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Synthesis of 2-mercaptobenzothiazole and 2-mercaptobenzimidazole derivatives condensed with carbohydrates as a potential antimicrobial agents

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The thiazole and imidazole nucleus, as well as carbohydrates are important classes of compounds found in many natural and synthetic products with a wide range of biological activities. Due to the importance of these classes of compounds as antimicrobial agents, the present article reports the synthesis of a new series of nine compounds based on the coupling of 2-mercaptobenzothiazole and 2-mercaptobenzimidazole with different carbohydrates.

Keywords: Antimicrobial agents; 2-Mercaptobenzothiazole; 2-Mercaptobenzimidazole; Carbohydrates

1. Introduction

The classes of heterocyclic compounds known as thiazole and imidazole (figure 1) are found in many natural and synthetic products with a wide range of biological activities, such as antiviral, anticancer, antibacterial, antifungal, anticonvulsant, anti-Parkinsonian and anti-inflammatory activities that can be well illustrated by the large number of drugs in the market containing this nucleus [1, 2]. Thiazole **1** and imidazole **2** rings also find important applications in other fields, such as polymers [3], liquid crystals [4], photonucleases [5], fluorescent dyes [6, 7], insecticides [8] and antioxidants [9]. In the case of natural products, thiazole and imidazole rings [1, 2] are present as subunit in a large number of terrestrial and marine compounds, with different biological activities that represent a very important field in drug discovery.

Although not present in every bacterial species, the cell wall is very important as a cellular component. For example, in the bacteria *Mycobacterium tuberculosis*, the cell wall is extremely hydrophobic and forms an exceptionally strong permeability barrier rendering mycobacteria naturally resistant, protecting this bacterium to a wide variety of antimicrobial agents [10, 11]. The constituents of cell walls including predominantly galactose and

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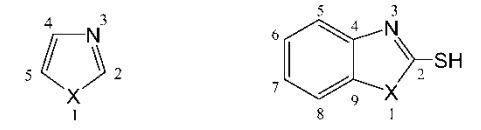


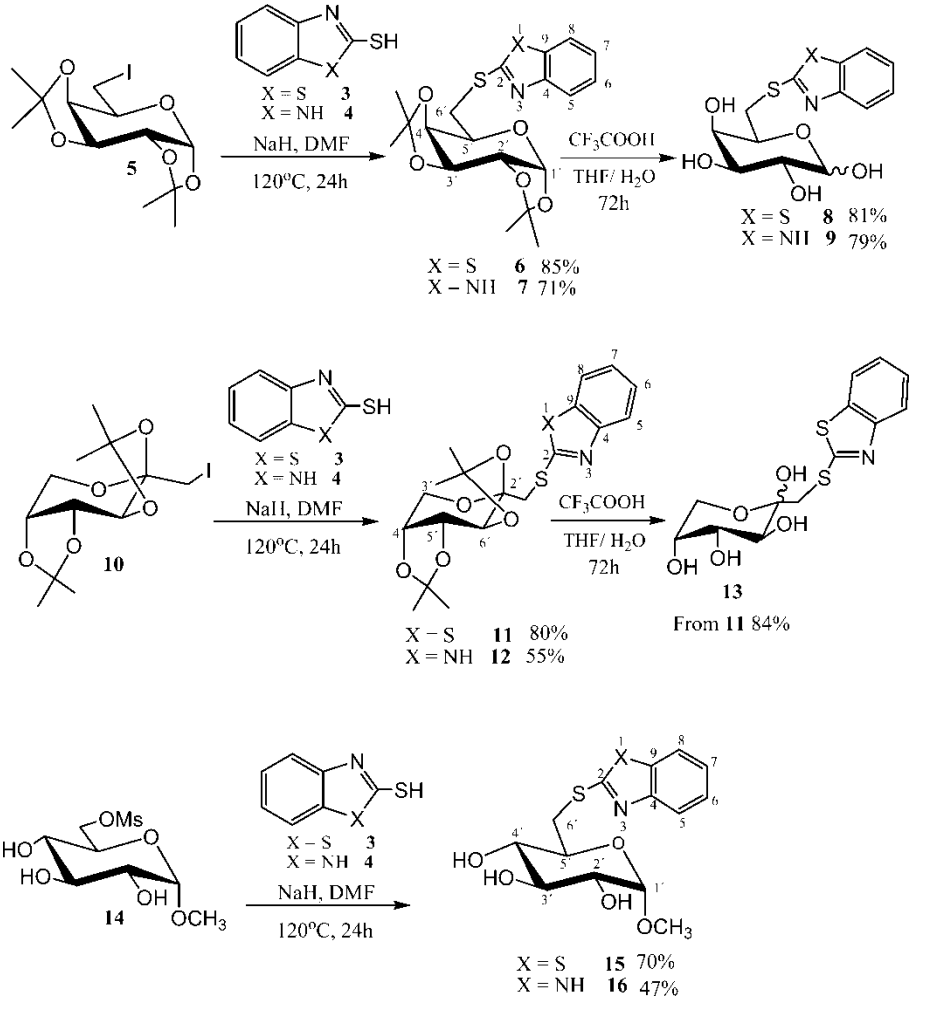
X – S - Thiazole **1**
X = N - Imidazole **2**

