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RESEARCH ARTICLE

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Thiazoles in glycosylation reactions: Novel synthesis of thiazole thioglycosides

Mamdouh A. Abu-Zaied[1] | **Galal H. Elgemeie**[2]

[1]Green Chemistry Department, National Research Centre, Giza, Egypt

[2]Chemistry Department, Faculty of Science, Helwan University, Helwan, Cairo, Egypt

Correspondence
Galal H. Elgemeie, Chemistry Department, Faculty of Science, Helwan University, Helwan, Cairo, Egypt.
Email: elgemeie@yahoo.com

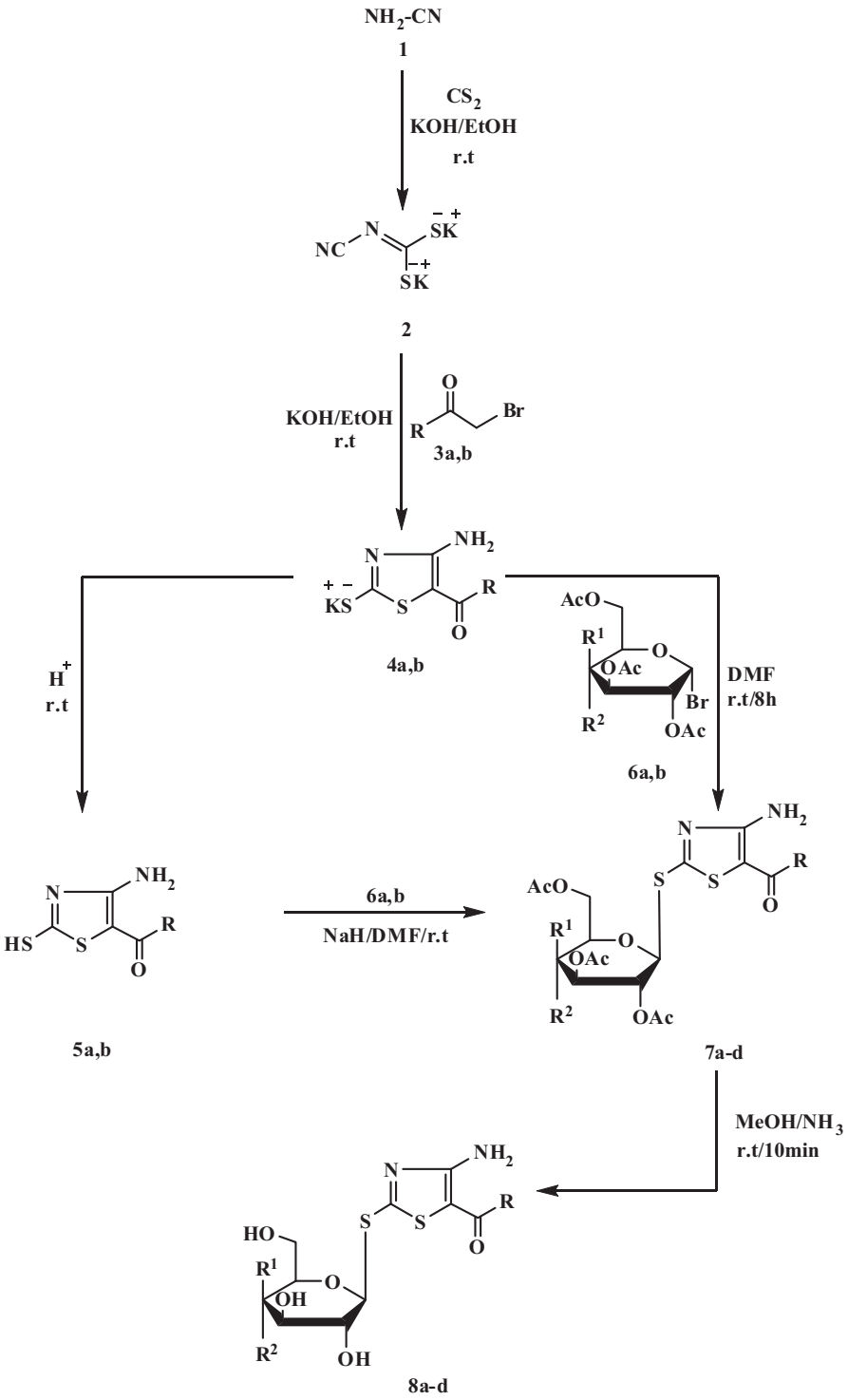
Abstract

This research reports a novel method for synthesizing new thiazole thioglycosides. This series of thiazole thioglycosides were designed by the reaction of potassium cyanocarbonimidodithioate **2** with benzoyl acetonitrile **3a** and ethyl bromoacetate **3b** in the presence of ethanol-KOH to give the corresponding potassium 4-amino-5-sub stituted-thiazole-2-thiolates **4a,b**. The latter compounds were treated with peracetylated sugar bromides **6a,b** in DMF to give high yields of the corresponding thiazole thioglycosides **7a-d**. Treatment of thiazole salts **4a,b** with hydrochloric acid gave the corresponding 3-mercaptothiazole derivatives **5a,b**. The latter compounds were reacted with peracetylated sugars **6** in sodium hydride in DMF to produce the *S*-glycosyl compounds **7a-d**. Ammonolysis of the protected thiazole thioglycosides **6a-h** gave the corresponding free thiazole thioglycosides **8a-d**. The compounds have been characterized by ^{13}C NMR, ^{1}H NMR, and IR.

1 | INTRODUCTION

