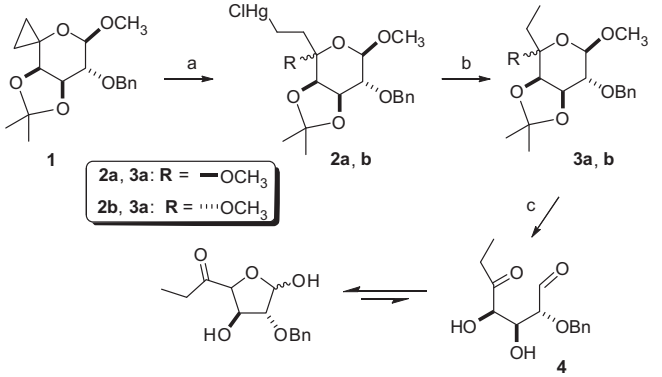
Among monosaccharide derivatives containing two carbonyl groups (dialdoses, diuloses and aldosuloses), aldosuloses, although yet poorly investigated, are an important class of natural dicarbonyl monosaccharides.[1] These compounds have been postulated as intermediates in the biosynthesis of cyclitols,[2] and are also useful synthetic intermediates for the preparation of high value-added compounds such as iminosugars[3] (1-deoxynojirimycin and its stereoisomeric analogues), carbasugars (gabosine derivatives),[4] cyclitols (*epi*- and D-*chiro*-inositol),[5] or polyhydroxycyclopentanes.[6]

A general approach to aldohexos-5-uloses was developed using as a key reaction the epoxidation–methanolysis of 4-deoxy-hex-4-eno-[7] or 6-deoxy-hex-5-enopyranosides,[8] two classes of unsaturated sugars. Recently, the chemistry of 5,6-unsaturated pyranosides has had some interesting developments in the reduction and functionalization of their double bond, such as the oxidation to an epoxide.[8b] However, the chain extension by the cyclopropanation of the *exo*-double bond has not been thoroughly explored, although the resulting spirocyclopropyl-functionalized sugars are very important as synthetic building blocks, glycosidase inhibitors or useful scaffolds for carbohydrates mimics.[9]

As part of a project on the elaboration of these 5-methylene pyranosides, in the last few years, we have studied the reactivity of the double bond towards the methylene–zinc iodide complex, dichlorocarbene and rhodium ethoxycarbonyl complex addition. These studies were carried out to clarify the stereochemical aspects of these reactions,[10] and to obtain 1,5-dicarbonyl intermediates analogues to L-*arabino*-heptos-5-ulose, previously reported.[7a] As an extension of these studies, in this paper we describe, for the first time, a simple sequence of reactions that use a cyclopropanation reaction aimed at transforming a hexose into a heptose thorough the spirocyclopropyl pyranoside ring-opening sequence.

The spirocyclopropyl galactopyranoside **1**, obtained in a nearly quantitative yield starting from the 5-methylene derivative with the Simmons–Smith modified cyclopropanation, following our previously reported method,[10] was treated with mercuric trifluoroacetate in dry methanol to give, after exchange with NaCl saturated solution, a crude material containing the two organomercuric chlorides **2a**,**b**. The mixture was purified by flash chromatography, affording the pure organomercuric derivatives **2a** and **2b** in a good total yield (78%) in a 1:1.8 ratio (Scheme 1).

The structure and the stereochemistry of these compounds were deduced from their ^{1}H and ^{13}C NMR, COSY and NOE spectra. In particular, in the ^{1}H NMR spectrum, diagnostic signals were those of the methylene protons of the CH_2HgCl group (H-7a and



Scheme 1. Reagents: (a) (i) $Hg(CF_3COO)_2$, MeOH; (ii) NaCl satd sol; (b) $LiAlH_4$, THF; (c) CF_3COOH, CH_3CN–H_2O.

* Corresponding author. Tel.: +39 095 7385017; fax: +39 095 580138.
E-mail address: vpistara@unict.it (V. Pistarà).