X = S 2-mercaptobenzothiazole **3**
X = NH 2-mercaptobenzoimidazole **4**

Figure 1. Thiazoles and imidazoles.

arabinose, mainly present as arabino-D-galactan and lipoarabinomannans are important targets for selective drug discovery against mycobacteria species [12, 13].

Due to the importance of the thiazole and imidazole nucleus and carbohydrate derivatives as antimicrobial agents, we report the synthesis of a series of nine compounds based on the coupling of 2-mercaptobenzothiazole **3** and 2-mercaptobenzimidazole **4** with different carbohydrates (scheme 1).



SCHEME 1

2. Results and discussion

The 2-mercaptobenzothiazole and 2-mercaptobenzimidazole derivatives **6–9**, **11–13**, **15** and **16** were prepared in 47–85% yield by reacting 2-mercaptobenzothiazole **3** and 2-mercaptobenzimidazole **4** with carbohydrates **5**, **10** and **14** in presence of sodium hydride in *N,N*-dimethylformamide at 120 °C for 24 hours (scheme 1). In all cases the best yields were obtained when 2-mercaptobenzothiazole **3** was used as nucleophilic species. This could be explained by the dimerization of 2-mercaptobenzimidazole **4** observed in the reactions involving this compound. Carbohydrates **5**, **10** and **14** were prepared by classical carbohydrate chemistry methods. The compounds **5** and **10** were obtained in 78% and 90% overall yield by reacting D-galactose and D-fructose, respectively, with zinc chloride, sulfuric acid and acetone [14] followed by iodination at C-6 position (for galactose) and at C-1 position (for fructose) by treatment with triphenylphosphine, iodine and imidazole in toluene [15]. Carbohydrate **14** was obtained in 40% yield by reaction of methyl α-D-glucopyranoside with methanesulfonyl chloride in pyridine [16]. The methyl-2,3,4-tri-*O*-acetyl-6-deoxy-6-iodo-α-D-glucopyranoside have also been prepared and its reaction with 2-mercaptobenzothiazole **3** and 2-mercaptobenzimidazole **4** in the same conditions described above gave a mixture of compounds, which have not been isolated and identified. This observation is probably due to hydrolysis of the acetyl group present in the starting material.

3. Conclusions

The present article has reported an efficient synthesis in satisfactory yield of a new series of nine compounds based on the coupling of 2-mercaptobenzothiazole and 2-mercaptobenzimidazole with different carbohydrates.

4. Experimental

Melting points were determined with a Thomas-Hoover apparatus and are uncorrected. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were determined in deuterated solvents containing *ca.* 1% tetramethylsilane as an internal standard on a Bruker DRX 300 spectrometers. Coupling constants (J) are given in Hertz (Hz). The $[\alpha]_D$ were recorded on Perkin-Elmer 241-MC sodium absorption at 20 °C. Infrared spectra were obtained on a Bomem FT IR MB-102 spectromer in KBr pellets. Elemental analyses were carried at University of São Paulo (USP).