The thiazole nucleus plays an important role in medicinal chemistry, making it one of the intensively studied heterocycles.[1] Tiazofurin (2-(β-D-ribofuranosyl)thiazole) is a well-known synthetic C-nucleoside with interesting anticancer activity in a variety of tumor systems (Figure 1).[2] The Tiazofurin biological activity is rendered to its potential to inhibit inosine monophosphate dehydrogenase which will lead to shutdown of guanine nucleotide synthesis.[3] In spite of the known efficacy of Tiazofurin, its high toxicity and lack of specificity represent a problem for its clinical use.[4] For this reason, many Tiazofurin analogues were synthesized aiming to produce derivatives with reduced toxicity.[5] As a part of our recent program directed toward syntheses of catabolically stable nucleoside analogues, we have recently reported on the synthesis and antiviral activity of a number of heterocyclic thioglycosides that have an interesting cytotoxic activity such as pyridine thioglycosides,[6] pyrimidine thioglycosides,[7] imidazole thioglycosides,[8] oxadiazole thioglycosides,[9] thiophene thioglycosides,[10] quinoline thioglycosides,[11] and thienopyrazole thioglycosides.[12] We have reported that the thioglycosides of dihydropyridine show a strong P-glycoprotein antagonist activity as well as against human colon carcinoma cells.[13] In light of the above findings and previous reports on thiazole thioglycosides,[14,15] the purpose of this work was to design, synthesize, and investigate the biological activity of novel thiazole thioglycosides carrying carbohydrate residues by forming *S*-glycosidic bonds.