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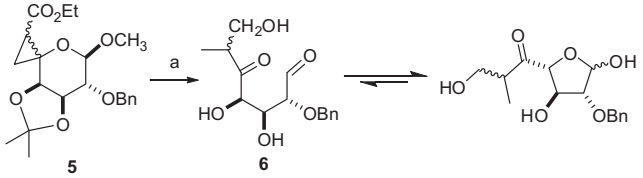
H-7b), which resonate as multiplets centred at 1.82 and 2.20 ppm for **2a**, and at 2.10 and 2.19 ppm in the case of **2b**. NOE experiments easily allowed the stereochemical assignation of these adducts. For example, in the case of derivative **2a**, a positive enhancement (about 1.4%) was apparent on the signal of the C-5 methoxy group protons (3.31 ppm) by irradiating the protons of the C-1 methoxy group (3.57 ppm) and vice versa, whereas the same methoxy groups of the opposite stereoisomer **2b** did not show any appreciable NOE effect.

Reductive demercuration with lithium aluminium hydride of the diastereomers **2a** and **2b** produced, after flash chromatography, the corresponding 6,7-dideoxy-1,5-bis-glycosides **3a** (75% yield) and **3b** (77% yield) (Scheme 1). The latter compounds were finally hydrolyzed (CF_3COOH–H_2O–CH_3CN 0.1:0.5:1, rt, 12 h) affording the 6,7-dideoxy-1,5-dicarbonyl heptose **4**, which exists in CD_3CN as an 1:2.7 α- and β-furanose mixture. In the ^1H NMR spectrum the H-1 proton signal appeared at 5.33 ppm (J = 0.5 Hz) for the α-anomer and at 5.42 ppm (J = 4.0 Hz) for the β-anomer.

The electrophilic ring-opening reaction, by methoxymercuration–demercuration sequence, leading to **3a**,**b** from **1**, was also carried out without the purification of the organomercuric derivatives **2a**,**b**. In this case 1,5-bis-glycosides **3a**,**b** were obtained in 71% global yield over two steps from **1**. Keeping in mind our simple procedure[10] for the synthesis of spirocyclopropane carboxylates **5** (a mixture of four stereoisomers, global yield 89%) from the addition of ethoxycarbonyl carbene (generated from the metal (Rh^{2+}) catalyzed decomposition of ethyldiazoacetate) to 5-methylene galactopyranosides, and the high yield of **3** from the ring-opening procedure conducted without purification on adducts **2**, we decided to apply the same reactions to the syntheses of hydroxymethyl derivatives of heptoses **6**, after the mixture of stereoisomers **5** was reduced with lithium aluminium hydride (Scheme 2). The methoxymercuration–demercuration sequence of the obtained hydroxymethyl derivatives produced the corresponding 1,5-bis-glycosides, analogues to **3**, which upon hydrolysis afforded a mixture of diastereomeric 6-deoxy-6-methyl-D,L-*arabino*-heptos-5-uloses **6** (Scheme 2). The ^1H NMR spectrum in CD_3CN–D_2O solution of the unseparated diastereomeric mixture of **6** is further complicated because of the interconverting anomers showing doublets (in the range 1.08 and 1.14 ppm, J = 7.0–7.5 Hz) for the protons of the methyl groups. This indicates that heptos-5-uloses **6** exist, almost exclusively, as a mixture of 1:2 α- and β-furanosic forms with the H-1 proton resonating as doublets centred at 5.50 ppm (J = 0.5 Hz) and 5.48 ppm (J = 3.5 Hz), respectively.

In conclusion this paper describes a new route for the preparation of a δ-dicarbonyl heptoses thorough the ring-opening by a methoxymercuration–demercuration procedure of a 5-spirocyclopropanated D-galactose derivative, which represents, to our best knowledge, the first reported example of the elongation of 5-spirocyclopropanated sugars to a higher carbon sugar. The same reaction sequence should be of considerable importance as it can be applied to spirocyclopropanated lactose (analogous to the spirogalactopyranoside derivative investigated here). This will expand the applications of this natural disaccharide, a by-product of the cheese-industry obtained in great amounts from whey, opening new prospects for its utilization. The results of these studies will be contained in a future publication.