The progress of all reactions was monitored by thin-layer chromatography, which was performed on 2.0 cm × 6.0 cm aluminum sheets precoated with silica gel 60 (HF-254, Merck) to a thickness of 0.25 mm. The developed chromatograms were viewed under an ultraviolet light. For column chromatography, Merck silica gel (70–230 mesh) was used. Solvents used in the reactions were generally redistilled prior to use.

4.1 *General procedure to prepare compounds 6, 7, 11, 12, 15 and 16*

To a solution of 2-mercaptobenzothiazole **3** or 2-mercaptobenzimidazole **4** (3.3 mmol) in anhydrous DMF (5 mL) was added at 0 °C sodium hydride 60% dispersion in mineral oil (3.3 mmol). After ten minutes under stirring at room temperature a solution of the respective carbohydrate (3 mmol) in DMF (5 mL) was added. The reaction mixture was stirred at 120 °C

for 24 hours, water was added (20 mL), and extracted with ether (3 × 50 mL). The organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure to furnish a crude residue. Purification by flash chromatography using as eluent a gradient of hexane and ethyl acetate gave the desired products **6** (1.05 g, 85%), **7** (0.84 g, 71%), **11** (0.92 g, 80%), **12** (0.66 g, 55%), **15** (0.72 g, 70%) and **16** (0.51 g, 47%).

4.1.1 6′-Deoxy-1′,2′,3′,4′-di-*O*-isopropylidene-6′-*S*-(2-mercaptobenzothiazoyl)-α-D-galactopyranose (6). Yield 85%, $[\alpha]_D = -72,4$ (*c* 1.0, CH_2Cl_2); IR (KBr) 3061, 2985, 2936 and 1068 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.41–1.21 (s, 12H, 4 CH_3 isoprop.), 3.47–3.49 (d, 2H, $H_{6'}$, $H_{6''}$, $J = 6.9$), 4.24 (dd, 1H, $H_{2'}$ $J = 2.4, 5.0$), 4.28 (m, 1H, $H_{5'}$), 4.37 (dd, 1H, $H_{4'}$, $J = 7.9, 1.7$), 4.58 (dd, 1H, $H_{3'}$, $J = 7.9, 2.4$), 5.49 (d, 1H, $H_{1'}$, $J = 5.0$), 7.17 (ddd, 1H, H_7, $J = 8.0, 7.3, 1.3$), 7.33 (ddd, 1H, H_6, $J = 8.0, 7.3, 1.3$), 7.64 (dd, 1H, H_8, $J = 8.0, 1.3, 0.6$), 7.76 (ddd, 1H, H_5, $J = 8.0, 1.3, 0.6$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.0–26.5 (4 CH_3), 41.3 (C-6′), 61.2 (C-4′), 70.4 (C-2′), 70.8 (C-5′), 72.7 (C-3′), 102.6 (C-1′), 108.9 and 109.3 (C isoprop.), 121.1 and 121.4 (C-8, C-5), 124.3 and 126.0 (C-6, C-7), 136.0 (C-9), 153.0 (C-4), 167.0 (C-2). C H N (%): found C 55.99, H 5.97, N 3.25; $C_{19}H_{23}NO_5S_2$ requires C 55.70, H 5.68, N 3.42.