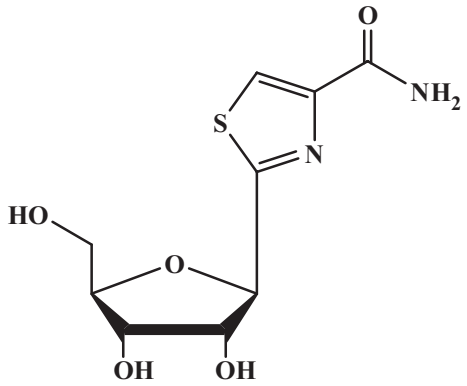
The synthesis was initiated by the condensation of cyanamide **1** and carbon disulfide in ethanolic potassium hydroxide in a simple one-step protocol to give the potassium cyanocarbonimidodithioate **2** (Scheme 1). Compound **2** is readily reacted with one equivalent of phenacyl bromide **3a** and ethyl bromoacetate **3b** in ethanol-KOH at room temperature for 24 hours to give the corresponding potassium 4-amino-5-substituted-thiazo le-2-thiolates derivatives **4a,b** in good yields. Acidification of the latter at room temperature has resulted in the formation of the corresponding 3-mercaptothiazole **5a,b**. Compounds **4a,b** undergoes reaction with tetra-*O*-acetyl-α-D-glucopyranosyl bromide **6a** and tetra-*O*-acetyl-α-D-galactopyranosyl bromide **6b** in DMF at ambient temperature to give an excellent yields of the corresponding thiazole *S*-glycosides **7a-d** (Scheme 1). It has been confirmed that the *cis*-(α) sugars maybe reacted through S_N2 reaction mechanism to give the β-glycoside reaction products. [16] The structures of **7a-d** were proved according to their



SCHEME 1 Synthetic pathway for thiazole thioglycosides 7a-d and 8a-d

spectral data (IR, ^{13}C NMR, ^{1}H NMR). For example, the anomeric proton in the ^{1}H NMR spectrum for **7a** appeared as a doublet at δ 5.33-5.34 ppm with a 10.2 Hz spin-spin coupling constant indicating the β-configuration. The glucose protons appeared at δ 3.98-4.92 ppm. Compounds **7a-d** can also be prepared by reaction of the thiazole-3-thiole derivatives **5a,b** with halo sugars **6** in DMF-sodium hydride at room temperature. The thioglycosides **7a-d** reacted with MeOH-NH_3 at ambient temperature to give the deprotected derivatives **8a-d** in good yields. The structures of **8a-d** were proved based on spectral data. Thus, the anomeric proton in the ^{1}H NMR spectrum for **8a** appeared as a doublet with $J_{1,2} = 10.5$ Hz at δ 4.41-4.42, confirming the presence of only the β-*D*-configuration (Scheme 1).

In conclusion, a novel synthesis of interesting new class of thiadiazoles and their corresponding thioglycosides is reported. The results represent a new, simple, and economically effective method for the synthesis of the Tiazofurin analogues. The simple and ambient temperature reaction



Tiazofurin

FIGURE 1 Structure of Tiazofurin

conditions, clean reaction products, and availability of starting materials make this approach as innovative and useful to the present methods for the formation of thiazole glycosides. Further investigations on the use of this method for the preparation of other biologically interesting glycosides will be investigated. The prepared thioglycosides are promising as good starting materials for the preparation of other interesting carbohydrate compounds.

2 | EXPERIMENTAL

All melting points were uncorrected on a Gallenkamp melting point apparatus. The **IR** Spectra were recorded on a Pye Unicam Spectra-1000 (KBr disk). NMR spectra were recorded on a Varian 500 MHz spectrometer in $(CD_3)_2$ SO using $Si(CH_3)_4$ as an internal standard. Elemental analyses were obtained from the Micro-analytical Data Center at Cairo University, Egypt. Progress of the reactions was judged by TLC using aluminum sheets coated with silica gel F_{254} (Merck) and viewing under a short-wavelength UV lamp. All evaporations were carried out under reduced pressure at 40°C.

2.1 | General procedure for the synthesis of (4a,b)

cyanocarbonimidodithioate **2** (10 mmol) was added to a stirred solution of compounds **3a,b** (10 mmol) in absolute ethanol (20 mL) containing KOH (10 mmol) at room temperature. The mixture was stirred magnetically until completion (TLC, 12 hours), then the resulting precipitate was collected by filtration and recrystallized from EtOH to give compounds **4a,b**.

