New *C*-aryl alditols from Diels-Alder adducts of sugar nitroalkenes

Noelia Araújo, Manuel Baños, María V. Gil, Luis E. Cáceres, Emilio Román,* and José A. Serrano

Departamento de Química Orgánica e Inorgánica, Facultad de Ciencias, Universidad de Extremadura, E-06071 Badajoz, Spain
E-mail: roman@unex.es

Abstract
2-Nitro-, 2-amino- and 2-acetamido-1-(penta-*O*-acetylpentitol-1′-yl)benzenes were prepared using previously reported Diels-Alder cycloadducts obtained from sugar-derived nitroalkenes with D-*galacto* and D-*manno* configurations as starting materials. Deacetylation and oxidative cleavage of the sugar side-chain of nitrobenzene pentitol peracetates yielded nitrobenzaldehydes. From 2-nitro-1-(D-*galacto*-pentitol-1′-yl)benzene also 1′,4′- and 2′,5′-anhydro derivatives were synthesized.

Keywords: Nitro compounds, *C*-aryl alditols, anhydro derivatives, *C*-nucleosides, aromatization

Introduction

Compounds with an open-chain monosaccharide unit linked through a C–C single bond to a hetero- or carboaromatic ring have received attention due to their diverse biological properties.[1–8] Thus, the nitrobenzene derivative chloramphenicol[1,2] inhibits protein synthesis, the methoxy–benzene derivative karacilin[3] possesses antiviral activity in vitro against herpes viruses. This type of substances, namely *C*-aryl alditols, can be considered as acyclo-*C*-nucleoside analogues that by intramolecular dehydration could provide *C*-nucleosides; some of the latter, either natural or synthetic, have been reported to have a broad range of useful antitumor, antifungal and antibiotic properties, thus encouraging the development of methodologies toward this class of products.[8-11] Besides, the *C*-aryl alditol substructure is also present in some natural products, like the 5-(4-aminophenyl)-1,2,3,4-tetrahydroxypentane moiety of methanopterin, a cofactor involved in the biological reduction of CO_2 to CH_4.[12]

Based on our previous experience with Diels-Alder reactions of sugar derivatives,[13–15] we report herein the synthesis of several *C*-aryl alditols. Cycloadducts obtained from D-*galacto*- and D-*manno*-3,4,5,6,7-penta-*O*-acetyl-1,2-dideoxy-1-nitrohept-1,2-enitols **1a,**[16] **1b**[17] (Figure 1) with furan, 1-acetoxy-, or 1-trimethylsilyloxybuta-1,3-dienes were used as starting materials. As an

example of an acid-catalyzed dehydration of the polyhydroxyalkyl chain in 1-(D-*galacto*-pentitol-1′-yl)-2-nitrobenzene **6c**, we describe the preparation of 2′,5′- and 1′,4′-anhydro derivatives **10** and **11**.

Results and Discussion

Upon treatment with DBU in dichloromethane at room temperature both the D-*galacto* cycloadduct **2a**[15] and a 50:50 mixture of **2a** and its stereoisomer **3a**[15] underwent aromatization by *anti*- and *syn*-E2 elimination of acetic acid, thus furnishing 1-(1′,2′,3′,4′,5′-penta-*O*-acetyl-D-*galacto*-pentitol-1′-yl)-2-nitrobenzene **6a** in good yields (Figure 1). Similarly, a 65:35 mixture of D-*manno* adduct **4b**[15] and its stereoisomer **5b**[15] afforded 1-(1′,2′,3′,4′,5′-penta-*O*-acetyl-D-*manno*-pentitol-1′-yl)-2-nitrobenzene **6b** (85%). By comparison with closely related reactions, the milder conditions now used for these processes are noticeable: Treatment of **2a** or **4b** with sodium acetate in boiling THF only induced *anti*-elimination of acetic acid, yielding nitrocyclohexadienes;[15] under these conditions, stereoisomers of **2a** and **4b** did not undergo the desired *syn*-elimination, probably because of the unfavorable conformation that has to be adopted by the cyclohexene ring.

Compound **6b** was also obtained by potassium carbonate-induced elimination of acetic acid from the crude mixture of 7-oxanorbornene stereoisomers **7b**,[13] followed by treatment of the resulting product with acetic anhydride in pyridine at room temperature. As previously reported,[18] this reaction could involve a base-induced β-elimination of the heteroatom bridge, followed by aromatization as the result of the elimination of acetic acid. The procedure is very simple and easy, and could be an alternative to other methods that have been used in related reactions, in which 7-oxabicyclo[2.2.1]hept-2-ene systems yielded substituted benzenes by treatment with $TiCl_4$-$LiAlH_4$.[19,20]

Determination of structures of nitrobenzene pentitol peracetates **6a** and **6b** is based on their analytical and spectroscopic data. The ^1H and ^{13}C NMR spectra of both compounds show four protons and six carbon atoms in the aromatic region; the values of the vicinal proton coupling constants in the sugar side-chain are similar to those of their starting materials,[15] thus supporting the same extended conformation in the acyclic carbohydrate moiety.

Treatment of **6a** and **6b** with potassium carbonate in 90% methanol yielded the deacetylated derivatives **6c** and **6d**, respectively. Oxidative cleavage of the pentahydroxypentyl side-chains in **6c** and **6d** with sodium metaperiodate in MeOH/H_2O (1:1) led to 2-nitrobenzaldehyde **6f**,[21] thus supporting the proposed structures of their respective starting materials and demonstrating that they differ merely in the configuration of their sugar chains.

Following the method described by Cowan,[22] reduction of the nitro group in nitrobenzene alditols **6a** and **6b** with $NaBH_4$/$Cu(OAc)_2$ in methanol yielded the corresponding aniline derivatives: **6b** afforded 2-(1′,2′,3′,4′,5′-penta-*O*-acetyl-D-*manno*-pentitol-1′-yl)aniline **8b** as the only product, whereas **6a** led to a 2:1 mixture of 2-(1′,2′,3′,4′,5′-penta-*O*-acetyl-D-*galacto*-

pentitol-1′-yl)aniline **8a** and 2-(2′,3′,4′,5′-tetra-*O*-acetyl-D-*galacto*-pentitol-1′-yl)acetanilide **9e**. The formation of the latter product is explained by an intramolecular migration of the acetyl group at C-1′ to the amino group. The difference in behavior of **6a** and **6b** suggests that the migration could be due to spatial proximity of C-1′ acetate and the amino group in the D-*galacto* configuration of the sugar side-chain, which is not the case with the D-*manno* configuration. Supporting evidence of the structure of acetanilide **9e** is provided by the chemical shift of H-1′ at δ 5.69 in **9e**, which is shifted downfield to δ 6.06 in the peracetylated derivative **9a**.[23]

In order to explore the dehydrating cyclization of *C*-aryl alditols, nitrobenzene pentitol **6c** was refluxed in 1% sulfuric acid in isopropyl alcohol. Compounds **10** (62%) and **11** (20%) with 2′,5′-anhydro and 1′,4′-anhydro rings, respectively, were isolated. These results agree with those previously reported:[24] When the sugar chain is linked to a π-deficient heterocycle, C-1′ is usually not involved in the cyclization process, and 2′,5′-anhydro derivatives are formed. Accordingly, the ^{1}H NMR spectrum of **11** in DMSO-d_6 displays a triplet signal corresponding to the hydroxyl group at C-5′; such a signal is absent in the spectrum of **10**. The ^{13}C NMR chemical shifts are similar to those reported for closely related compounds;[25] the signal for C-5′ appears at δ 73.1 for **10**, and at δ 60.0 for **11** in agreement with the type of cyclization proposed.