4.1.2 6′-Deoxy-1′,2′,3′,4′-di-*O*-isopropylidene-6′-*S*-(2-mercaptobenzimidazoyl)-α-D-galactopyranose (7). Yield 71%, m.p. (90–93 °C); $[\alpha]_D = -71,9$ (*c*1.0, CH_2Cl_2); IR (KBr) 3600–3200, 3066, 2935, 2904 and 1070–1000 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.56–1.23 (s, 12H, 4 CH_3), 3.45 (dd, 1H, $H_{6'}$ or $H_{6''}$, $J = 14.0, 5.5$), 3.55 (dd, 1H, $H_{6'}$ or $H_{6''}$, $J = 14.0, 8.0$), 4.22 (m, 1H, $H_{5'}$), 4.34 (dd, 1H, $H_{2'}$, $J = 5.0, 2.4$), 4.42 (dd, 1H, $H_{4'}$, $J = 8.0, 1.7$), 4.65 (dd, 1H, $H_{3'}$, $J = 8.0, 2.4$), 5.56 (d, 1H, $H_{1'}$, $J = 5.0$), 7.16–7.22 (m, 2H, H_6, H_7), 7.54–7.49 (m, 2H, H_5, H_8); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.5–26.2 (4 CH_3), 32.9 (C-6′), 67.5 (C-5′), 70.7 (C-4′), 70.9 (C-3′), 71.8 (C-2′), 96.8 (C-1′), 109.3 and 109.7 (C isoprop.), 114.3 (C-5, C-8), 122.7 (C-6, C-7), 138.9 (C-4, C-9), 150.0 (C-2). C H N (%): found C 58.30, H 5.90, N 7.24; $C_{19}H_{24}N_2O_5S$ requires C 58.10, H 6.16, N 7.14.

4.1.3 1′-Deoxy-2′,3′,4′,5′-di-*O*-isopropylidene-1′-*S*-(2-mercaptobenzothiazoyl)-β-D-fructopyranose (11). Yield 80%, $[\alpha]_D = -7.05$ (*c* 2.0, CH_2Cl_2); IR (KBr) 3062, 2988, 2935 and 992–1067 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.56–1.29 (s, 12H, 4 CH_3 isoprop.), 3.98–3.78 (m, 4H, $H_{1'-1''}$ and $H_{6'-6''}$), 4.26 (dd, 1H, H'_5, $J = 7.8, 2.5$), 4.39 (d, 1H, $H_{3'}$, $J = 2.5$), 4.69 (dd, 1H, $H_{4'}$, $J = 7.8, 2.5$), 7.23 (ddd, 1H, H_7, $J = 7.9, 7.3, 1.3$), 7.35 (ddd, 1H, H_6, $J = 7.9, 7.3, 1.3$), 7.68 (ddd, 1H, H_8, $J = 7.9, 1.3, 0.8$), 7.76 (ddd, 1H, H_5, $J = 7.9, 1.3, 0.8$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.5–26.7 (4 CH_3), 41.5 (C-1′), 61.9 (C-6′), 70.6 (C-5′), 70.7 (C-4′), 70.9 (C-3′), 72.9 (C-2′), 109.5 (C isoprop.), 121.3 (C-8), 121.7 (C-5), 124.4 (C-7), 126.2 (C-6), 135.8 (C-9), 153.3 (C-4), 167.4 (C-2). C H N (%): found C 56.04; H 5.24, N 3.29; $C_{19}H_{23}NO_5S_2$ requires C 55.70, H 5.66, N 3.42.

4.1.4 1′-Deoxy-2′,3′,4′,5′-di-*O*-isopropylidene-1′-*S*-(2-mercaptobenzimidazoyl)-β-D-fructopyranose (12). Yield 55%, IR (KBr) 3052, 2987, 2937 and 1067 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.27–1.56 (4s, 12H, 4 CH_3 isoprop.), 3.48 (d, 1H, $H_{1''}$, $J = 14.8$), 3.67 (d, 1H, $H_{1'}$, $J = 14.8$), 3.94 (d, 1H, $H_{6'}$, $J = 13.0$), 4.07 (d, 1H, $H_{6''}$, $J = 13.0$), 4.31 (dd, 1H, H'_5, $J = 7.9, 2.4$), 4.33 (d, 1H, $H_{3'}$, $J = 2.4$), 4.67 (dd, 1H, H'_4, $J = 7.9, 2.4$), 7.16–7.21 (m, 2H, H-6, H-7), 7.47–7.51 (m, 2H, H-5, H-8); ^{13}C NMR (75 MHz; $CDCl_3$) δ 19.0–21.4 (4 CH_3), 36.7 (C-1′), 56.4 (C-6′), 65.0 (C-5′), 65.3 (C-4′), 67.7 (C-3′), 97.1 (C-2′), 104.1 (C-5,

C-8), 109.5 (C isoprop.), 117.2 (C-6, C-7), 134.0 (C-4, C-9), 145.5 (C-2). C H N (%): found C 55.30, H 6.57, N 6.77; $C_{19}H_{24}N_2O_5S \cdot H_2O$ requires C 55.60, H 6.34, N 6.82.