2.1.1 | Sodium 4-amino-5-benzoylthiazole-2-thiolate (4a)

White solid (EtOH); yield (80%); mp >300°C; IR (KBr, cm^{-1}) υ 3346 (NH_2), 3039 (aromatic H), 1714 (C=O), 1608 (C=N). $C_{10}H_7KN_2OS_2$: C, 43.77; H, 2.57; N, 10.21; S, 23.37. Found: C, 43.60; H, 2.55; N, 10.12; S, 23.30%.

2.1.2 | Potassium 4-amino-5-(ethoxycarbonyl)thiazole-2-thiolate (4b)

White solid (EtOH); yield (76%); mp >300°C; IR (KBr, cm^{-1}) υ 3374 (NH_2), 1716 (C=O), 1598 (C=N). $C_6H_7KN_2O_2S_2$: C, 29.73; H, 2.91; N, 11.56; S, 26.46. Found: C, C, 29.63; H, 2.76; N, 11.40; S, 26.33%.

2.2 | General procedure for the synthesis of (5a-d)

To a solution of compound **4a,b** (10 mmol) in water, 5 drops of HCl (36%) was dropped at room temperature (25°C). After an additional stirring, a precipitate thus formed was collected by filtration and crystallized from EtOH to give **5a-d** as a white solid.

2.2.1 | 4-Amino-2-mercaptothiazol-5-yl) (phenyl)methanone (5a)

White solid (EtOH); yield (78%); mp 264°C; IR (KBr, cm^{-1}) υ 3379 (NH_2), 3028 (aromatic H), 1715 (C=O), 1593 (C=N); ^{1}H NMR (500 MHz, DMSO): δ 7.45 (s, D_2O exch., 2H, NH_2), 7.65-8.22 (m, 5H, C_6H_5), 13.26 (s, D_2O exch., 1H, SH).); ^{13}C NMR: δ 122.00 (C-5), 128.11-140.00 (6C, Ar-C), 146.22 (C-4), 155.21 (C-2), 168.00 (C=O). Anal. Calcd. For $C_{10}H_8N_2OS_2$: C, 50.83; H, 3.41; N, 11.85; S, 27.14. Found: C, 50.77; H, 3.28; N, 11.73; S, 27.11%.

2.2.2 | Ethyl 4-amino-2-mercaptothiazole-5-carboxylate (5b)

White solid (EtOH); yield (70%); mp 240°C; IR (KBr, cm^{-1}) υ 3389 (NH_2), 1716 (C=O), 1589 (C=N); ^{1}H NMR

3,4,5	R
a	C_6H_5
b	OEt

7	R	R^1	R^2
a	C_6H_5	H	OAc
b	OEt	H	OAc
c	C_6H_5	OAc	H
d	OEt	OAc	H

8	R	R^1	R^2
a	C_6H_5	H	OH
b	OEt	H	OH
c	C_6H_5	OH	H
d	OEt	OH	H

FIGURE 2 List of synthesized derivatives 3-5, 7a-d, 8a-d

(500 MHz, DMSO): δ 1.42 (t, 3H, J = 6.4 Hz, CH_3), 4.52 (q, 2H, CH_2), 7.25 (s, D_2O exch., 2H, NH_2), 13.22 (s, D_2O exch., 1H, SH); ^{13}C NMR: δ 16.23 (CH_3), 63.52 (CH_2), 124.64 (C-5), 147.36 (C-4), 157.71 (C-2), 169.46 (C=O). Anal. Calcd. For $C_6H_8N_2O_2S_2$: C, 35.28; H, 3.95; N, 13.71; S, 31.39. Found: C, C, 35.23; H, 3.79; N, 13.63; S, 31.24%.