Scheme 2. Reagents: (a) (i) $LiAlH_4$, THF; (ii) $Hg(CF_3COO)_2$, MeOH; (iii) NaCl satd sol; (iv) $LiAlH_4$, THF; (v) CF_3COOH, CH_3CN–H_2O.

1. Experimental

1.1. General methods

Melting points were determined with a Kofler hot-stage apparatus and are uncorrected. ^1H NMR spectra were recorded with a Varian Unity INOVA instrument at 200 and 500 MHz in $CDCl_3$ as a solvent, unless otherwise stated (Me_4Si was used as the internal standard). ^{13}C NMR spectra were recorded at 50 and 125 MHz. Assignments were made, when possible, with the aid of APT, COSY and HETCOR experiments and applying additivity rules.[11] All reactions were followed by TLC on Kieselgel 60 F_{254} with detection by UV light and/or with ethanolic 5% sulfuric acid, and heating. Kieselgel 60 (E. Merck, 230–400 mesh) was used for flash chromatography. Solvents were dried by distillation according to standard procedure,[12] and stored over 4 Å molecular sieves activated for at least 24 h at 400 °C. $MgSO_4$ was used as the drying agent for solutions. Spirocyclopropane galactopyranosides **1** and **5** were synthesized following our previously reported method.[10]

1.2. General method for the electrophilic ring-opening of 1

1.2.1. Methoxymercuration

To a stirred solution of **1** (1 g, 1.74 mmol) in dry MeOH (10.75 mL) mercury(II) trifluoroacetate (1.14 g, 2.47 mmol) was added at room temperature under a nitrogen atmosphere. The reaction was monitored by TLC (cyclohexane–EtOAc 4:1) until **1** disappeared. After about 2 h, the reaction was quenched by the addition of brine (5 mL), and the solution was stirred vigorously for 30 min and then extracted with dichloromethane (3 × 20 mL). The combined organic extracts were washed with water and dried (Na_2SO_4). After filtration, the solvent was removed under reduced pressure to give a residual syrup, which afforded **2a** and **2b** as pure samples (global yield 78%) by flash chromatography (cyclohexane–EtOAc 9:1).

1.2.1.1. Methyl 2-*O*-benzyl-7-chloromercurio-6,7-dideoxy-3,4-*O*-isopropilidene-5-*C*-methoxy-β-D-*galacto*-heptopyranoside, 2a. Amorphous solid, yield 35%; $[\alpha]_D$ −3.5 (*c* 0.8, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz): δ 7.27–7.40 (m, 5H, aromatics H), 4.83–4.78 (AB system, 2H, J = 11.5 Hz, CH_2Ph), 4.46 (d, 1H, J = 8.0 Hz, H-1), 4.26 (dd, 1H, J = 5.0, 8.0 Hz, H-3), 4.06 (d, 1H, J = 5.0 Hz, H-4), 3.75 (m, 2H, H-6a, H-6b), 3.57 (s, 3H, C_1–OCH_3), 3.73 (t, 1H, J = 8.0 Hz, H-2), 3.31 (s, 3H, C_5–OCH_3), 2.19 (m, 1H, H-7b), 2.10 (m, 1H, H-7a), 1.33 (s, 3H, CH_3), 1.25 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 138.56 (aromatic C), 127.48, 127.36, 127.26 (aromatics CH), 111.05 (C(CH_3)$_2$), 101.11 (C-1), 100.75 (C-5), 80.29, 78.30, 75.08 (C-2, C-3, C-4), 73.05 (CH_2Ph), 55.97 (C_1–OCH_3), 48.50 (C_5–OCH_3), 32.34 (CH_2), 26.67, 24.04 (2 × CH_3), 21.98 (CH_2Hg). Anal. Calcd for $C_{19}H_{27}ClHgO_6$: C, 38.85; H, 4.63. Found: C, 38.87; H, 4.59.

