Carbohydrate Research 344 (2009) 1289–1296

Contents lists available at ScienceDirect

Carbohydrate Research

journal homepage: www.elsevier.com/locate/carres

Synthesis, antifungal activities, and potential detoxification of *N*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)thiocarbamates

Yaling Zhou [a], Li Wang [a], Lixia Han [a], Fangui Meng [a,b], Chunlong Yang [a,b,*]

[a] Department of Chemistry, College of Science, Nanjing Agricultural University, Nanjing 210095, China
[b] Key Laboratory of Monitoring and Management of Crop Diseases and Pest Insects, Ministry of Agriculture, Nanjing Agricultural University, Nanjing 210095, China

ARTICLE INFO

Article history:
Received 25 January 2009
Received in revised form 28 April 2009
Accepted 6 May 2009
Available online 10 May 2009

Keywords:
Glucosyl thiocarbamates
Antifungal activities
Detoxification
Mercury

ABSTRACT

A series of *N*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)thiocarbamates were synthesized by the reaction of glucosyl isothiocyanates with monohydric and dihydric alcohols, and acetone oxime, using methods of both normal reaction and microwave-assisted synthesis. Antifungal activities of the title compounds were determined with three kinds of plant pathogenic fungi, *Fusarium graminearum*, *Rhizoctoria cerealis*, and *Colletotrichum orbiculare*. The synthesized glucosyl thiocarbamates easily reacted with $HgCl_2$ to give novel metal–organic compounds, bis[*O*-alkyl *N*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)thiocarbamato]mercury, in yields of 80%. This strong affinity of thiocarbamates for mercury showed their potential utility in medical or marine environmental detoxification.

1. Introduction

Thiocarbamates are remarkable for their biological activities and are widely used as bactericides,[1–3] pesticides,[4,5] and herbicides.[6–9] Many of the thiocarbamates that have been reported are *N*-alkyl[10] and *N*-phenyl or benzyl[11] compounds, few of which are *N*-glucosyl.[12,13] The linkage between the hydrophobic tail and the sugar head in *N*-glucosyl thiocarbamates appears to modify the physicochemical properties of non-ionic surfactants by changing their water solubility.[13] As was reported, many biologically important products have a sugar unit joined through an atom (O, S, N, or C) or a group of atoms.[14] Glucosyl isothiocyanates, proven to be excellent intermediates, have been used for the preparation of a variety of carbohydrate derivatives of synthetic, biological, and pharmaceutical interest,[15,16] since they easily undergo many important reactions, such as cycloadditions and nucleophilic additions.[17]

Furthermore, thiocarbamates and some metal atoms (such as rhodium, iridium, palladium, platinum, and gold) could form the metal complexes.[18] Some thiocarbamates can be used as sulfhydryl group antidotes, and these compounds may have potential utility in medical or marine environmental fields,[19] owing to their high affinity to heavy metal cations,[20] for example, Hg^{2+} and Pb^{2+}. Hg-related health risks do exist for consumers of bivalves.[21] Also some thiocarbamates can be used as reagents in ore flotation, since their strong affinity and good selectivity for certain ions.[22] For example, *O*-isopropyl-*N*-ethylthiocarbamate is more selective for copper sulfide against gangue iron sulfides; thus, it can perform copper/iron separation.[23]

The reports about D-glucopyranosyl thiocarbamates are quite infrequent, and only a few of them have been described in detail.[12,13] In this study, 20 different *N*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)thiocarbamates were synthesized by the reaction of 2,3,4,6-tetra- *O*-acetyl-β-D-glucopyranosyl isothiocyanate with the compounds linking with one or two hydroxyl groups, respectively (Scheme 1). Their antifungal activities against three plant pathogenic fungi were evaluated. Furthermore, the potential utility of these glucosyl thiocarbamates for detoxification was investigated by reacting with $HgCl_2$.