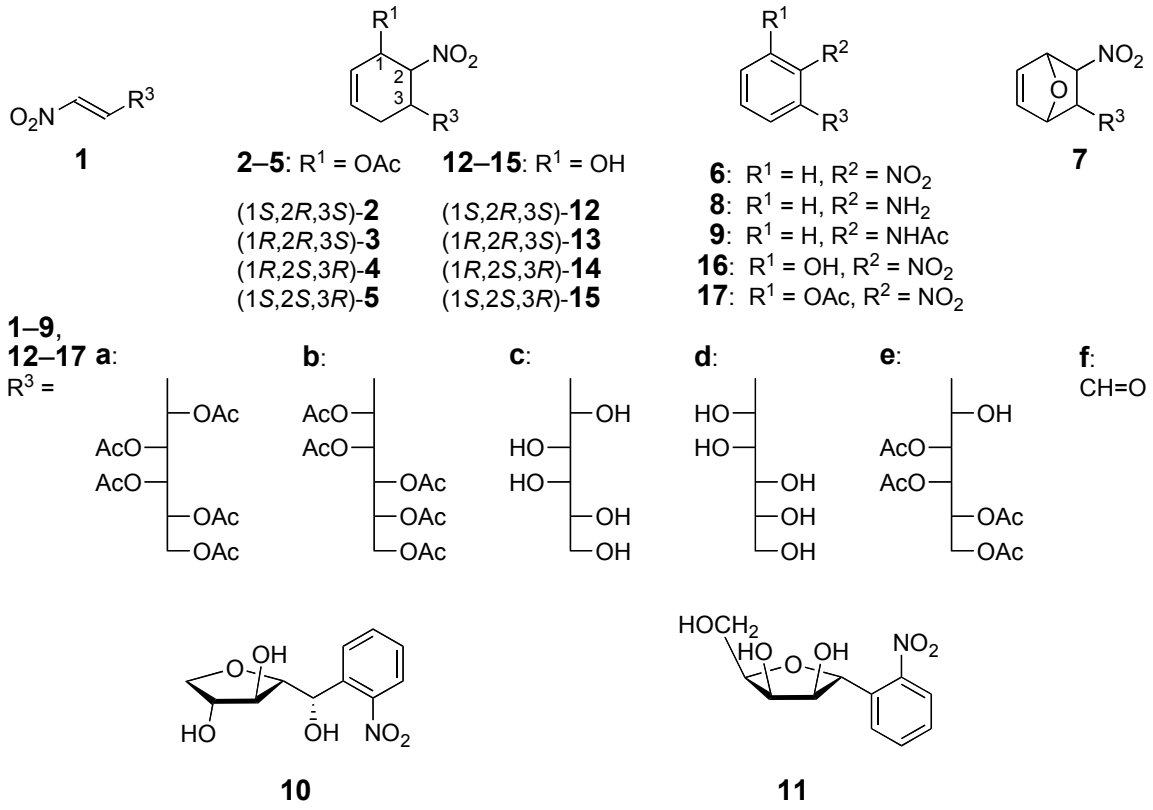

Figure 1

Concerning the dehydration mechanism, we believe that the formation of **10** probably involves an attack of the C-2′ hydroxyl group at C-5′ displacing its protonated hydroxyl group.[26] The magnitude of the coupling constant ($J_{2',3'}$ = 3.5 Hz) in **10** supports the α-anomeric configuration; this is within the range of related 3,6-anhydro-D-galactose derivatives:[27] A small coupling constant (^3J = 0.5–4.0 Hz) has been observed between the proton at the ring carbon bearing the *C*-substituent and the proton at the vicinal ring carbon.

Probably, the cyclization leading to **11** involves a benzylic carbocation intermediate generated in acid medium, and accordingly, proof of its structure cannot be based on mechanistic grounds. The α-anomeric configuration is in agreement with the absence of a NOESY effect between the H-1′ and H-4′, and is consistent with the steric hindrance that would be present in the transition state leading to the β-anomer with all substituents in the furanoid ring *cis* oriented; also, the coupling constant ($J_{1',2'}$ = 7.8 Hz) is similar to that previously reported (^3J = 8.0 Hz) for 1-benzyl-4,5,6,7-tetrahydro-2-α-D-*lyxo*-furanosyl-6,6-dimethylindol-4-one.[28]

On the other hand, 3-glyco-2-nitrophenols **16a** and **16b** were prepared from crude hydrolysis mixtures[15] of the corresponding cycloadducts **12**–**15** by treatment with dimethylsulfoxide and acetic anhydride. As described previously,[29] these reagents oxidize primary or secondary alcohols to carbonyl compounds, whereas in our case the oxidation led to nitrophenols **16a** and **16b**, probably through the enol form of the initially formed cyclohexenone. The assignment of structures **16a** and **16b** is based on spectroscopic data as well as on those obtained from the respective hexaacetylated derivatives **17a** and **17b**, or the deacetylated derivatives **16c** and **16d**. Oxidative cleavage of the pentahydroxypentyl chains of the latter two compounds with sodium metaperiodate in MeOH/H_2O (1:1) afforded, in both cases, the known 3-hydroxy-2-nitrobenzaldehyde **16f**,[30] thus providing additional support for structures **16a** and **16b**.

In conclusion, Diels-Alder cycloadducts obtained from sugar-derived nitroalkenes with furan, 1-acetoxy-, or 1-trimethylsilyloxybuta-1,3-diene are suitable precursors of *C*-aryl alditols. Intramolecular cyclization of the sugar chains leads to *C*-nucleoside analogues. The potential of the nitro group, easily convertible to other functionalities, opens an access to a variety of this class of compounds.