1.2.1.2. Methyl 2-*O*-benzyl-7-chloromercurio-6,7-dideoxy-3,4-*O*-isopropilidene-5-*C*-methoxy-β-L-*galacto*-heptopyranoside, 2b. Amorphous solid, yield 43%; $[\alpha]_D$ −19.1 (*c* 0.6, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz): δ 7.28–7.39 (m, 5H, aromatics H), 4.83–4.75 (AB system, 2H, J = 11.5 Hz, CH_2Ph), 4.52 (d, 1H, J = 7.5 Hz, H-1), 4.30 (dd, 1H, J = 7.0, 8.5 Hz, H-3), 4.19 (d, 1H, J = 8.5 Hz, H-4), 4.12 (dd, 1H, J = 7.0, 7.5 Hz, H-2), 3.74 (m, 1H, H-6b), 3.48 (s, 3H, C_1–OCH_3), 3.28 (s, 3H, C_5–OCH_3), 3.18 (dd, 1H, J = 6.0, 8.0 Hz, H-6a), 2.20 (dq, 1H, J = 3.5, 6.0, 15.0 Hz, H-7b), 1.82 (dq, 1H, J = 4.0, 8.0, 15.0 Hz, H-7a), 1.50 (s, 3H, CH_3), 1.35 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 138.16 (aromatic C), 128.05, 127.99, 127.53 (aromatics CH), 109.64 (C(CH_3)$_2$), 100.60 (C-1), 98.86 (C-5), 78.42, 76.86, 77.72 (C-2, C-3, C-4), 73.40 (CH_2Ph), 56.84 (C_1–OCH_3), 47.32 (C_5–OCH_3),

29.55 (CH_2), 27.72, 26.54 (2 × CH_3), 22.56 (CH_2Hg). Anal. Calcd for $C_{19}H_{27}ClHgO_6$: C, 38.85; H, 4.63. Found: C, 38.91; H, 4.65.

1.2.2. Demercuration

To a stirred suspension of lithium aluminium hydride (6.75 mmol, 5 equiv) in dry THF (8.5 mL) at the temperature of an ice bath, a solution of **2a** or **2b** (1 equiv) in anhydrous THF (8.5 mL) was slowly added under a nitrogen atmosphere, monitoring the reaction by TLC (cyclohexane–EtOAc 4:1). After about 2 h, the starting material disappeared and the solution was diluted with Et_2O (10 mL) and a minimal amount of H_2O (0.25 mL) and then 0.25 mL of a NaOH 15% aqueous solution was added. The resulting mixture was stirred for an additional 30 min and then filtered over Celite; the solvent was removed at reduced pressure and the obtained crude was purified by flash chromatography (cyclohexane–EtOAc 75:25), affording **3a** (74% yield) or **3b** (75% yield).

1.2.2.1. Methyl (5*S*)-2-*O*-benzyl-6,7-dideoxy-3,4-*O*-isopropylidene-5-*C*-methoxy-α-L-*arabino*-heptopyranoside, 3a. Amorphous solid, yield 74%; $[\alpha]_D$ −12.5 (*c* 1.2, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz): δ 7.40–7.23 (m, 5H, aromatics H), 4.84–4.78 (AB system, 2H, *J* = 12.0 Hz, C*H*$_2$Ph), 4.46 (d, 1H, *J* = 8.0 Hz, H-1), 4.22 (ddd, 1H, *J* = 5.5, 7.5, 8.0 Hz, H-3), 4.00 (d, 1H, *J* = 5.5 Hz, H-4), 3.71 (dd, 1H, *J* = 8.0, 7.5 Hz, H-2), 3.57 (s, 1H, C_1–OC*H*$_3$), 3.25 (s, 3H, C_5–OC*H*$_3$), 1.84 (dd, 2H, *J* = 5.5, 7.5 Hz, *CH*$_2$CH$_3$), 1.33 (s, 3H, CH_3), 1.32 (s, 3H, CH_3), 0.89 (t, 3H, *J* = 7.5 Hz, *CH*$_3$CH$_2$); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 139.42 (aromatic C), 128.85, 128.40, 128.13 (aromatics CH), 109.90 (*C*(CH$_3$)$_2$), 101.85 (C-5), 99.53 (C-1), 79.60, 78.53, 75.66 (C-2, C-3, C-4), 74.24 (*C*H$_2$Ph), 57.57 (C_1–OCH$_3$), 47.75 (C_5–OCH$_3$), 28.54, 26.96 (2 × CH_3), 25.04 (*C*H$_2$CH$_3$), 7.87 (*C*H$_3$CH$_2$). Anal. Calcd for $C_{19}H_{28}O_6$: C, 64.75; H, 8.01. Found: C, 64.81; H, 7.98.