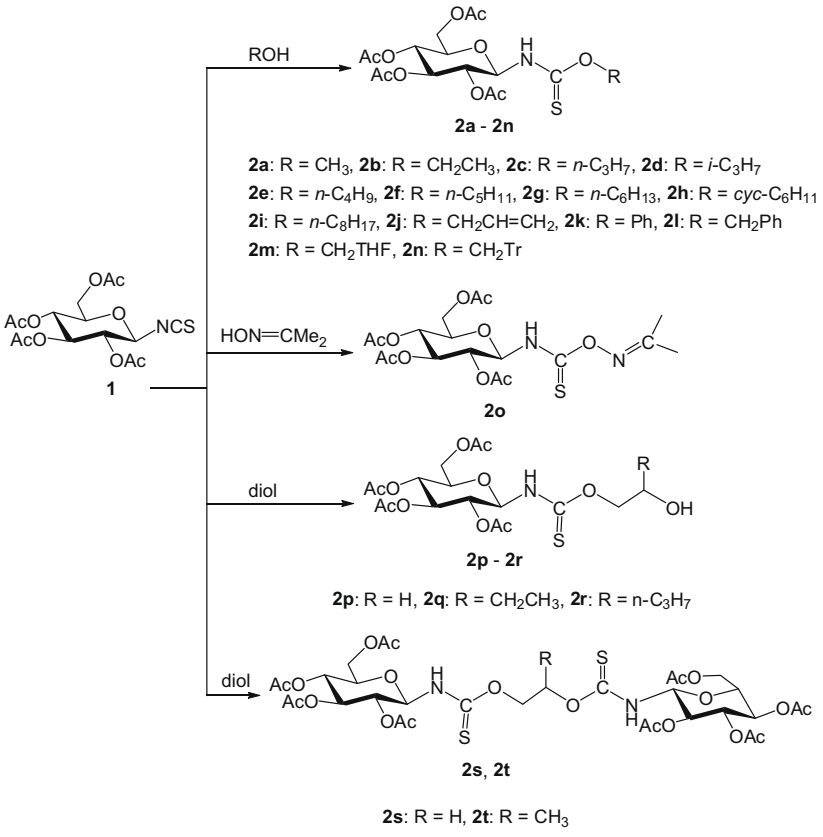
2. Results and discussion

2.1. The synthesis of glucosyl thiocarbamates

Glucosyl isothiocyanates were synthesized in moderate yield by the reaction of an acylated glucosyl bromide with lead thiocyanate according to the literature,[24–28] and the acylated glucosyl bromide was prepared by methods described in the literature.[29,30] Glucosyl isothiocyanates reacted with the acyclic and heterocyclic monohydric alcohols to give the thiocarbamates **2a**–**2j** and **2m,** for the most part, in yields of over 80%, except for **2n** and **2o**, which were obtained by the reaction of glucosyl isothiocyanates with 1-(hydroxymethyl)-1*H*-1,2,4-triazole and acetoxime, respectively.

* Corresponding author. Address: Key Laboratory of Monitoring and Management of Crop Diseases and Pest Insects, Ministry of Agriculture, Nanjing Agricultural University, Nanjing 210095, China. Tel./fax: +86 025 84395255.
E-mail address: chunlongyang@yahoo.com.cn (C. Yang).

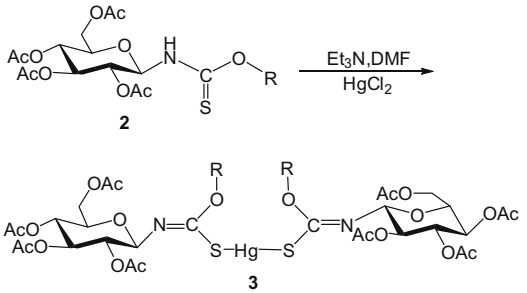
0008-6215/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carres.2009.05.008



Scheme 1. Preparation of the title compounds.

However, phenol and benzyl alcohol were more difficult to react with the glucosyl isothiocyanates owing to their easy oxidation at high reaction temperatures (100 °C) and long reaction times (5 h). To limit the oxidation, microwave-assisted synthesis was used, and compounds **2k** and **2l** were obtained. In the reaction of glucosyl isothiocyanates with dihydric alcohols, monothiocarbamates **2p**–**2r**, which are linked with only one glucosyl group, with the other hydroxyl group left open, as well as the bridged bisthiocarbamates **2s** and **2t**, which are linked with two glucosyl groups, were prepared (Scheme 1). In preparation of monothiocarbamates **2p**–**2r**, the molar ratio of diols and *N*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)isothiocyanates was 2:1, while in preparation of the bisthiocarbamates **2s** and **2t**, the ratio of two reactants was just the opposite.