2.3 | General procedure for the synthesis of (7a-d)

2.3.1 | Method A

To a solution of **4a,b** (10 mmol) in dry DMF (20 mL), a solution of 2,3,4,6-tetra-*O*-acetyl-α-D-gluco or (galacto) pyranosyl bromide **6a**,**b** (10 mmol) in DMF was dropped within 30 minutes. Stirring was continued for 6 hours. After completion, the reaction mixture was poured into ice water, and the resulting precipitate was collected by filtration, dried, and recrystallized from EtOH to give compounds **7a-d.**

2.3.2 | Method B

To a solution of **5a-b** (10 mmol) in dry DMF (20 mL), NaH (15 mmol) was added portionwise through 15 minutes, and the solution was stirred at room temperature for another 30 minutes. Then, a solution of 2,3,4,6-tetra-*O*-acetyl-α-D-gluco or (galacto) pyranosyl bromide **6a**,**b** (10 mmol) in DMF was dropped within 30 minutes, and the reaction mixture was stirred at room temperature until completion (TLC, 5-10 hours). After completion, the reaction mixture was poured on ice water, and the resulting precipitate was collected by filtration, dried, and recrystallized from EtOH to give compounds **7a-d.**

2.3.3 | 4-Amino-2-(2′,3′,4′,6′-tetra-*O*-acetyl-β-D-glucopyranosylthio) thiazol-5-yl)(phenyl) methanone (7a)

White solid; (EtOH) yield (84%); mp 220°C; $[\alpha]_D^{25}$ = +9.6 (c = 1 g/dL, EtOH); IR (KBr, cm^{-1}) υ 3385 (NH_2), 3035 (aromatic H), 2933 (CH), 1756 (4C=O), 1718 (C=O), 1597 (C=N); ^1H NMR (500 MHz, DMSO): δ 1.98-2.08 (4s, 12H, 4xOAc), 3.98 (m, 2H, 2H-6′), 4.52 (m, 1H, H-5′), 4.61 (t, 1H, J = 9.2 Hz, H-4′), 4.83 (t, 1H, J = 9.3 Hz, H-3′), 4.92 (t, 1H, J = 9.3 Hz, H-2′), 5.33-5.34 (d, 1H, $J_{1'-2'}$ = 10.2 Hz, H-1′), 7.46 (s, D_2O exch., 2H, NH_2), 7.72-7.94 (m, 5H, C_6H_5); ^{13C} NMR: δ 21.31 (4xOAc), 62.33 (C-6′), 66.95 (C-4′), 67.86 (C-2′), 75.86 (C-3′), 78.64 (C-5′), 84.65 (C-1′), 125.17 (C-5), 130.63-139.64 (6C, Ar-C), 146.17(C-4), 168.54 (C-2), 173.38 (4C=O), 204.29 (C=O). Anal. Calcd. For $C_{24}H_{26}N_2O_{10}S_2$: C, 50.87; H, 4.63; N, 4.94; S, 11.32. Found: C, 50.64; H, 4.55; N, 4.78; S, 11.19%.

2.3.4 | Ethyl 4-amino-2-(2′,3′,4′,6′-tetra-*O*-acetyl-β-D-glucopyranosylthio)thiazole-5-carboxylate (7b)

White solid (EtOH) yield (80%); mp 234°C; $[\alpha]_D^{25}$ = +11.2 (c = 1 g/dL, EtOH); IR (KBr, cm^{-1}) υ 3378 (NH_2), 2967 (CH), 1756 (4C=O), 1715 (C=O); ^1H NMR (500 MHz, DMSO): δ 1.42(t, 3H, J = 6.4 Hz, CH_3), 2.03-2.26 (4s, 12H, 4xOAc), 4.12 (m, 2H, 2H-6′), 4.26 (m, 1H, H-5′), 4.38 (q, 2H, CH_2), 4.42 (t, 1H, J = 9.2 Hz, H-4′), 4.54 (t, 1H, J = 9.1 Hz, H-3′), 4.84 (t, 1H, J = 9.2 Hz, H-2′), 5.42-5.43 (d, 1H, $J_{1'-2'}$ = 9.5 Hz, H-1′), 7.34 (s, D_2O exch., 2H, NH_2); ^{13}C NMR: δ 16.42 (CH_3), 22.19 (4xOAc), 61.14(CH_2), 62.44 (C-6′), 68.28 (C-5′), 72.54 (C-4′), 73.64 (C-3′), 77.64 (C-2′), 84.26 (C-1′), 127.19 (C-5), 145.64 (C-4), 168.48 (C-2), 169.84 (C=O), 174.56 (4C=O). Anal. Calcd. For $C_{20}H_{26}N_2O_{11}S_2$: C, 44.94; H, 4.90; N, 5.24; S, 12.00. Found: C, 44.84; H, 4.84; N, 5.16; S, 11.92%.