1.2.2.2. Methyl (5*R*)-2-*O*-benzyl-6,7-dideoxy-3,4-*O*-isopropylidene-5-*C*-methoxy-α-L-*arabino*-heptopyranoside, 3b. Amorphous solid, yield 75%; $[\alpha]_D$ −38.2 (*c* 0.8, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz): δ 7.40–7.24 (m, 5H, aromatics H), 4.84–4.76 (AB system, 2H, *J* = 12.0 Hz, C*H*$_2$Ph), 4.49 (d, 1H, *J* = 7.0 Hz, H-1), 4.23 (d, 1H, *J* = 7.0 Hz, H-4), 4.08 (dd, 1H, *J* = 7.0, 8.0 Hz, H-3), 3.48 (s, 1H, C_1–OC*H*$_3$), 3.28 (s, 1H, C_5–OC*H*$_3$), 3.24 (dd, 1H, *J* = 6.0, 7.0 Hz, H-2), 1.85 (q, 1H, *J* = 7.5, 8.0 Hz, *CH*$_2$CH$_3$), 1.69 (q, 1H, *J* = 7.5 Hz, *CH*$_2$CH$_3$), 1.20 (dd, 3H, *J* = 7.5, 8.0 Hz, *CH*$_3$CH$_2$); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 138.44 (aromatic C), 128.09, 127.66, 127.40 (aromatics CH), 110.44 (*C*(CH$_3$)$_2$), 101.42 (C-1), 101.15 (C-5), 78.93, 76.92, 77.10 (C-2, C-3, C-4), 73.10 (*C*H$_2$Ph), 55.74 (C_1–OCH$_3$), 48.69 (C_5–OCH$_3$), 27.50, 26.67 (2 × CH_3), 25.15 (*C*H$_2$CH$_3$), 7.57 (*C*H$_3$CH$_2$). Anal. Calcd for $C_{19}H_{28}O_6$: C, 64.75; H, 8.01. Found: C, 64.69; H, 8.03.

1.3. General method for the direct methoxymercuration–demercuration of 1

The reaction mixture obtained from the methoxymercuration step (Section 1.2.1) was used directly without separating the two organomercuric chlorides **2a**,**b**, for the demercuration with $LiAlH_4$, following the above reported procedure (Section 1.2.2). The resulting reaction mixture was filtered through Celite and the solvent was removed at reduced pressure. The obtained crude material was then purified by flash chromatography yielding the expected bis-glycosides **3a**,**b** with a 71% global yield.

