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Carbohydrate Research 342 (2007) 119–123
Carbohydrate RESEARCH

Note

One-pot synthesis of 2-C-glycosylated benzimidazoles from the corresponding methanal dimethyl acetals

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Received 7 June 2006; received in revised form 16 October 2006; accepted 22 October 2006
Available online 27 October 2006

Abstract—A series of 2-glycosyl-benzimidazoles with α-D-arabinopyranosyl, β-D-galactopyranosyl, β-D-glucopyranosyl, β-D-mannopyranosyl, and β-L-rhamnopyranosyl configurations were obtained in 52–73% yields from the corresponding *C*-glycosylmethanal dimethyl acetals and *o*-phenylenediamine under catalysis with hydrogen chloride or a strongly acidic cation-exchange resin. Intermediate benzimidazolines were spontaneously oxidized by air to produce the final products in the one-pot procedure. The prepared compounds did not show any inhibitory effect on the growth of 12 strains of five different species of pathogenic yeasts.
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Keywords: Benzimidazole, 2-glycosyl; 2,6-Anhydroaldose dimethyl acetal; Strongly acidic cation-exchange resin, catalysis; Benzimidazoline, oxidation; Pathogenic yeasts, growth inhibition effect

The significance of sugar benzimidazoles (BIA) has dramatically increased since the earliest synthesis was described.[1] Initially, benzimidazoles were used for identification and/or isolation of aldoses[2] and aldonic acids.[3] A particular advancement in BIA synthesis has been made since the finding that BIA show an array of pharmacological effects. Some BIA are active against viral enzymes.[4] Imidazoles substituted at C-2 are anticancer agents.[5] BIA, both those with or without a sugar moiety, exhibit antifungal and antibacterial properties.[6] Halogenated BIA are effective agents against amoebae, which can cause serious health damage in humans.[7] Additionally, 2-alkylsulfanyl derivatives of BIA are active against *Mycobacterium tuberculosis*.[8] BIA substituted with a sugar residue at C-2 are potent inhibitors of glycogen phosphorylase and have became the targets for new drug development for treatment of diabetes mellitus.[9]

The wide-spread importance of BIA has led to a correspondingly extensive development of their synthetic methods, which are described in the review.[10] The latest progress in the continuous, yet intensive, area of study has been concisely summarized in recent papers.[11–15] Essentially, 2-substituted BIA are being synthesized by two methods. The first method utilizes an acid-catalyzed condensation of *o*-phenylenediamine (OPD) with carboxylic acids or their derivatives. The second method involves the condensation of aldehydes with OPD followed by oxidation of intermediate benzimidazolines. A significant simplification was introduced using air as oxidant and preferably dioxane as solvent to yield a direct, one-pot synthesis of BIA from substituted aromatic 1,2-diamines and aldehydes.[12]

Both synthetic approaches have also been applied in preparing a C-2 substitution of BIA with a carbohydrate residue. Acid-catalyzed condensations of OPD with either aldonic acids[2] or aldoses in the presence of cupric acetate,[3] providing acyclic sugar BIA, are pioneering works in the field. The first 2-glycosylated BIA, viz. 2-(α-L-arabinofuranosyl)benzimidazole has been obtained by the condensation of OPD with the corresponding intermediate anhydroaldonic acid, which was prepared stepwise from starting 2,5-anhydro-3,4,6-tri-*O*-benzoyl-L-mannose dimethyl acetal by its aldehyde deprotection

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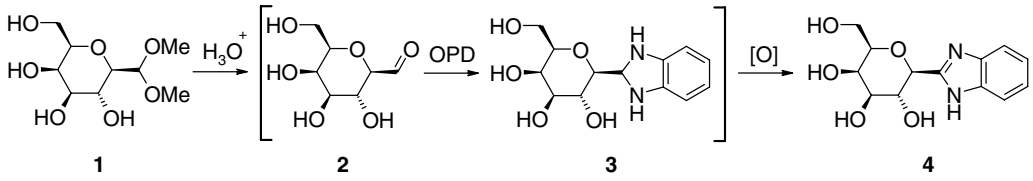
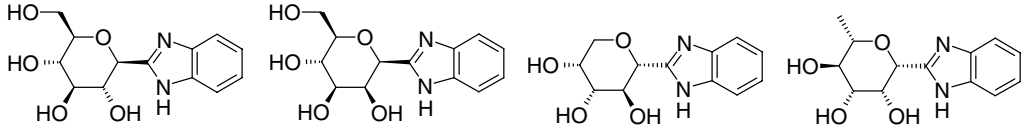
doi:10.1016/j.carres.2006.10.019