Experimental Section

General. Solutions were concentrated at reduced pressure below 40 °C. Silica Gel 60 (Merck, 230-400 mesh ASTM) was used for column chromatography, which was carried out using a dry-column mode.[31] Thin layer chromatography (TLC) was performed on precoated Merck Kieselgel 60 GF_{254} aluminium-backed plates; visualization with UV light or iodine vapor. Preparative thin layer chromatography (PTLC) was performed using silica gel (Merck 60 GF_{254}). Reagents were used as supplied by Aldrich Chemical Co. NMR spectra were recorded on a Bruker AC/PC spectrometer (400.13 MHz for ^1H, 100.62 MHz for ^{13}C) with TMS or residual $CHCl_3$ or DMSO as internal standards. Evaluation of NMR signals is based on spin decoupling, heteronuclear

chemical shift correlation spectroscopy and DEPT experiments. IR spectra were recorded on Perkin-Elmer 399 and FT-IR MIDAC Corporation spectrophotometers. Solid samples were examined as KBr disks, and liquids as thin films on NaCl plates. Melting points were determined in open capillary tubes on an Electrothermal 8100 capillary melting point apparatus. Optical rotations were determined at 20±2 °C with a Perkin-Elmer 241 polarimeter.

1-(1′,2′,3′,4′,5′-Penta-*O*-acetyl-D-*galacto*-pentitol-1′-yl)-2-nitrobenzene (6a). To a stirred solution of (1*S*,2*R*,3*S*)-1-*O*-acetyl-3-(1′,2′,3′,4′,5′-penta-*O*-acetyl-D-*galacto*-pentitol-1′-yl)-2-nitrocyclohex-5-en-1-ol[15] (**2a**; 0.70 g, 1.28 mmol) in CH_2Cl_2 (6 mL) was added DBU (0.15 mL, 1.00 mmol). After 16 h at room temperature, the mixture was poured onto ice-cold water (50 mL), extracted with CH_2Cl_2 (3 × 25 mL); the combined extracts were washed successively with HCl (1 M, 2 × 25 mL), saturated aqueous $NaHCO_3$ (2 × 25 mL), and water (2 × 25 mL). The organic layer was decolorized with activated charcoal, dried ($MgSO_4$), filtered and evaporated to yield **6a** as a pale yellow oil that crystallized from Et_2O/petroleum ether (0.51 g, 82%); mp 91–93 °C; R_f 0.29 (Et_2O/petroleum ether, 2:1); $[\alpha]_D$ +5.6 (*c* 0.50, $CHCl_3$); IR (KBr) $\tilde{\nu}_{max}$ (cm^{-1}): 3020 (H–C_{ar}), 1735 (C=O), 1540, 1375 (NO_2), 1230, 1060 (C–O–C); ^{1}H NMR ($CDCl_3$): δ 8.12 (1H, dd, $J_{3,5}$ = 1.3 Hz, $J_{3,4}$ = 8.1 Hz, H-3), 7.7–7.4 (3H, m, H-4, H-5, H-6), 6.55 (1H, d, $J_{1',2'}$ = 1.2 Hz, H-1′), 5.69 (1H, dd, $J_{2',3'}$ = 10.1 Hz, $J_{1',2'}$ = 1.2 Hz, H-2′), 5.59 (1H, dd, $J_{3',4'}$ = 1.8 Hz, $J_{2',3'}$ = 10.1 Hz, H-3′), 5.38 (1H, m, H-4′), 4.34 (1H, dd, $J_{4',5'}$ = 4.8 Hz, $J_{5',5''}$ = 11.5 Hz, H-5′), 3.90 (1H, dd, $J_{4',5''}$ = 7.6 Hz, $J_{5',5''}$ = 11.5 Hz, H-5′′), 2.20, 2.17, 2.04, 2.01, 1.83 (each 3H, 5 s, 5 CH_3); ^{13}C NMR ($CDCl_3$): δ 170.4, 170.3, 170.0, 169.6, 168.8 (O*C*OCH_3), 147.0 (C-2), 132.9 (C-1), 133.3, 129.2, 127.9, 125.4 (C-3, C-4, C-5, C-6), 68.9, 68.1, 68.0, 67.6 (C-1′, C-2′, C-3′, C-4′), 62.1 (C-5′), 20.7, 20.6, 20.5, 20.1 (CH_3). Anal. Calcd. for $C_{21}H_{25}NO_{12}$: C, 52.17; H, 5.21; N, 2.90. Found: C, 52.06; H, 5.27; N, 2.76.

Following this procedure, a 50:50 mixture of **2a** and diastereoisomer **3a** yielded **6a** (75%).

1-(1′,2′,3′,4′,5′-Penta-*O*-acetyl-D-*manno*-pentitol-1′-yl)-2-nitrobenzene (6b).

Method A: Following the procedure as described above for the preparation of **6a**, a 65:35 mixture of (1*R*,2*S*,3*R*)- and (1*S*,2*S*,3*R*)-1-*O*-acetyl-3-(1′,2′,3′,4′,5′-penta-*O*-acetyl-D-*manno*-pentitol-1′-yl)-2-nitrocyclohex-5-en-1-ol[15] (**4b** and **5b**) afforded **6b** (85%) as an oil; R_f 0.23 (Et_2O/petroleum ether, 2:1); $[\alpha]_D$ +2.5 (*c* 0.40, $CHCl_3$); IR (film) $\tilde{\nu}_{max}$ (cm^{-1}): 3040 (H–C_{ar}), 1750 (C=O), 1545, 1380 (NO_2), 1230, 1070 (C–O–C); ^{1}H NMR ($CDCl_3$): δ 7.86 (1H, d, $J_{3,4}$ = 7.8 Hz, H-3), 7.61 (1H, d, $J_{5,6}$ = 4.8 Hz, H-6), 7.47 (1H, dd, $J_{4,5}$ = 3.4 Hz, $J_{3,4}$ = 7.8 Hz, H-4), 7.44 (1H, dd, $J_{4,5}$ = 3.4 Hz, $J_{5,6}$ = 4.7 Hz, H-5), 6.50 (1H, d, $J_{1',2'}$ = 9.9 Hz, H-1′), 5.61 (dd, 1H, $J_{3',4'}$ = 9.4 Hz, $J_{2',3'}$ = 1.7 Hz, H-3′), 5.52 (1H, dd, $J_{2',3'}$ = 1.8 Hz, $J_{1',2'}$ = 10.0 Hz, H-2′), 5.08 (1H, ddd, $J_{3',4'}$ = 9.5 Hz, $J_{4',5'}$ = 2.7 Hz, $J_{4',5''}$ = 4.8 Hz, H-4′), 4.24 (1H, dd, $J_{4',5'}$ = 2.7 Hz, $J_{5',5''}$ = 10.0 Hz, H-5′), 4.13 (1H, dd, $J_{4',5''}$ = 4.7 Hz, $J_{5',5''}$ = 10.0 Hz, H-5′′), 2.21, 2.11, 2.06, 2.04, 1.80 (each 3H, 5 s, 5 CH_3); ^{13}C NMR ($CDCl_3$): δ 170.3, 169.7, 169.6, 169.4, 169.3 (O*C*OCH_3), 148.9 (C-2), 132.9, 129.3, 128.3, 124.2 (C-3, C-4, C-5, C-6), 131.1 (C-1), 70.6 (C-1′), 67.6, 67.2, 66.1 (C-2′, C-3′, C-4′), 61.7 (C-5′), 20.5, 20.4, 20.2 (CH_3).