1.4. General method for the hydrolysis of bis-glycosides 3a,b

A solution of **3a**,**b** (456 mg, 1.25 mmol) in a 2:1 (v/v) mixture of CH_3CN–H_2O (10 mL) was added of CF_3COOH (2.5 mL) and stirred at 50 °C until the TLC analysis (cyclohexane–EtOAc 1:1) showed the complete disappearance of the starting material (5 h). The mixture was concentrated and repeatedly co-evaporated with toluene (5 × 10 mL) under reduced pressure. The crude residue was partitioned between brine (10 mL) and EtOAc (20 mL) and the aqueous phase was extracted with EtOAc (3 × 20 mL). The organic phases collected and dried were concentrated under reduced pressure to give a residue (385 mg), which was directly purified by flash chromatography (cyclohexane–EtOAc, 7:3), to give **4** (184 mg, 55% yield) as colourless syrup. The δ-dicarbonyl heptose **4** exists almost exclusively as 1:2.7 mixture of α- and β-furanosic forms.

1.4.1. 6,7-Dideoxy-2-*O*-benzyl-L-*arabino*-heptos-5-ulose, 4. Syrup, yield 55%; $[\alpha]_D$ +9.1 (*c* 0.7, $CHCl_3$); ^1H NMR (CD_3CN, 500 MHz) α-furanosic anomer: δ 7.21–7.38 (m, 5H, aromatics H), 5.38 (d, 1H, *J* = 0.5 Hz, H-1), 4.50 (s, 2H, C*H*$_2$Ph), 4.40 (d, 1H, *J* = 5.0 Hz, H-4), 4.22 (m, 1H, H-3), 3.71 (dd, 1H, *J* = 0.5, 4.5 Hz, H-2), 2.55 (q, 2H, *J* = 7.2 Hz, CH_2), 0.87 (t, 3H, *J* = 7.2 Hz, CH_3); β-furanosic anomer: δ 7.21–7.38 (m, 5H, aromatics H), 5.42 (d, 1H, *J* = 5.0 Hz, H-1), 4.55 (s, 2H, C*H*$_2$Ph), 4.42 (d, 1H, *J* = 5.0 Hz, H-4), 4.32 (t, 1H, *J* = 5.0 Hz, H-3), 3.76 (dd, 1H, *J* = 4.0, 5.0 Hz, H-2), 2.56 (q, 2H, *J* = 7.2 Hz, CH_2), 0.91 (t, 3H, *J* = 7.5 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 50 MHz) α-furanosic anomer: δ 211.39 (C=O), 138.57 (aromatic C), 129.90, 129.11, 128.55 (aromatics CH), 102.45 (C-1), 90.39 (C-4), 87.99 (C-2), 78.02 (C-3), 72.07 (CH_2Ph), 32.27 (CH_2), 7.21 (CH_3); β-furanosic anomer: δ 212.60 (C=O), 138.63 (aromatic C), 129.34, 128.81, 128.73 (aromatics CH), 98.35 (C-1), 88.15 (C-4), 83.68 (C-2), 76.78 (C-3), 72.75 (CH_2Ph), 32.34 (CH_2), 7.34 (CH_3). Anal. Calcd for $C_{14}H_{18}O_5$: C, 63.15; H, 6.81. Found: C, 63.21; H, 6.86.

1.5. General method for the electrophilic ring-opening of 5

1.5.1. Reduction

A mixture of the four stereoisomers of spirocyclopropane carboxylates **5** (1 mmol) and $LiAlH_4$ (1.5 mmol) in dry THF (20 mL) was stirred at 0 °C for 1.5 h. The reaction mixture was then diluted with Et_2O (10 mL) and then quenched by the addition of H_2O (0.25 mL) and 15% aqueous solution of NaOH (0.25 mL). After the stirring for another 30 min, the reaction mixture was filtered over Celite, and the solvent was removed under reduced pressure to give a crude mixture that was purified by flash chromatography (cyclohexane–EtOAc 4:1). The corresponding hydroxymethyl derivatives were afforded as a mixture of four stereoisomers (85% yield), which were not separated. Their structures were confirmed form the ^1H NMR spectrum ($CDCl_3$, 500 MHz), which showed the cyclopropane methyl group protons (dd, *J* = 6.5, 10.5 Hz) in the range 0.60–1.09 ppm, four multiplets at about 1.70–1.90 ppm for the H-6 protons, and other multiplets in the range 3.24–3.52 and 3.72–3.93 ppm for the hydroxymethyl groups protons.