Scheme 1.

and oxidation.[16] 2-Glycosylated BIA have also been prepared from the corresponding cyanides, either via intermediate anhydroaldonic acids[17] or thioformimidates.[18] Intramolecular cyclodehydration of acyclic sugar BIA was also employed.[19] Recently, the synthesis of 2-(β-D-glucopyranosyl)benzimidazole from the corresponding carbonitrile oxide and 2-substituted anilines was reported.[20]

This contribution describes a new, one-pot method to synthesize 2-glycosylated BIA by acid-catalyzed condensation of OPD with 2,6-anhydroaldoses (*C*-glycopyranosylmethanals), which were generated in situ from the corresponding dimethyl acetals[†] that are easily available from parent *C*-glycopyranosylnitromethanes (2,6-anhydro-1-deoxy-1-nitroalditols) through a modified Nef reaction.[22] Strongly acidic cation-exchange resin in the H^+ form (or hydrochloric acid) was used as the catalyst for hydrolyzing the starting acetals, as well as for subsequent condensation reactions with OPD, and air oxygen was employed as an oxidant of intermediate benzimidazolines. Also, a screening of the inhibitory effect of the prepared BIA on growth of pathogenic yeasts is described.



Conversion of starting β-D-galactopyranosylmethanal dimethyl acetal (**1**) to 2-(β-D-galactopyranosyl)benzimidazole (**4**, Scheme 1) served as a model transformation. A series of treatments of **1** with a strongly acidic cation-exchange resin in the H^+ form in boiling water or in boiling 1 M HCl and in the presence of an excess of OPD led to almost complete consumption of **1** and moderate (44–58%) yields of **4**. The observation of higher yields following portionwise addition of OPD prompted starting the transformation of **1** with deaerated solvents and catalysts by boiling them prior to addition of reactants in order to avoid evitable oxidative dimerization and polymerization of OPD.[23] This led to an increase in yields of **4** up to 62–73%.

The new method of synthesizing **4** by applying H^+ form to the catalytic resin for the condensation to generated in situ sugar aldehyde **2** with OPD enabled a simple isolation of BIA **4**. This was accomplished by washing the resin, which allowed removal of residual starting sugar, followed by treatment with triethylamine that released a basic product **4** from the resin. Otherwise, when a classic catalysis employing HCl was used, a neutralization and subsequent salt removal was necessary prior to flash chromatography separation of **4** from residual OPD and less-mobile, high-molecular weight by-products, which were not further investigated.

Both optimized procedures were then applied in the preparation of 2-glycosylated BIA **5**–**8**, which were obtained in 52–73% yields. Also, the newly introduced catalysis with H^+ resin gave slightly lower yields (about 10%) in all cases when compared to the classic catalysis of the transformation with HCl, which might have been caused by incomplete desorption of BIA from the resin.

The structures of 2-glycopyranosylated BIA **4** and **6**–**8** were proved by their ^1H and ^{13}C NMR spectra. The chemical shifts of the modified C-2 carbon atoms were observed in the range of δ 153–154, which is the same as the value of the C-2 carbon atom of BIA **5** described previously (δ 153.1).[18] This observation suggests that the final BIA **4**–**8** are the products of oxidation of the respective intermediate benzimidazolines with atmospheric oxygen allowed to interact with the reaction mixture during the course of the condensation, as exemplified for benzimidazoline **3** (Scheme 1). The values of the $J_{1',2'}$ proton–proton coupling constants of the 2-glycosyl moiety prove that their original pyrano-equatorial configurations remained unchanged.

A series of 12 pathogenic yeast strains within five species was used for the examination of their susceptibility against BIA **4**–**8**. It was found that any of these BIA did not cause formation of inhibitory zones at both the con-

[†] Similarly like 2,5-anhydro-3,4,6-tri-*O*-benzoyl-L-mannose dimethyl acetal,[16] a tiophene aldehyde dimethyl acetal has also been used for preparation of the corresponding BIA, however, again in a procedure that first involved isolation of an intermediate aldehyde.[21]

centrations tested and thus, does not have an inhibitory effect on these yeast pathogens. Nevertheless, the results helped us to obtain the first knowledge about the reaction of the yeast strains on the presence of these 2-glycosylated BIA.