2.3.5 | 4-Amino-2-(2′,3′,4′,6′-tetra-*O*-acetyl-β-D-galactopyranosylthio) thiazol-5-yl)(phenyl) methanone (7c)

White solid (EtOH) yield (80%); mp 246°C; $[\alpha]_D^{25}$ = +19.5 (c = 1 g/dL, EtOH); IR (KBr, cm^{-1}) υ 3384 (NH_2), 3041 (aromatic H), 2922 (CH), 1756 (4C=O), 1594 (C=N); ^1H NMR (500 MHz, DMSO): δ 2.03-2.16 (4s, 12H, 4xOAc), 3.88 (m, 2H, 2H-6′), 4.36 (m, 1H, H-5′), 4.69 (t, 1H, J = 9.4 Hz, H-4′), 4.75 (t, 1H, J = 9.4 Hz, H-3′), 4.89 (t, 1H, J = 9.2 Hz H-2′), 5.46-5.47 (d, 1H, $J_{1'-2'}$ = 10.6 Hz, H-1′), 7.59 (s, D_2O exch., 2H, NH_2), 7.71-7.92 (m, 5H, C_6H_5); ^{13}C NMR: δ 22.15 (4xOAc), 62.65 (C-6′), 67.71 (C-4′), 69.74 (C-2′), 74.68 (C-3′), 76. 44 (C-5′), 84.78 (C-1′), 124.05 (C-5), 129.49-140.62 (6C, Ar-C), 145.25 (C-4), 169.36 (C-2), 172.28 (4C=O), 201.43 (C=O). Anal. Calcd. For $C_{24}H_{26}N_2O_{10}S_2$: C, 50.87; H, 4.63; N, 4.94; S, 11.32. Found: C, 50.82; H, 4.48; N, 4.82; S, 11.14%.

2.3.6 | Ethyl 4-amino-2-(2′,3′,4′,6′-tetra-*O*-acetyl-β-D-galactopyranosylthio)thiazole-5-carboxylate (7d)

White solid (EtOH) yield (86%); mp 234°C; $[\alpha]_D^{25}$ = +20.0 (c = 1 g/dL, EtOH); IR (KBr, cm^{-1}) υ 3371 (NH_2), 3032 (aromatic H), 2929 (CH), 1752 (4C=O), 1722 (CO), 1598 (C=N); ^1H NMR (500 MHz, DMSO): δ 1.34 (t, 3H, J = 6.4 Hz, CH_3), 2.01-2.13 (4s, 12H, 4xOAc), 3.96 (m, 2H, 2H-6′), 4.36 (q, 2H, CH_2), 4.47(m, 2H, H-6′),4.58(m, 1H,H-5′), 4.65 (t, 1H, J = 9.2 Hz, H-4′), 4.79 (t, 1H, J = 9.3 Hz, H-3′), 4.86 (t, 1H, J = 9.4 Hz, H-2′), 5.58-5.59 (d, 1H, $J_{1'-2'}$ = 8.7 Hz, H-1′), 6.98 (s, D_2O exch., 2H, NH_2); ^{13}C NMR: δ 16.21 (CH_3), 22.43 (4xOAc), 61.47(CH_2), 62.42 (C-6′), 68.26 (C-4′), 70.54

(C-2′), 74.28 (C-3′), 76.18 (C-5′), 84.56 (C-1′), 121.45 (C-5), 148.24 (C-4), 168.29 (C-2), 169.66 (C=O), 172.16 (4C=O). Anal. Calcd. For $C_{20}H_{26}N_2O_{11}S_2$: C, 44.94; H, 4.90; N, 5.24; S, 12.00. Found: C, 44.82; H, 4.80; N, 5.18; S, 12.12%.