Compounds with the general structure **2** were characterized by IR, ^{1}H, and ^{13}C NMR spectroscopy and by elemental analysis. In the IR spectrum an absorbance at about 3300 cm^{-1} showed the presence of an NH group, and the absorbance at about 1520 cm^{-1} indicated the NH(C=S) group. In the ^{1}H NMR spectra the NH of monothiocarbamates appeared as doublet at δ 6.16–7.03 , while the NH of bisthiocarbamates appeared as broad peak at δ 7.08. H-1, H-2, H-3, and H-4 appeared as doublet of doublets (overlapped to appear as three-line patterns), respectively, while H-6a and H-6b appeared as two-line patterns. As a result of the complex coupling with H-4, H-6a and H-6b, H-5 appeared as a multiplet. In the ^{13}C NMR spectra, the C=S of *N*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)thiocarbamates appeared at about δ 191–192, and four acetyl C=O groups on the glucosyl ring appeared at about δ 169–171. C-1 appeared at about δ 83, C-2–C-6 appeared at about δ 61–73. The elemental analysis data were in accord with the structure of compounds **2**.



3a: R = CH_3, **3b**: R = CH_2CH_3, **3c**: R = *n*-C_3H_7, **3d**: R = *i*-C_3H_7, **3e**: R = *n*-C_4H_9
3f: R = *n*-C_5H_{11}, **3g**: R = *n*-C_6H_{13}, **3h**: R = *cyc*-C_6H_{11}, **3i**: R = *n*-C_8H_{17}

Scheme 2. Reaction of the thiocarbamates with $HgCl_2$.

2.2. Antifungal activities of glucosyl thiocarbamates

Antifungal activities of compounds **2** against three kinds of plant pathogenic fungi (*Fusarium graminearum*, *Rhizoctoria cerealis*, and *Colletotrichum orbiculare*) were evaluated by a radial growth inhibition technique with three repeats for each sample according to the literature procedure.[31] As shown in Table 1, most of compounds **2** showed weak antifungal activities at 500 μg mL^{-1}, but some of the compounds, such as **2c**, **2f**, **2s**, and **2t** exhibited somewhat stronger antifungal activities. It is interesting that there might be certain relationship between antifungal activities and the number of carbon atoms in the alcohol position of compounds **2** synthesized by straight-chain fatty alcohols, that is, compounds **2a**, **2c**, and **2f** with odd-numbered carbon atoms have stronger antifungal activities than compounds **2b**, **2e**, and **2g** with even-numbered carbon atoms. By comparing **2s** and **2t** with **2p**,

Table 1
Antifungal activities of compounds **2** against three kinds of plant pathogenic fungi

Compd	Inhibition % (500 μg·mL^{-1})		
	F. graminearum	*R. cerealis*	*C. orbiculare*
2a	22.4	13.3	43.3
2b	13.8	10.2	31.0
2c	41.6	15.4	41.4
2d	23.3	0	36.7
2e	18.1	15.6	25.5
2f	46.6	41.7	46.1
2g	31.0	0	20.6
2h	32.8	23.1	48.3
2i	17.0	20.0	22.0
2j	34.5	58.3	23.3
2k	29.7	37.5	35.5
2l	23.7	10.7	40.0
2m	38.5	43.5	16.5
2n	30.8	25.4	10.0
2o	31.0	40.0	38.6
2p	15.4	17.9	12.0
2q	37.9	15.4	33.3
2r	31.4	12.2	30.0
2s	38.5	43.5	45.5
2t	39.0	45.0	43.0
p	100	100	100

p = propiconazole.

2q, and **2r**, it was also revealed that the antifungal activities of bisthiocarbamates are a bit stronger than those of the monothiocarbamates.

2.3. The reaction of glucosyl thiocarbamates with $HgCl_2$

In an attempt to further study the affinity of glucosyl thiocarbamates with $HgCl_2$, nine corresponding compounds **3** were synthesized (Scheme 2). The reaction was obviously influenced by the length of the carbon chain in the alcohol position. Taking compounds **2a** and **2i** as examples, **2a** reacted with $HgCl_2$ for at least 5.5 h, and the reaction temperature was increased to 35 °C to give **3a** in a yield of 80%, while **2i** reacted with $HgCl_2$ for only 2 h at a lower temperature of 0 °C to obtain **3i** in a yield of 84% (Scheme 2).