4.1.5 Methyl 6′-deoxy-6′-*S*-(2-mercaptobenzothiazoyl)-α-D-glucopyranoside (15). Yield 70%, m.p. (90–93°C); $[\alpha]_D = +98.3$ (*c* 1.0, MeOH); IR (KBr) 3471–3000, 2917, 2844, 1426, 1046 and 751 cm^{-1}; ^1H NMR (300 MHz, DMSO d_6) δ 3.42 (s, 3H, OCH_3), 3.34 (t, 1H, H'_3, $J = 9.2$), 3.49 (dd, 1H, H'_2, $J = 9.6, 3.3$), 3.58 (m, 1H, $H_{5'}$), 3.68 (t, 1H, $H_{4'}$ $J = 9.1$), 3.97–3.86 (m, 2H, $H_{6'}$, $H_{6''}$), 4.69 (d, 1H, $H_{1'}$, $J = 3.6$), 7.46–7.34 (m, 2H, H_6, H_7), 7.86 (t, 2H, H_5, H_8, $J = 7.7$); ^{13}C NMR (75 MHz, DMSO d_6) δ 36.9 (C-6′), 55.8 (OCH_3), 71.8 (C-4′), 73.6 (C-2′), 74.8 (C-5′), 75.0 (C-3′), 101.4 (C-1′), 122.1 (C-5), 122.4 (C-8), 125.9 (C-6), 127.5 (C-7), 136.3 (C-9), 154.2 (C-4), 169.9 (C-2). C H N (%): found C 46.65, H 4.77, N 4.08; $C_{14}H_{17}NO_5S_2$ requires C 46.96, H 4.99, N 4.08.

4.1.6 Methyl 6′-deoxy-6′-*S*-(2-mercaptobenzimidazoyl)-α-D-glucopyranoside (16). Yield 47%, m.p. (106–108°C); $[\alpha]_D = +38.6$ (*c* 1.1, MeOH). IR (KBr) 3381–3000, 2929, 2838, 1440, 1408, 1049 and 744 cm^{-1}; ^1H NMR (300 MHz, D_2O) δ 3.20 (s, 4H, $H_{3'}$, OCH_3), 3.31 (t, 1H, H'_4, $J = 9.5$), 3.45 (dd, 1H, H'_2, $J = 9.6, 3.7$), 3.60–3.51 (m, 2H, $H_{6'}$, $H_{6''}$), 3.74 (m, 1H, $H_{5'}$), 4.57 (d, 1H, $H_{2'}$, $J = 3.6$), 4.69 (d, 1H, $H_{1'}$, $J = 3.6$), 7.06–7.10 (m, 2H, H_6, H_7), 7.31–7.28 (m, 2H, H_5, H_8); ^{13}C NMR (75 MHz, D_2O) δ 36.3 (C-6′), 57.5 (OCH_3), 72.7 (C-4′), 73.8 (C-2′), 74.8 (C-5′), 75.3 (C-3′), 101.8 (C-1′), 116.3 (C-8, C-5), 125.2 (C-7), 140.6 (C-4, C-6), 153.1 (C-2). C H N (%): found C 46.25, H 5.81, N 7.29; $C_{14}H_{18}N_2O_5S \cdot 2H_2O$ requires C 46.40, H 6.07, N 7.73.