2.4 | General procedure for the synthesis of (8a-d)

Dry gaseous ammonia was passed through a solution of protected nucleoside **7a-d** (10 mmol) in dry methanol (20 mL) for 10 minutes with cooling and stirring, then the reaction mixture was stirred at room temperature until the reaction was judged complete by TLC (9-10 hours) using ($CHCl_3$/MeOH 9:1) (*R*f, 0.54-0.56). The resulting mixture was concentrated under reduced pressure to afford a solid residue which is washed several times by boiling chloroform. The residue was dried and recrystallized from EtOH to give corresponding compounds **8a-d**.

2.4.1 | 4-Amino-2-(β-D-glucopyranosylthio) thiazol-5-yl)(phenyl)methanone (8a)

White solid (EtOH); yield (66%); mp 180°C; $[\alpha]_D^{25} = +17.4$ ($c = 1$ g/dL, EtOH); IR (KBr, cm^{-1}) υ 3542 (OH), 3432 (NH_2), 3052 (aromatic H), 2936 (CH), 1710 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.43-3.46 (m, 2H, 2H-6′), 3.52 (m.1H, H-5′), 3.76 (t, 1H, $J = 9.3$ Hz, H-4′), 3.92 (t, 1H, $J = 9.1$ Hz, H-3′), 4.02 (t, 1H, $J = 9.2$ Hz, H-2′), 4.41-4.42 (d, 1H, $J_{1'\text{-}2'} = 10.5$ Hz, H-1′), 4.84 (s, D_2O exch., 1H, 6′-OH), 4.98-5.14 (s, D_2O exch., 3H, 2′-OH, 3′-OH, and 4′-OH), 7.34 (s, D_2O exch., 2H, NH_2), 7.72-8.14 (m, 5H, C_6H_5); ^{13}C NMR: δ 62.26 (C-6′), 69.42 (C-5′), 70.37 (C-4′), 74.26 (C-3′), 76.44 (C-2′), 85.47 (C-1′), 125.34 (C-5), 132.14-141.42 (6C, Ar-C), 147.34 (C-4), 169.23 (C-2), 203.45 (C=O). Anal. Calcd. For $C_{16}H_{18}N_2O_6S_2$: C, 48.23; H, 4.55; N, 7.03; S, 16.09. Found: C, 48.10; H, 4.42; N, 7.01; S, 15.88%.

2.4.2 | Ethyl 4-amino-2-(β-D-glucopyranosylthio)thiazole-5-carboxylate (8b)

White solid (EtOH); yield (80%); mp 177°C; $[\alpha]_D^{25} = +15.8$ ($c = 1$ g/dL, EtOH); IR (KBr, cm^{-1}) υ 3541 (OH), 3367 (NH_2), 2,933 (CH), 1711 (C=O); ^{1}H NMR (500 MHz, DMSO): δ 1.36(t, 3H, $J = 6.51$ Hz, CH_3), 3.64 (m, 2H, 2H-6′), 3.76 (m, 1H, H-5′), 4.03 (t, 1H, $J = 9.1$ Hz, H-4′), 4.11 (t, 1H, $J = 9.3$ Hz, H-3′), 4.34 (t, 1H, $J = 9.2$ Hz, H-2′), 4.52 (q, 2H, CH_2), 5.33-5.34 (d, 1H, $J_{1'\text{-}2'} = 10.3$ Hz, H-1′), 7.62 (s, D_2O exch., 2H, NH_2); ^{13}C NMR: δ 15.54 (CH_3), 59.68 (CH_2), 61.14(CH_2),62.15 (C-6′), 69.36 (C-5′), 73.31 (C-4′), 76.29 (C-3′), 79.44 (C-2′), 86.47 (C-1′), 125.22 (C-5), 146.31 (C-4), 166.18 (C-2), 168.45 (C=O). Anal. Calcd. For $C_{12}H_{18}N_2O_7S_2$: C, 39.34; H, 4.95; N, 7.65; S, 17.50. Found: C, 39.23; H, 4.82; N, 7.58; S, 17.38%.