1. Experimental

1.1. General methods and materials

Melting points were measured on a Kofler stage. Optical rotations were measured with a Perkin–Elmer 141 polarimeter at 20 °C. Microanalyses were obtained using a Fisons EA-1108 instrument. NMR spectra were recorded at 295 K on a Bruker AVANCE DPX 300 spectrometer [300.13 MHz and internal sodium (trimethylsilyl)propionate-2,2,3,3-d_4, δ 0.00 for ^{1}H; 75.47 MHz and internal MeOH, δ 50.15 for ^{13}C]. Homo- and hetero-nuclear correlation spectroscopy experiments were performed as well. Mass spectra were obtained with a Shimadzu-Kratos Analytical MALDI TOF IV instrument (matrix 2,5-dihydroxybenzoic acid). TLC was run on Merck silica gel 60 F254 pre-coated aluminum plates; visualization of spots was effected by a 254/365 nm UV lamp and by spraying the chromatograms with alkaline silver nitrate. Flash chromatography was performed using an Acros silica gel (0.037–0.075 mm). For chromatographic separations, the solvent mixture (volume ratios) was used: ethyl acetate–butan-1-ol–MeOH–water 18:9:7:3. Starting glycopyranosylmethanal dimethyl acetals with α-D-arabino, β-D-galacto, β-D-gluco, β-D-manno, and β-L-rhamno configurations were prepared according to the published procedure.[22] OPD was recrystallized from hot water. Screening of the inhibitory effect was performed with a series of 12 pathogenic yeast strains of five species: *Candida albicans* CCY 29-3-32, CCY 29-3-104, CCY 29-31-1, CCY 29-31-3, *Candida tropicalis* CCY 29-7-1, CCY 29-7-5, *Cryptococcus neoformans* CCY 17-1-2, CCY 17-1-5, *Malassezia pachydermatis* CCY 85-1-4, CCY 85-1-9, and *Trichosporon cutaneum* CCY 30-5-10, CCY 30-5-31 obtained from Culture Collection of Yeasts, Slovak Academy of Sciences, Bratislava, Slovakia.

1.2. Synthesis of 2-glycosylated BIA using strongly acidic cation-exchange resin in the H^+ form as catalyst (Procedure A)

Nearly saturated methanolic solutions of a *glyco*pyranosylmethanal dimethyl acetal (1.26 mmol; 0.26 g of α-L-arabino, or 0.30 g of β-D-galacto or β-D-gluco or β-D-manno, or 0.28 g of β-L-rhamno) and *o*-phenylenediamine (OPD, 0.12 g, 1.11 mmol) were successively added to a boiling and stirred suspension of Dowex 50 W X-8 (50–100 mesh, H^+ form; 4 mL) in water (14 mL). The suspension was boiled and stirred for 4 h. Two other portions of OPD (each 0.05 g, 0.46 mmol) were added to the suspension at the beginning of the 2nd and 3rd hour of the reaction. Then the liquid phase of the cold suspension was removed by filtration and the resin was washed successively with water and MeOH (each 3×10 mL). The residue (ca. 20 mg) obtained by evaporation of the combined filtrate under reduced pressure contained mostly residual starting sugar acetal. The resin was extracted at 40 °C for 1 h with Et_3N (3×20 mL). The combined extracts were evaporated until a black, partly crystalline syrup formed (ca. 0.35 g). The syrup was dissolved in MeOH (50 mL) and treated with charcoal (5 g). Final filtration and evaporation gave a brown crystalline residue (ca. 0.30 g), which was purified by flash chromatography on a silica gel.

1.3. Synthesis of 2-glycosylated BIA using HCl as catalyst (Procedure B)

The same quantities of a glycopyranosylmethanal dimethyl acetal and OPD and in the same manner as in Procedure A were successively added to a boiling 1 M HCl (5 mL) solution while the reaction mixture was continuously maintained boiling for 4 h. After cooling off, solid $NaHCO_3$ was added until neutral and the final reaction mixture was evaporated under reduced pressure to dryness. The residue was triturated with MeOH (3×20 mL) and the combined extracts were further worked up as in Procedure A.