Compounds with the general structure **3** were characterized by IR, ^{1}H, and ^{13}C NMR spectroscopy, elemental analysis and additional concentration analysis of the mercury atom. In the IR spectrum, the absorption at about 3300 cm^{-1} disappeared, which indicated the absence of an NH group in compounds **3**, while the absorption at about 1620 cm^{-1} showed the presence of a C=N group; furthermore, disappearance of the absorption at about 1520 cm^{-1} showed the absence of the NH(C=S) group in compounds **3**. In the ^{1}H NMR spectra, the NH proton at δ 6.16–7.03 disappeared, which was in agreement with their IR spectra. In the ^{13}C NMR spectra, the four acetyl C=O groups on the glucosyl ring appeared at about δ 169–171, while the C–S of bis[*O*-alkyl *N*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)thiocarbamato] mercury appeared at about δ 162–163. By determining the concentration of mercury, it could be concluded that one mercury atom was linked with two glucosyl thiocarbamates as shown in Scheme 2. Moreover, the structures of compounds **3** were confirmed by elemental analysis.

3. Experimental

3.1. General methods

Melting points were determined with a digital melting point apparatus (WRS-1B) without correction. IR spectra (Bruker Tensor27 FTIR) were recorded for samples on KBr plates. The ^{1}H and ^{13}C NMR spectra (Bruker DRX-500) were recorded using tetramethylsilane (TMS, δ 0.00) and chloroform ($CDCl_3$, δ 77.30) as internal standards, respectively. Optical rotations were measured on an ATAGO Automatic Polarimeter (AP-100) at room temperature (20 °C). Microwave-assisted synthesis was carried out in a microwave reactor (MAS-I). Elemental analyses were carried out on an elemental analyzer (Vario EL III). The concentration of mercury was determined with a cold-vapor atomic absorption spectrometer (HG-3000). Thin-layer chromatography (TLC) was performed on precoated plates (GF_{254}) in 0.6% carboxymethyl cellulose sodium (CMC) with subsequent heating and detection by UV light. Column chromatography was conducted on silica gel C-300.

3.2. General procedure for the synthesis of *N*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)thiocarbamates

2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl isothiocyanate (**1**, 0.4 g, 1 mmol), which was prepared according to reported procedures,[26] was added to a monohydric or dihydric alcohol (20 mL), respectively, warmed at 90–100 °C (reflux temperature for **2a**–**2d**) and stirred for 2–4 h, until the starting material **1** disappeared on TLC. Then the excess reactant was evaporated, and the residue was recrystallized from EtOH. The clear filtrate was left at room temperature, and a white solid powder was obtained by filtration. Some solids of the compounds (**2n**–**2t**) could not be obtained directly by recrystallization, and then the crude products were purified by column chromatography on silica gel eluting with 1:1 EtOAc–petroleum ether. Fractions containing the product were combined, and the solvent was removed to afford **2n**–**2t** as white solids.

3.2.1. *O*-Methyl *N*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)thiocarbamate (2a)

White powder; yield 95%; mp 188.8–189.5 °C; $[\alpha]_D$ +11.62 (*c* 2.0, $CHCl_3$); IR (KBr) ν/cm^{-1}: 3303 (m, NH), 1745 (s, C=O), 1532 (m, NH(C=S)), 1254 and 1070 (s, C–O–C); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.90 (d, 1H, *J* 8.5 Hz, NH), 5.57 (t, 1H, *J* 8.5, 9.0 Hz, H-1), 5.37 (t, 1H, *J* 9.5, 9.5 Hz, H-2), 5.08 (t, 1H, *J* 9.5, 10.0 Hz, H-3), 5.00 (t, 1H, *J* 9.5, 9.5 Hz, H-4), 4.32 (dd, 1H, *J* 4.0, 4.5 Hz, H-6a), 4.11 (t, 1H, *J* 11.0, 12.5 Hz, H-6b), 4.03 (s, 3H, OCH_3), 3.86 (m, 1H, H-5), 2.19, 2.18, 2.16, 2.14 (4s, 12H, $4CH_3CO$); ^{13}C NMR (300 MHz, $CDCl_3$): δ 193.22 (C=S), 171.37, 170.88, 170.10, and 169.81 (4C, $4COCH_3$), 83.50 (C-1), 73.81 (C-5), 72.87 (C-3), 70.63 (C-2), 68.40 (C-4), 61.82 (C-6), 57.95 (OCH_3), 20.97, 20.93, and 20.81 (4C, $4COCH_3$). Anal. Calcd for $C_{16}H_{23}NO_{10}S$ (421.42): C, 45.60; H, 5.50; N, 3.32; S, 7.61. Found: C, 45.54; H, 5.45; N, 3.28; S, 7.67.