2.4.3 | 4-Amino-2-(β-D-galactopyranosylthio) thiazol-5-yl)(phenyl)methanone (8c)

White solid (EtOH); yield (72%); mp 166°C; $[\alpha]_D^{25} = +14.1$ ($c = 1$ g/dL, EtOH); IR (KBr, cm^{-1}) υ 3522 (OH), 3427 (NH_2), 3049 (aromatic H), 2939 (CH), 1708 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.37-3.46 (m, 2H, 2H-6′), 3.58 (m.1H, H-5′), 3.62 (t, 1H, $J = 9.1$ Hz, H-4′), 3.87 (t, 1H, $J = 9.4$ Hz, H-3′), 4.15 (t, 1H, $J = 9.1$ Hz, H-2′), 4.36-4.37 (d, 1H, $J_{1'\text{-}2'} = 10.2$ Hz, H-1′), 4.81 (s, D_2O exch., 1H, 6′-OH), 4.92-5.08 (s, D_2O exch., 3H, 2′-OH, 3′-OH, and 4′-OH), 7.29 (s, D_2O exch., 2H, NH_2), 7.65-8.17 (m, 5H, C_6H_5); ^{13}C NMR: δ 62.56 (C-6′), 68.29 (C-5′), 72.82 (C-4′), 74.63 (C-3′), 79.62 (C-2′), 84.58 (C-1′), 126.92 (C-5), 130.53-142.36 (6C, Ar-C), 148.44 (C-4), 167.68 (C-2), 206.24 (C=O). Anal. Calcd. For $C_{16}H_{18}N_2O_6S_2$: C, 48.23; H, 4.55; N, 7.03; S, 16.09. Found: C, 48.10; H, 4.42; N, 7.01; S, 15.88%.

2.4.4 | Ethyl 4-amino-2-(β-D-galactopyranosylthio)thiazole-5-carboxylate (8d)

White solid (EtOH); yield (80%); mp 178°C; $[\alpha]_D^{25} = +16.7$ ($c = 1$ g/dL, EtOH); IR (KBr, cm^{-1}) υ 3507 (OH), 3421 (NH_2), 2951 (CH), 1713 (C=O); ^{1}H NMR (500 MHz, DMSO): δ 1.43 (t, 3H, $J = 6.6$ Hz, CH_3), 3.46 (m, 2H, 2H-6′), 3.64 (m, 1H, H-5′), 3.77 (t, 1H, $J = 9.4$ Hz, H-4′), 4.33 (t, 1H, $J = 9.2$ Hz, H-3′), 4.46 (t, 1H, $J = 9.1$ Hz H-2′), 4.48 (q, 2H, CH_2), 5.26-5.27 (d, 1H, $J_{1'\text{-}2'} = 10.9$ Hz, H-1′), 7.53 (s, D_2O exch., 2H, NH_2); ^{13}C NMR: δ 15.27 (CH_3), 60.42 (CH_2), 61.59(CH_2),62.62 (C-6′), 67.26 (C-5′), 75.471 (C-4′), 77.35 (C-3′), 79.36 (C-2′), 86.39 (C-1′), 126.46 (C-5), 148.26 (C-4), 166.23 (C-2), 169.31 (C=O). Anal. Calcd. For $C_{12}H_{18}N_2O_7S_2$: C, 39.34; H, 4.95; N, 7.65; S, 17.50. Found: C, 39.23; H, 4.82; N, 7.58; S, 17.38%.

ORCID

Galal H. Elgemeie http://orcid.org/0000-0003-3268-5975

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