1.4. 2-(β-D-Galactopyranosyl)benzimidazole (4)

Yield 0.19 g (54%, A), 0.26 g (73%, B); mp 220–222 °C (dec; MeOH); $[\alpha]_D^{20}$ +31 (*c* 0.5, MeOH); R_f 0.37; ^{1}H NMR (MeOH-d_4), δ 7.52–7.59 (m, 2H, H-4, H-7), 7.20–7.27 (m, 2H, H-5, H-6), 4.45 (d, 1H, $J_{1',2'}$ 9.7 Hz, H-1′), 3.94–4.02 (m, 2H, H-2′, H-4′); 3.82 (dd, 1H, $J_{5',6'a}$ 8.4 Hz, $J_{6'a,6'b}$ 12.3 Hz, H-6′a), 3.71–3.78 (m, 2H, H-5′, H-6′b), 3.65 (dd, 1H, $J_{2',3'}$ 9.4 Hz, $J_{3',4'}$ 3.2 Hz, H-3′); ^{13}C NMR (MeOH-d_4), δ 154.0 (C-2), 139.2 (C-3a, C-7a), 123.7 (C-5, C-6), 116.0 (C-4, C-7), 81.1 (C-5′), 78.1 (C-1′), 76.0 (C-3′), 71.9 (C-2′), 71.0 (C-4′), 63.0 (C-6′); MALDI-TOFMS, *m*/*z* 281.2 $[M+H]^+$, 303.2 $[M+Na]^+$, 319.3 $[M+K]^+$. Anal. Calcd for $C_{13}H_{16}N_2O_5$: C, 55.71; H, 5.75; N, 9.99. Found: C, 55.52; H, 5.85; N, 9.79.

1.5. 2-(β-D-Glucopyranosyl)benzimidazole (5)

Yield 0.19 g (54%, A), 0.25 g (70%, B); mp 267–268 °C (dec; MeOH); $[\alpha]_D^{20}$ +26 (*c* 0.5, MeOH), lit.[18] +25; R_f 0.56; ^{1}H NMR (MeOH-d_4), δ 7.53–7.60 (m, 2H, H-4, H-7), 7.19–7.26 (m, 2H, H-5, H-6), 4.50 (d, 1H, $J_{1',2'}$ 9.5 Hz, H-1′), 3.90 (dd, 1H, $J_{5',6'a}$ 1.5 Hz, $J_{6'a,6'b}$ 11.9 Hz, H-6′a), 3.76 (dd, 1H, $J_{5',6'b}$ 4.5 Hz, H-6′b),

3.65 (t, 1H, $J_{2',3'}$ 8.7 Hz, H-2′), 3.45–3.60 (m, 3H, H-3′, H-4′, H-5′); ^{13}C NMR (MeOH-d_4), δ 153.9 (C-2), 139.2 (C-3a, C-7a), 123.7 (C-5, C-6), 116.1 (C-4, C-7), 82.2 (C-4′), 79.3 (C-3′), 77.4 (C-1′), 74.9 (C-2′), 71.3 (C-5′), 62.8 (C-6′); MALDI-TOFMS, *m*/*z* 281.0 $[M+H]^+$, 303.1 $[M+Na]^+$, 319.1 $[M+K]^+$.

1.6. 2-(β-D-Mannopyranosyl)benzimidazole (6)

Yield 0.20 g (56%, A), 0.23 g (65%, B); mp 249–250 °C (dec; MeOH); $[\alpha]_D^{20}$ +52 (*c* 0.5, MeOH); R_f 0.52; ^{1}H NMR (MeOH-d_4), δ 7.51–7.58 (m, 2H, H-4, H-7), 7.18–7.25 (m, 2H, H-5, H-6), 4.91 (d, 1H, $J_{1',2'}$ 1.2 Hz, H-1′), 4.33 (dd, 1H, $J_{2',3'}$ 2.9 Hz, H-2′), 3.98 (dd, 1H, $J_{5',6'a}$ 2.4 Hz, $J_{6'a,6'b}$ 11.9 Hz, H-6′a), 3.84 (dd, 1H, $J_{5',6'b}$ 5.9 Hz, H-6′b), 3.72 (dd, 1H, $J_{3',4'}$ 9.4 Hz, H-3′), 3.70 (t, 1H, $J_{4',5'}$ 9.4 Hz, H-4′), 3.47–3.51 (m, 1H, H-5′); ^{13}C NMR (MeOH-d_4), δ 154.0 (C-2), 139.5 (C-3a, C-7a), 123.5 (C-5, C-6), 115.8 (C-4, C-7), 82.3 (C-5′), 77.1 (C-1′), 75.9 (C-4′), 72.8 (C-2′), 68.4 (C-3′), 63.1 (C-6′); MALDI-TOFMS, *m*/*z* 281.3 $[M+H]^+$, 303.2 $[M+Na]^+$, 319.1 $[M+K]^+$. Anal. Calcd for $C_{13}H_{16}N_2O_5$: C, 55.71; H, 5.75; N, 9.99. Found: C, 55.44; H, 5.95; N, 9.72.