Method B: To a solution of the crude mixture of oxanorbornenes **7**[13] (0.30 g, 0.60 mmol) in MeOH (90%, 8 mL) was added K_2CO_3 (0.35 g, 2.53 mmol). After stirring for 1 h at room temperature the resulting solution was neutralized with Amberlite IR-120 (H^+) resin, then filtered and the filtrate concentrated to a residual oil that was treated with pyridine (1.5 mL) and Ac_2O (1.5 mL). After 14 h at room temperature, the crude product was poured onto ice cold water (50 mL), extracted with CH_2Cl_2 (3 x 25 mL). The extracts were combined, washed succesively with HCl (1 M, 2 x 25 mL), saturated aqueous $NaHCO_3$ (2 x 25 mL), and water (2 x 25 mL). Upon drying ($MgSO_4$) and concentration a pure (by TLC) oil **6b** was obtained (0.27 g, 94%).

2-Nitro-1-(D-*galacto*-pentitol-1′-yl)benzene (6c). To a solution of 1-(1′,2′,3′,4′,5′-penta-*O*-acetyl-D-*galacto*-pentitol-1′-yl)-2-nitrobenzene (**6a**, 1.50 g, 3.10 mmol) in MeOH (90%, 38 mL) was added K_2CO_3 (1.70 g, 12.30 mmol). After stirring for 24 h at room temperature the reaction mixture was neutralized with Amberlite IR-120 (H^+) and evaporated to yield a colorless oil **6c** (0.74 g, 88%). R_f 0.32 (benzene/MeOH, 3:1); $[\alpha]_D$ –120.0 (*c* 0.50, pyridine); IR (film) $\tilde{\nu}_{max}$ (cm^{-1}) 3600–3100 (O-H), 3020 (H–C_{ar}), 1550, 1360 (NO_2), 1215, 1080 (C–O–C); ^{1}H NMR (DMSO-d_6): δ 7.90 (1H, d, $J_{3,4}$ = 6.9 Hz, H-3), 7.85 (1H, dd, $J_{5,6}$ = 8.0 Hz, $J_{4,6}$ = 1.0 Hz, H-6), 7.68 (1H, t, $J_{3,4}$ = $J_{4,5}$ = 7.2 Hz, H-4), 7.46 (1H, t, $J_{4,5}$ = $J_{5,6}$ = 7,6 Hz, H-5), 5.48 (1H, s, H-1′), 4.5–3.9 (5H, m, 5 OH, D_2O exchangeable), 3.8–3.4 (5H, m, H-2′, H-3′ H-4′, H-5′, H-5′′); ^{13}C NMR (DMSO-d_6): δ 147.8 (C-2), 139.0 (C-1), 132.2, 130.7, 127.6, 123.3 (C-3, C-4, C-5, C-6), 72.5 (C-1′), 70.1, 69.8, 66.6 (C-2′, C-3′, C-4′), 63.2 (C-5′).

2-Nitro-1-(D-*manno*-pentitol-1′-yl)benzene (6d). Following the procedure as described for the preparation of **6c**, 1-(1′,2′,3′,4′,5′-penta-*O*-acetyl-D-*manno*-pentitol-1′-yl)-2-nitrobenzene (**6b**, 0.80 g, 1.65 mmol) gave a colorless oil **6d** (0.37 g, 82%); R_f 0.34 (benzene/MeOH, 3:1); $[\alpha]_D$ –2.2 (*c* 0.50, pyridine); IR (film) $\tilde{\nu}_{max}$ (cm^{-1}) 3400–3200 (O-H), 3020 (H–C_{ar}), 1560, 1400 (NO_2), 1020 (C–O–C); ^{1}H NMR (DMSO-d_6): δ 7.83 (1H, d, $J_{3,4}$ = 7.8 Hz, H-3), 7.75 (1H, d, $J_{5,6}$ = 8.0 Hz, H-6), 7.65 (1H, t, $J_{3,4}$ = $J_{4,5}$ = 7.6 Hz, H-4), 7.44 (1H, t, $J_{4,5}$ = 7.6 Hz, H-5), 5.29 (1H, d, $J_{1',2'}$ = 8.9 Hz, H-1′), 5.0–3.0 (5H, m, 5 OH, D_2O exchangeable), 3.8–3.2 (5H, m, H-2′, H-3′, H-4′, H-5′, H-5′′); ^{13}C NMR (DMSO-$d_{6:}$): δ 150.0 (C-2), 139.6 (C-1), 132.6, 128.9, 127.7, 123.4 (C-3, C-4, C-5, C-6), 73.6 (C-1′), 71.4, 69.6, 67.1 (C-2′, C-3′, C-4′), 64.0 (C-5′).

2-Nitrobenzaldehyde (6f).[21] To a stirred solution of 2-nitro-1-(D-*galacto*-pentitol-1′-yl)benzene (**6c**; 0.15 g, 0.55 mmol) in MeOH (50%, 12 mL) was added $NaIO_4$ (0.53 g, 2.48 mmol). After 15 min at room temperature, the mixture was extracted with CH_2Cl_2 (3 x 20 mL), the extracts were combined, washed with water (2 x 20 mL), dried ($MgSO_4$), and evaporated to yield an oil (0.068 g, 82%); IR and ^{1}H NMR data match those reported for 2-nitrobenzaldehyde.[21]

This procedure converted also 1-(D-*manno*-pentitol-1′-yl)-2-nitrobenzene (**6d**) into **6f** (77%).

2-(1′,2′,3′,4′,5′-Penta-*O*-acetyl-D-*galacto*-pentitol-1′-yl)aniline (8a) and **2-(2′,3′,4′,5′-tetra-*O*-acetyl-D-*galacto*-pentitol-1′-yl)acetanilide (9e).** To a stirred solution of 1-(1′,2′,3′,4′,5′-penta-*O*-acetyl-D-*galacto*-pentitol-1′-yl)-2-nitrobenzene (**6a**, 2.00 g, 4.00 mmol) in MeOH (60 mL) was added a saturated solution of $Cu(AcO)_2$ (16 mL). The mixture was treated with $NaBH_4$ (2.10 g, stepwise; 3 x 0.70 g, each five min). After 30 min, the reaction mixture was filtered, and the filtrate was diluted with Et_2O (120 mL) and washed with saturated aqueous $NaHCO_3$ (3 x 50

mL). The aqueous layer was extracted with Et_2O (100 mL), the combined organic extracts were dried ($MgSO_4$) and evaporated to yield an oil (1.70 g, 91%), which was shown to be a 2:1 mixture of **8a** and **9e**; R_f 0.32 and 0.41, respectively (Et_2O/petroleum ether, 3:1). Although attempts to separate these two products were unsuccessful, their respective NMR data could be obtained from enriched samples (PTLC).