4.2 *General procedure to prepare compounds 8, 9 and 13*

To a solution of compounds **6**, **7** or **11** (1.0 mmol) in THF (5 mL) was slowly added a solution of CF_3CO_2H/H_2O (9:1) (2 mL). The reaction was stirred 96 hours at room temperature, in the case of the compounds **6** and **7** and 12 hours at 60 °C for compound **11**. The reaction mixture was evaporated under reduced pressure and the crude residue was purified by flash chromatography using a mixture of CH_2Cl_2/MeOH as eluent to furnish compounds **8** (0.27 g, 81%), **9** (0.26 g, 79%) and **13** (0.27 g, 84%).

4.2.1 6′-Deoxy-6′-*S*-(2-mercaptobenzothiazoyl)-D-galactopyranose (8). Yield 81%, m.p. (185–189 °C); IR (KBr) 3347, 2935, 2852, 1456, 1427, 1067 and 1003 cm^{-1}; ^1H NMR (300 MHz, DMSO d_6) δ 2.49–4.14 (m, 18H, $H_{2'}$, $H_{6'}$ and OH), 4.22 (d, 1H, $H_{1'\beta}$, $J = 6.8$), 4.95 (d, 1H, $H_{1'\alpha}$, $J = 2.8$), 7.31–7.47 (m, 4H, $H_{6\alpha\beta}$, $H_{7\alpha\beta}$), 7.82–7.99 (m, 4H, $H_{5\alpha\beta}$, $H_{8\alpha\beta}$); ^{13}C NMR (75 MHz, DMSO d_6) δ 43.6 (C-6′α), 43.8 (C-6′β), 78.0 (C-4′$\alpha\beta$), 78.7 (C-2′α), 79.1 (C-3′β), 79.8 (C-5′α), 81.3 (C-5′β), 82.2 (C-3′α), 82.8 (C-3′β), 102.5 (C-1′α), 107.2 (C-1′β), 131.4 and 130.7 (C-5, C-8), 136.0 and 134.1 (C-6, C-7), 144.2 (C-9), 162.3 (C-4), 176.6 (C-2). C H N (%): found C 47.75, H 4.89, N 4.16; $C_{13}H_{15}NO_5S_2 \cdot 2H_2O$ requires C 47.41, H 4.55; N 4.25.

4.2.2 6′-Deoxy-6′-*S*-(2-mercaptobenzimidazoyl)-D-galactopyranose (9). Yield 79%, IR (KBr) 3600–3200, 2929, 1441, 1390, 1100-1000 cm^{-1}; ^1H NMR (300 MHz, CD_3OD) δ 2.0 (s, 8H, OH), 3.24–4.17 (m, 12H, $H_{2'}$-$H_{6'}$), 4.87 (s, 1H, $H_{1'\beta}$), 5.12 (d, 1H, $H_{1'\alpha}$ $J = 3.0$),

7.13–7.41 (m, 4H, $H_{5\alpha,\beta}$-$H_{8\alpha,\beta}$); ^{13}C NMR (75 MHz, CD_3OD) δ 36.1 (C-6′β, C-6′α), 47.6–68.4 (C-2′α, β-C-5′α, β), 97.6 (C-1′α), 101.8 (C-1′β), 113.6 (C-6, C-7), 123.37 (C-5, C-8), 142.0 (C-4, C- 9), 150.8 (C-2).

4.2.3 1′-Deoxy-1′-*S*-(2-mercaptobenzothiazoyl)-D-fructopyranose (13). Yield 84%, IR (KBr) 3663, 2922, 2852 and 1100–1000 cm^{-1}; ^{1}H NMR (300 MHz, CD_3OD) δ 3.23–3.96 (m, 14H, $H_{1',1'',2',3',5',6',6''}$), 4.87 (m, 1H, $H_{4'}$), 7.28–7.39 (m, 2H, H_6, H_7), 7.73–7.80 (m, 2H, H_5-H_8); ^{13}C NMR (75 MHz, CD_3OD) δ 38.1 (C-1′), 64.9 (C-6′), 71.1–71.6 (C-3′-C-5′), 99.0 (C-2), 100.0 (C-2′), 121.9–122.5 (C-5, C-8), 125.9–127.6 (C-6, C-7), 155.0 (C-4, C-9).

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