1.7. 2-(α-D-Arabinopyranosyl)benzimidazole (7)

Yield 0.19 g (61%, A), 0.22 g (70%, B); mp 245–246 °C (dec; MeOH); $[\alpha]_D^{20}$ −36 (*c* 0.5, MeOH); R_f 0.50; ^{1}H NMR (MeOH-d_4), δ 7.53–7.60 (m, 2H, H-4, H-7), 7.20–7.27 (m, 2H, H-5, H-6), 4.36 (d, 1H, $J_{1',2'}$ 9.6 Hz, H-1′), 4.04 (dd, 1H, $J_{4',5'a}$ 2.1 Hz, $J_{5'a,5'b}$ 12.4 Hz, H-5′a), 3.94–4.02 (m, 2H, H-2′, H-4′), 3.78 (dd, 1H, $J_{4',5'b}$ 1.0 Hz, H-5′b), 3.66 (dd, 1H, $J_{2',3'}$ 9.3 Hz, $J_{3',4'}$ 3.3 Hz, H-3′); ^{13}C NMR (MeOH-d_4), δ 153.9 (C-2), 139.3 (C-3a, C-7a), 123.7 (C-5, C-6), 116.1 (C-4, C-7), 78.6 (C-1′), 75.4 (C-3′), 72.0 (C-5′), 71.8 (C-2′), 70.8 (C-4′); MALDI-TOFMS, *m*/*z* 250.9 $[M+H]^+$, 273.0 $[M+Na]^+$, 289.0 $[M+K]^+$. Anal. Calcd for $C_{12}H_{14}N_2O_4$: C, 57.59; H, 5.64; N, 11.19. Found: C, 57.90; H, 5.59; N, 10.93.

1.8. 2-(β-L-Rhamnopyranosyl)benzimidazole (8)

Yield 0.17 g (51%, A), 0.22 g (66%, B); mp 234–235 °C (dec; MeOH); $[\alpha]_D^{20}$ −52 (*c* 0.5, MeOH); R_f 0.59; ^{1}H NMR (MeOH-d_4), δ 7.63–7.70 (m, 2H, H-4, H-7), 7.36–7.43 (m, 2H, H-5, H-6), 5.04 (d, 1H, $J_{1',2'}$ 1.3 Hz, H-1′), 4.28 (dd, 1H, $J_{2',3'}$ 3.3 Hz, H-2′), 3.67 (dd, 1H, $J_{3',4'}$ 9.2 Hz, H-3′), 3,46–3.54 (m, 2H, H-4′, H-5′), 1.46 (d, 3H, *J* 5.7 Hz, H-6′a, H-6′b, H-6′c); ^{13}C NMR (MeOH-d_4), δ 153.3 (C-2), 135.7 (C-3a, C-7a), 125.3 (C-5, C-6), 115.4 (C-4, C-7), 78.5 (C-4′), 76.1 (C-1′), 75.4 (C-3′), 73.6 (C-5′), 72.8 (C-2′), 18.4 (C-6′); MALDI-TOFMS, *m*/*z* 265.3 $[M+H]^+$, 287.3 $[M+Na]^+$, 303.2 $[M+K]^+$. Anal. Calcd for $C_{13}H_{16}N_2O_4$: C, 59.08; H, 6.10; N, 10.60. Found: C, 58.90; H, 6.33; N, 10.41.

1.9. Screening of the inhibitory effect of BIA 4–8 on the growth of pathogenic yeasts

The effect of BIA **4**–**8** on growth of the 12 pathogenic yeast strains introduced in the methods and materials section was studied on agar plates containing malt agar and suspension of the yeast strain tested (10^6 cells per mL). Sterile filter paper disks soaked with BIA solutions in EtOH were dried and then placed on the agar surfaces and inhibitory zones of a restricted growth of the yeast strains were evaluated after 3 and 5 days of cultivation at 28 and 37 °C. Two concentrations (1% and 0.5%, weight per volume) were examined. The growth medium was sterilized by autoclaving at 121 °C. Ethanolic solutions of BIA **4**–**8** were sterilized by filtration.

Acknowledgements

This work was supported in part by the APVT-51-039802 and VEGA-2/6129/26 grants.

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