8a: ^{1}H NMR ($CDCl_3$): δ 7.66 (1H, d, $J_{5,6}$ = 3.4 Hz, H-6), 7.3–7.0 (1H, m, H-3), 7.13 (1H, br d, $J_{4,5}$ = 7.2 Hz, H-5), 6.69 (1H, m, H-4), 6.28 (1H, d, $J_{1',2'}$ = 5.2 Hz, H-1′), 5.65 (1H, dd, $J_{1',2'}$ = 5.2 Hz, $J_{2',3'}$ = 8.3 Hz, H-2′), 5.39 (1H, dd, $J_{3',4'}$ = 2.3 Hz, $J_{2',3'}$ = 8.2 Hz, H-3′), 5.30 (1H, m, H-4′), 4.4-3.8 (2H, m, 2 NH, D_2O exchangeable), 4.20 (dd, 1 H, $J_{4',5'}$ = 5.1 Hz, $J_{5',5''}$ = 11.7 Hz, H-5′), 3.85 (1H, dd, $J_{4',5''}$ = 7.1 Hz, $J_{5',5''}$ = 11.9 Hz, H-5′′), 2.07, 2.03, 2.01, 1.99, 1.94 (each 3H, 5 s, 5 CH_3); ^{13}C NMR ($CDCl_3$): δ 170.3, 170.1, 169.9, 169.1 (O*C*OCH$_3$), 144.4 (C-1), 129.5 (C-3), 128.5 (C-5), 119.8 (C-2), 118.5 (C-4), 117.0 (C-6), 70.6 (C-1′), 68.8, 68.6, 67.9 (C-2′, C-3′, C-4′), 61.8 (C-5′), 20.6, 20.5, 20.3 (CH_3).

9e: ^{1}H NMR ($CDCl_3$): δ 7.96 (1H, d, $J_{5,6}$ = 1.8 Hz, H-6), 7.3–7.0 (1H, m, H-3), 7.28 (1H, s, NH, D_2O exchangeable), 7.06 (1H, br d, $J_{4,5}$ = 7.5 Hz, H-5), 6.69 (1H, m, H-4), 5.69 (2H, m, H-1′, H-2′), 5.30 (2H, m, H-3′, H-4′), 4.33 (1H, dd, $J_{4',5'}$ = 4.8 Hz, $J_{5',5''}$ = 11.5 Hz, H-5′), 3.85 (1H, dd, $J_{4',5''}$ = 7.1 Hz, $J_{5',5''}$ = 11.5 Hz, H-5′′), 3.43 (1H, s, OH, D_2O exchangeable), 2.27, 2.13, 1.90, 1.79 (each 3H, 4 s, 4 CH_3); ^{13}C NMR ($CDCl_3$): δ 170.2, 169.9, 169.8, 169.7, 168.7 (O*C*OCH$_3$), 160.8 (NH*C*OCH$_3$), 139.3 (C-1), 135.7 (C-4), 128.2 (C-3), 127.4 (C-5), 119.8 (C-2), 118.5 (C-6), 71.1 (C-1′), 68.2, 67.8, 67.5 (C-2′, C-3′, C-4′), 62.0 (C-5′), 20.8, 20.5, 20.0 (OCO*C*H$_3$, NHCO*C*H$_3$).

2-(1′,2′,3′,4′,5′-Penta-*O*-acetyl-D-*galacto*-pentitol-1′-yl)acetanilide (9a). To a solution of a *c.a.* 2:1 mixture of 2-(1′,2′,3′,4′,5′-penta-*O*-acetyl-D-*galacto*-pentitol-1′-yl)aniline (**8a**) and 2-(2′,3′,4′,5′-tetra-*O*-acetyl-D-*galacto*-pentitol-1′-yl)acetanilide (**9e**) (0.40 g, 0.88 mmol) in pyridine (4 mL) was added Ac_2O (2 mL). After 18 h at 0 ºC the reaction mixture was poured onto water (100 mL) and extracted with CH_2Cl_2 (2 x 50 mL). The combined organic extracts were washed with HCl (1 M, 50 mL) and saturated aqueous $NaHCO_3$ (50 mL), dried ($MgSO_4$), and concentrated to yield **9a** as an oil, which crystallized from Et_2O/petroleum ether (0.37 g, 86%); mp 93–95 °C; R_f 0.14 (Et_2O/petroleum ether, 2:1); $[\alpha]_D$ +14.4 (*c* 0.50, $CHCl_3$); IR (KBr) $\tilde{\nu}_{max}$ (cm^{-1}) 3420 (NH), 1745 (C=O), 1365, 1225 (C–N), 1225, 1080 (C–O–C); ^{1}H NMR ($CDCl_3$): δ 8.44 (1H, s, D_2O exchangeable NH), 7.74 (1H, d, $J_{5,6}$ = 7.6 Hz, H-6), 7.33 (2H, m, H-3, H-4), 7.18 (1H, t, $J_{4,5}$ = $J_{5,6}$ = 7.6 Hz, H-5), 6.06 (1H, d, $J_{1',2'}$ = 5.9 Hz, H-1′), 5.73 (1H, t, $J_{2',3'}$ = $J_{1',2'}$ = 5.9 Hz, H-2′), 5.25 (2H, m, H-3′, H-4′), 4.10 (1H, dd, $J_{4',5'}$ = 5.3 Hz, $J_{5',5''}$ = 11.3 Hz, H-5′), 3.82 (1H, dd, $J_{4',5''}$ = 7.0 Hz, $J_{5',5''}$ = 11.3 Hz, H-5′′), 2.24, 2.06, 1.99, 1.96, 1.95, 1.94 (each 3H, 6 s, NHCOCH$_3$, 5 OCOCH$_3$); ^{13}C NMR ($CDCl_3$): δ 170.1, 170.0, 169.8, 169.5, 168.9, 168.5 (5 O*C*OCH$_3$, NH*C*OCH$_3$), 135.4 (C-1), 129.3, 127.9, 125.2 (C-3, C-4, C-5, C-6), 127.0 (C-2), 70.2, 69.3, 68.2, 67.2 (C-1′, C-2′, C-3′, C-4′), 61.4 (C-5′), 23.7, 20.4, 20.2, 20.1, 19.9 (NHCO*C*H$_3$, 5 OCO*C*H$_3$). Anal. Calcd for $C_{23}H_{29}NO_{11}$: C, 55.75; H, 5.90; N, 2.83. Found: C, 55.97; H, 6.06; N, 2.78.