1.5.2. Methoxymercuration–demercuration and hydrolysis

To a stirred mixture of the four stereoisomers of hydroxymethyl spirocyclopropane (1 equiv, 2 mmol) in dry MeOH (10 mL), mercury(II) trifluoroacetate (1.4 equiv) was added at room temperature and under a nitrogen atmosphere and the reaction progress was monitored by TLC (cyclohexane–EtOAc, 85:15) until starting material disappeared (about 2 h). The reaction was quenched by the addition of brine and then extracted with dichloromethane (3 × 20 mL); the combined organic extracts were washed with H_2O and dried (Na_2SO_4). After filtration, the solvent was removed under reduced pressure to give a residue (1 equiv) that was dissolved in anhydrous THF (8.5 mL). The resulting mixture was slowly added to a stirred suspension of $LiAlH_4$ (6.75 mmol, 5 equiv) in dry THF (8.5 mL), under a nitrogen atmosphere at the temperature of an ice bath, and then monitored by TLC (cyclohexane–EtOAc 85:15) until the starting material disappeared (about 2 h). The reaction mixture was diluted with Et_2O (10 mL) and then quenched by the addition of H_2O (0.25 mL) and a 15% aqueous solution NaOH (0.25 mL). After stirring for other 30 min, the solu-

tion was filtered over Celite; the solvent was removed under reduced pressure and the obtained crude material was hydrolyzed following the above reported method for bis-glycosides **3a**,**b** (Section 1.4). Purification by flash chromatography (cyclohexane–EtOAc 60:40) gave 6-deoxy-2-*O*-benzyl-6-*C*-methyl-D,L-*arabino*-heptos-5-ulose **6** as a 1:2 α- and β-furanosic anomeric mixture.

1.5.2.1. 6-Deoxy-2-*O*-benzyl-6-*C*-methyl-D,L-*arabino*-heptos-5-ulose, 6. As α- and β-furanosic anomeric mixture: syrup, yield 55%; $[\alpha]_D$ +11.2 (*c* 0.4, $CHCl_3$); ^1H NMR (CD_3Cl, 500 MHz): δ 7.36–7.19 (m, 20H, aromatics H), 5.51 (d, 1H, *J* = 0.5 Hz, H-1α), 5.50 (d, 1H, *J* = 0.5 Hz, H-1α), 5.48 (d, 1H, *J* = 5.5 Hz, H-1β), 5.47 (d, 1H, *J* = 5.5 Hz, H-1β), 4.74–4.66 (AB system × 2, each 2H, *J* = 11.5 Hz, C*H*$_2$Ph), 4.40–4.38 (m, 4H, H-4), 4.19 (m, 4H, H-3), 4.05–3.98 (m, 4H, H-2), 3.90–3.78 (AB system × 2, each 2H, *J* = 11.0 Hz, C*H*$_2$OH), 3.01–2.97 (dd × 4, each 1H, *J* = 6.0, 7.5 Hz, H-6), 1.12–1.10 (d × 2, each 3H, *J* = 7.0 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 212.79, 211.21, 211.10, 210.85 (C=O), 138.57, 138.51, 138.43, 138.22 (aromatic C), 129.91, 129.57, 129.41 129.31, 128.89, 128.5 (aromatics CH), 102.45, 102.10, 98.81, 98.44 (C-1), 91.36, 90.39, 89.66 (C-4), 85.99, 84.56, 83.10, 82.78 (C-2), 78.02, 76.22, 74.54, 74.15 (C-3), 73.65, 72.07, 71.81 (CH_2Ph), 67.22, 66.15, 65.22, 65.05 (CH_2OH), 45.60, 45.34 42.72, 42.17 (*C*H–CH_3), 13.21, 12.44, 11.37 (CH_3). Anal. Calcd for $C_{15}H_{20}O_6$: C, 60.80; H, 6.80. Found: C, 60.86; H, 6.82.

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