2-(1′,2′,3′,4′,5′-Penta-*O*-acetyl-D-*manno*-pentitol-1′-yl)aniline (8b). By the same procedure as described for the preparation of **8a** and **9e**, 1-(1′,2′,3′,4′,5′-penta-*O*-acetyl-D-*manno*-pentitol-1′-yl)-2-nitrobenzene (**6b**, 0.40 g, 0.83 mmol) yielded **8b** as an oil, which crystallized from Et_2O/petroleum ether (0.25 g, 67%); mp 150–152 °C; R_f 0.15 (Et_2O/petroleum ether, 2:1); $[\alpha]_D$ +67.3 (*c* 0.60, $CHCl_3$); IR (KBr) $\tilde{\nu}_{max}$ (cm^{-1}) 3490, 3440 (NH_2), 3020 (H–C_{ar}), 1750 (C=O), 1375, 1240 (C–N), 1240, 1040 (C–O–C); ^{1}H NMR ($CDCl_3$): δ 7.16 (1H, d, $J_{3,4}$ = 7.5 Hz, H-3), 7.08 (1H, t, $J_{4,5}$ = $J_{5,6}$ = 7.5 Hz, H-5), 6.71 (1H, t, $J_{3,4}$ = $J_{4,5}$ = 7.5 Hz, H-4), 6.62 (1H, d, $J_{5,6}$ = 7.5 Hz, H-6), 5.81 (2H, m, H-1′, H-2′), 5.62 (1H, dd, $J_{2',3'}$ = 1.1 Hz, $J_{3',4'}$ = 9.1 Hz, H-3′), 5.10 (1H, m, H-4′), 4.22 (1H, dd, $J_{4',5'}$ = 2.5 Hz, $J_{5',5''}$ = 12.4 Hz, H-5′), 4.16 (2H, m, 2 NH, D_2O exchangeable), 4.09 (1H, dd, $J_{4',5''}$ = 5.0 Hz, $J_{5',5''}$ = 12.5 Hz, H-5′′), 2.15, 2.07, 2.05, 2.04, 1.79 (each 3H, 5 s, 5 CH_3); ^{13}C NMR ($CDCl_3$): δ 170.4, 169.7, 169.5, 169.0 (O*C*OCH_3), 145.2 (C-1), 129.5, 128.8 (C-3, C-5), 119.5 (C-2), 118.1, 116.6 (C-4, C-6), 69.1, 68.8, 67.9, 67.3 (C-1′, C-2′, C-3′, C-4′), 61.7 (C-5′), 20.6, 20.4, 19.9 (CH_3). Anal. Calcd for $C_{21}H_{27}NO_{10}$: C, 55.62; H, 6.00; N, 3.09. Found: C, 55.87; H, 5.93; N, 3.06.

(2*R*,3*R*,4*S*)-2-[(*S*)-hydroxy[2-nitrophenyl]methyl]tetrahydrofuran-3,4-diol (10) and (2*R*,3*S*,4*R*,5*R*)-2-(hydroxymethyl)-5-(2-nitrophenyl)tetrahydrofuran-3,4-diol (11). To a solution of 2-nitro-1-(D-*galacto*-pentitol-1′-yl)benzene (**6c**; 0.10 g, 0.37 mmol) in *i*-PrOH (10 mL) was added H_2SO_4 (1%, 100 mL), and the mixture was refluxed for 4 days. The reaction mixture was neutralized with saturated aqueous $NaHCO_3$, the solvent was evaporated, and the crude residue was subjected to column chromatography (EtOAc/EtOH, 6:1). Concentration of fractions with R_f 0.71 and 0.64 afforded oils, which were characterized as **10** (0.058 g, 62%) and **11** (0.019 g, 20%), respectively.

10: $[\alpha]_D$ +29.1 (*c* 0.51, DMSO); IR (film) $\tilde{\nu}_{max}$ (cm^{-1}) 3500–3100 (O–H), 3030 (H–C_{ar}), 1540, 1370 (NO_2), 1215, 1095 (C–O); ^{1}H NMR (DMSO-d_6): δ 7.85 (1H, d, $J_{3,4}$ = 8.0 Hz, H-3), 7.81 (1H, d, $J_{5,6}$ = 7.8 Hz, H-6), 7.69 (1H, t, $J_{4,5}$ = $J_{5,6}$ = 7.5 Hz, H-5), 7.50 (1H, t, $J_{4,5}$ = $J_{3,4}$ = 7.8 Hz, H-4), 5.83 (1H, d, *J* = 5.1 Hz, OH, D_2O exchangeable), 5.23 (2H, br s, 2 OH, D_2O exchangeable), 5.19 (1H, d, $J_{1',2'}$ = 3.4 Hz, H-1′), 3.91 (2H, br s, H-3′, H-4′), 3.81 (1H, t, $J_{2',3'}$ = 3.5 Hz, H-2′), 3.77 (1H, dd, $J_{5',5''}$ = 9.1 Hz, $J_{4',5'}$ = 4.2 Hz, H-5′), 3.60 (1H, dd, $J_{4',5''}$ = 2.7 Hz, H-5′′); ^{13}C NMR (DMSO-d_6): δ 148.2 (C-2), 136.9 (C-1), 132.5, 130.2, 128.2, 123.6 (C-3, C-4, C-5, C-6), 87.2 (C-2′), 77.9, 76.6 (C-3′, C-4′), 73.1 (C-5′), 67.4 (C-1′). Anal. Calcd. for $C_{11}H_{13}NO_6$: C, 51.77; H, 5.13; N, 5.49. Found: C, 51.69; H, 5.08; N, 5.45.

11: $[\alpha]_D$ –34.5 (*c* 0.55, DMSO); IR (film) $\tilde{\nu}_{max}$ (cm^{-1}): 3500–3100 (O–H), 3030 (H–C_{ar}), 1545, 1375 (NO_2), 1220, 1150, 1080 (C–O); ^{1}H NMR (DMSO-d_6): δ 7.78 (1H, d, $J_{3,4}$ = 7.8 Hz, H-3), 7.66 (2H, m, H-5, H-6), 7.51 (1H, t, $J_{4,5}$ = $J_{3,4}$ = 7.6 Hz, H-4), 5.17 (1H, d, *J* = 7.1 Hz, 2′-OH, D_2O exchangeable), 5.06 (1H, d, $J_{1',2'}$ = 7.8 Hz, H-1′), 4.99 (1H, d, *J* = 3.4 Hz, 3′-OH, D_2O exchangeable), 4.62 (1H, t, *J* = 4.9 Hz, 5′-OH, D_2O exchangeable), 4.11 (1H, m, H-4′), 4.05 (1H, t, $J_{2',3'}$ = $J_{3',4'}$ = 4.0 Hz, H-3′), 4.00 (1H, dd, $J_{1',2'}$ = 7.8 Hz, $J_{2',3'}$ = 4.0 Hz, H-2′), 3.65 (1H, dd, $J_{5',5''}$ = 10.7 Hz, $J_{4',5'}$ = 5.1 Hz, H-5′), 3.50 (1H, dd, $J_{4',5''}$ = 5.6 Hz, $J_{5',5''}$ = 10.8 Hz, H-5′′); ^{13}C NMR (DMSO-d_6): δ 149.0 (C-2), 139.2 (C-1), 132.4, 128.5, 128.3, 123.6 (C-3, C-4, C-5, C-

6), 82.1, 78.8, 78.2, 71.2 (C-1′, C-2′, C-3′, C-4′), 60 (C-5′). Anal. Calcd. for $C_{11}H_{13}NO_6$: C, 51.77; H, 5.13; N, 5.49. Found: C, 51.60; H, 5.22; N, 5.35.

3-(1′,2′,3′,4′,5′-Penta-*O*-acetyl-D-*galacto*-pentitol-1′-yl)-2-nitrophenol (16a). A mixture of (1*S*,2*R*,3*S*)- and (1*R*,2*R*,3*S*)-3-(1′,2′,3′,4′,5′-penta-*O*-acetyl-D-*galacto*-pentitol-1′-yl)-2-nitrocyclohex-5-en-1-ol[15] (**12a** and **13a**, each 1.00 g, 1.99 mmol) was dissolved in DMSO (12.0 mL) and Ac_2O (7.8 mL). After 24 h, the crude mixture was concentrated affording **16a** as an oil, which was purified by column chromatography (Et_2O/petroleum ether, 1:1) (0.81 g, 82%); R_f 0.21 (Et_2O/petroleum ether, 2:1); $[\alpha]_D$ +20.0 (*c* 0.45, $CHCl_3$); IR (film) $\tilde{\nu}_{max}$ (cm^{-1}): 3340 (OH), 3025 (H–C_{ar}), 1750 (C=O), 1217, 1045 (C–O–C); ^{1}HNMR ($CDCl_3$): δ 9.85 (1H, br s, phenolic OH, D_2O exchangeable), 7.51 (1H, dd, $J_{4,6}$ = 1.1 Hz, $J_{5,6}$ = 7.6 Hz, H-6), 7.33 (1H, t, $J_{5,6}$ = $J_{4,5}$ = 7.6 Hz, H-5), 7.25 (1H, dd, $J_{4,5}$ = 7.6 Hz, $J_{4,6}$ = 1.1 Hz, H-4), 6.60 (1H, d, $J_{1′,2′}$ = 2.0 Hz, H-1′), 5.69 (1H, dd, $J_{2′,3′}$ = 10.0 Hz, $J_{1′,2′}$ = 2.1 Hz, H-2′), 5.62 (1H, dd, $J_{3′,4′}$ = 1.6 Hz, $J_{2′,3′}$ = 9.9 Hz, H-3′), 5.34 (1H, m, H-4′), 4.33 (1H, dd, $J_{4′,5′}$ = 5.0 Hz, $J_{5′,5′′}$ = 11.5 Hz, H-5′), 3.88 (dd, 1 H, $J_{4′,5′′}$ = 4.0 Hz, $J_{5′,5′′}$ = 11.5 Hz, H-5′′), 2.20, 2.18, 2.02, 1.99, 1.79 (each 3H, 5 s, 5 CH_3); ^{13}C NMR ($CDCl_3$): δ 170.4–168.7 (O*C*OCH_3), 152.6 (C-1), 149.6 (C-2), 128.6 (C-3), 125.1 (C-5), 121.4 (C-4), 110.8 (C-6), 69.5, 68.5, 68.1, 67.7 (C-1′, C-2′, C-3′, C-4′), 62.0 (C-5′), 20.7, 20.5, 20.2, 20.1 (CH_3).

1-Acetoxy-3-(1′,2′,3′,4′,5′-penta-*O*-acetyl-D-*galacto*-pentitol-1′-yl)-2-nitrobenzene (17a). Acetylation of **16a** (0.10 g, 0.20 mmol) with pyridine (1.0 mL) and acetic anhydride (0.5 mL) quantitatively gave hexaacetate **17a** as an oil; R_f 0.54 (Et_2O/petroleum ether, 2:1); $[\alpha]_D$ +28.5 (*c* 0.60, $CHCl_3$); IR (film) $\tilde{\nu}_{max}$ (cm^{-1}): 3040 (H–C_{ar}), 1745 (C=O), 1225, 1050 (C–O–C); ^{1}H NMR ($CDCl_3$): δ 7.85 (1H, dd, $J_{4,6}$ = 1.2 Hz, $J_{5,6}$ = 7.7 Hz, H-6), 7.47 (1H, t, $J_{5,6}$ = $J_{4,5}$ = 7.7 Hz, H-5), 7.49 (1H, dd, $J_{4,6}$ = 1.2 Hz, $J_{4,5}$ = 7.6 Hz, H-4), 6.62 (1H, d, $J_{1′,2′}$ = 1.9 Hz, H-1′), 5.71 (1H, dd, $J_{2′,3′}$ = 9.8 Hz, $J_{1′,2′}$ = 2.0 Hz, H-2′), 5.63 (1H, dd, $J_{3′,4′}$ = 1.8 Hz, $J_{2′,3′}$ = 9.8 Hz, H-3′), 5.36 (1H, m, H-4′), 4.38 (1H, dd, $J_{4′,5′}$ = 4.8 Hz, $J_{5′,5′′}$ = 12.0 Hz, H-5′), 3.91 (1H, dd, $J_{4′,5′′}$ = 4.2 Hz, $J_{5′,5′′}$ = 11.8 Hz, H-5′′), 2.27, 2.20, 2.18, 2.02, 1.99, 1.79 (each 3H, 6 s, 6 CH_3); ^{13}C NMR ($CDCl_3$): δ 170.2–168.0 (O*C*OCH_3), 154.6 (C-2), 135.8 (C-1), 130.2 (C-4), 127.7 (C-3), 124.1 (C-5), 116.5 (C-6), 69.1, 68.4, 68.1, 67.6 (C-1′, C-2′, C-3′, C-4′), 62.0 (C-5′), 20.6, 20.5, 20.2, 19.9 (CH_3).

3-(1′,2′,3′,4′,5′-Penta-*O*-acetyl-D-*manno*-pentitol-1′-yl)-2-nitrophenol (16b). Following the procedure described above for the preparation of **16a**, a mixture of (1*S*,2*R*,3*S*)-, (1*R*,2*R*,3*S*)-, (1*R*,2*S*,3*R*)-, and (1*S*,2*S*,3*R*)-3-(1′,2′,3′,4′,5′-penta-*O*-acetyl-D-*manno*-pentitol-1′-yl)-2-nitrocyclohex-5-en-1-ol[15] (**12b**–**15b**) afforded **16b** as an oil, which was purified by column chromatography (Et_2O/petroleum ether, 1:1) (68%); R_f 0.26 (Et_2O/petroleum ether, 2:1); $[\alpha]_D$ –18.0 (*c* 0.50, $CHCl_3$); IR (film) $\tilde{\nu}_{max}$ (cm^{-1}): 3370 (OH), 3030 (H–C_{ar}), 1750 (C=O), 1215, 1065 (C–O–C); ^{1}HNMR ($CDCl_3$): δ 9.93 (1H, br s, phenolic OH, D_2O exchangeable), 7.47 (1H, t, $J_{5,6}$ = $J_{4,5}$ = 7.9 Hz, H-5), 7.19 (1H, t, $J_{4,6}$ = 1.0 Hz, H-6), 7.01 (1H, dd, $J_{4,6}$ = 1.0 Hz, $J_{4,5}$ = 8.0 Hz, H-4), 6.54 (1H, d, $J_{1′,2′}$ = 9.6 Hz, H-1′), 5.64 (1H, dd, $J_{3′,4′}$ = 9.0 Hz, $J_{2′,3′}$ = 1.7 Hz, H-3′), 5.51 (1H, dd, $J_{2′,3′}$ = 1.7 Hz, $J_{1′,2′}$ = 9.6 Hz, H-2′), 5.06 (1H, m, H-4′), 4.22 (1H, dd, $J_{4′,5′}$ = 2.8 Hz, $J_{5′,5′′}$ = 10.5 Hz, H-5′), 4.10 (1H, dd, $J_{4′,5′′}$ = 4.7 Hz, $J_{5′,5′′}$ = 10.5 Hz, H-5′′), 2.19, 2.10, 2.06, 2.02, 1.82, (each 3H, 5 s, 5 CH_3); ^{13}C NMR ($CDCl_3$): δ 170.5, 169.8, 169.6, 169.4, 169.3

(O*C*OCH$_3$), 152.9 (C-1), 147.4 (C-2), 128.6 (C-3), 128.4 (C-5), 121.2 (C-4), 112.8 (C-6), 70.3 (C-1′), 68.2, 67.5, 66.9 (C-2′, C-3′, C-4′), 61.8 (C-5′), 21.0, 20.5, 20.3, 20.1 (CH$_3$).

1-Acetoxy-3-(1′,2′,3′,4′,5′-penta-*O*-acetyl-D-*manno*-pentitol-1′-yl)-2-nitrobenzene (17b). Acetylation of **16b** (0.10 g, 0.20 mmol) with pyridine (1.0 mL) and acetic anhydride (0.5 mL) quantitatively gave hexaacetate **17b** as an oil; R_f 0.57 (Et$_2$O/petroleum ether, 2:1); $[\alpha]_D$ –26.0 (*c* 0.50, CHCl$_3$); IR (film) $\tilde{\nu}_{max}$ (cm^{-1}): 3030 (H–C$_{ar}$), 1750 (C=O), 1225, 1045 (C–O–C); ^{1}HNMR (CDCl$_3$): δ 7.52 (1H, dd, $J_{4,6}$ = 1.2 Hz, $J_{5,6}$ = 7.7 Hz, H-6), 7.58 (1H, t, $J_{5,6}$ = $J_{4,5}$ = 7.6 Hz, H-5), 7.26 (1H, dd, $J_{4,6}$ = 1.2 Hz, $J_{4,5}$ = 7.6 Hz, H-4), 6.55 (1H, d, $J_{1',2'}$ = 9.2 Hz, H-1′), 5.73 (1H, dd, $J_{2',3'}$ = 1.6 Hz, $J_{1',2'}$ = 9.2 Hz, H-2′), 5.63 (1H, dd, $J_{3',4'}$ = 8.8 Hz, $J_{2',3'}$ = 1.6 Hz, H-3′), 5.06 (1H, m, H-4′), 4.24 (1H, dd, $J_{4',5'}$ = 2.8 Hz, $J_{5',5''}$ = 12.1 Hz, H-5′), 4.11 (1H, dd, $J_{4',5''}$ = 4.7 Hz, $J_{5',5''}$ = 12.2 Hz, H-5′′), 2.26, 2.20, 2.19, 2.01, 1.99, 1.80 (each 3H, 6 s, 6 CH$_3$); ^{13}C NMR (CDCl$_3$): δ 170.3–168.1 (O*C*OCH$_3$), 152.3 (C-2), 136.1 (C-1), 128.7 (C-4), 128.3 (C-5), 127.7 (C-3), 118.4 (C-6), 70.0 (C-1′), 68.3, 67.4, 66.7 (C-2′, C-3′, C-4′), 62.0 (C-5′), 20.8, 20.4, 20.4, 20.0 (CH$_3$).

3-Hydroxy-2-nitrobenzaldehyde (16f).[30] To a solution of 3-(1′,2′,3′,4′,5′-penta-*O*-acetyl-D-*galacto*-pentitol-1′-yl)-2-nitrophenol (**16a**, 0.50 g, 1.00 mmol) in MeOH (90%, 15 mL) was added K_2CO_3 (0.50 g, 3.62 mmol). After stirring at room temperature for 24 h, TLC (Et$_2$O-petroleum ether, 2:1) showed complete consumption of **16a** with one product at R_f 0.20 present. Neutralization with Amberlite IR-120 (H$^+$) and evaporation of the solvent gave a colorless oil, which was dissolved in MeOH (50%, 20 mL). The solution was stirred with $NaIO_4$ (1.00 g, 4.67 mmol) at room temperature for 15 min. Then, the mixture was extracted with CH_2Cl_2 (3 x 20 mL), the combined extracts were washed with water (3 x 20mL), dried and evaporated to yield an oil, which was purified by column chromatography (Et$_2$O-petroleum ether, 1.5:1). Crystallization from petroleum ether afforded a solid identified as 3-hydroxy-2-nitrobenzaldehyde (0.090 g, 54%); mp 150–152 ºC (lit.[30] mp 150–151 ºC); R_f 0.29 (Et$_2$O/petroleum ether, 2:1); IR (KBr) $\tilde{\nu}_{max}$ (cm^{-1}): 3600 (OH), 3030 (H–C$_{ar}$), 2815 (C–H aldehyde) 1715 (C=O), 1530, 1330 (NO$_2$); ^{1}H NMR (CDCl$_3$): δ 10.19 (1H, s, C*H*O), 9.75 (1H, s, D$_2$O exchangeable OH), 7.71 (1H, t, $J_{5,6}$ = 7.5 Hz, H-5), 7.62 (1H, d, $J_{5,6}$ = 7.5 Hz, H-6), 7.25 (1H, d, $J_{4,5}$ = 7.5 Hz, H-4); ^{13}C NMR (CDCl$_3$): δ 193.4 (*C*HO), 155.3 (C-3), 140.0 (C-2), 136.2 (C-5), 132.3 (C-1), 124.3, 122,5 (C-4, C-6).

By this procedure, 3-hydroxy-2-nitrobenzaldehyde (**16f**; 61%) was also obtained from **16b**.

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