3.2.2. Preparation of *O*-ethyl *N*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)thiocarbamate (2b)

White crystals; yield 92%; mp 156.2–156.8 °C; lit.[32] 156–158 °C; $[\alpha]_D$ +10.75 (*c* 2.0, $CHCl_3$); IR (KBr) ν/cm^{-1} : 3318 (m, NH), 1744 (s, C=O), 1524 (m, NH(C=S)), 1217 and 1038 (s, C–O–C); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.82 (d, 1H, *J* 8.0 Hz, NH), 5.57 (t, 1H, *J* 9.5, 9.0 Hz, H-1), 5.34 (t, 1H, *J* 9.5, 9.5 Hz, H-2), 5.06 (t, 1H, *J* 10.0, 9.0 Hz, H-3), 4.97 (t, 1H, *J* 9.5, 9.5 Hz, H-4), 4.48 (q, 2H, *J* 1.5, 7.5, 7.0 Hz, OCH_2), 4.31 (d, 1H, *J* 12.5 Hz, H-6a), 4.10 (d, 1H, *J* 12.5 Hz, H-6b), 3.84 (t, 1H, *J* 1.5, 8.0 Hz, H-5), 2.07, 2.06, 2.04, 2.03 (4s, 12H, $4CH_3CO$), 1.30 (t, 3H, *J* 4.5, 6.5 Hz, CH_2CH_3); ^{13}C NMR (300 MHz, $CDCl_3$): δ 192.39 (C=S), 171.13, 170.81, 170.05, and 169.76 (4C, $4COCH_3$), 83.22 (C-1), 73.73 (C-5), 72.98 (C-3), 70.60 (C-2), 68.39 (C-4), 67.41 (OCH_2), 61.84 (C-6), 20.86, 20.87, and 20.75 (4C, $4COCH_3$), 14.17 (CH_3). Anal. Calcd for $C_{17}H_{25}NO_{10}S$ (435.45): C, 46.89; H, 5.79; N, 3.22; S, 7.36. Found: C, 46.83; H, 5.81; N, 3.18; S, 7.31.

3.2.3. *O*-Propyl *N*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)thiocarbamate (2c)

White powder; yield 91%; mp 108.2–108.9 °C; $[\alpha]_D$ +9.87 (*c* 2.0, $CHCl_3$); IR (KBr) ν/cm^{-1}: 3325 (m, NH), 1749 (s, C=O), 1534 (m, NH(C=S)), 1232 and 1042 (s, C–O–C); ^1H NMR ($CDCl_3$, 500 MHz): δ 6.83 (d, 1H, *J* 9.5 Hz, NH), 5.60 (t, 1H, *J* 9.0, 9.0 Hz, H-1), 5.37 (t, 1H, *J* 9.5, 9.5 Hz, H-2), 5.08 (t, 1H, *J* 9.5, 9.5 Hz, H-3), 5.00 (t, 1H, *J* 9.5, 9.5 Hz, H-4), 4.38 (m, 2H, OCH_2), 4.33 (dd, 1H, *J* 5.0, 5.0 Hz, H-6a), 4.11 (d, 1H, *J* 12.0 Hz, H-6b), 3.86 (m, 1H, H-5), 2.11, 2.09, 2.06, 2.05 (4s, 12H, $4CH_3CO$), 1.70 (m, 2H, CH_2CH_3), 0.97 (t, 3H, *J* 7.5, 7.5 Hz, CH_2CH_3); ^{13}C NMR (300 MHz, $CDCl_3$): δ 192.54 (C=S), 171.32, 170.87, 170.09, and 169.80 (4C, $4COCH_3$), 83.32 (C-1), 73.80 (C-5), 73.19 (C-3), 72.90 (C-2), 70.62 (C-4), 68.39 (OCH_2), 61.80 (C-6), 21.96 (CH_2), 20.97, 20.91, and 20.81 (4C, $4COCH_3$), 10.51 (CH_3). Anal. Calcd for $C_{18}H_{27}NO_{10}S$ (449.47): C, 48.10; H, 6.05; N, 3.12; S, 7.13. Found: C, 48.16; H, 6.09; N, 3.10; S, 7.07.

3.2.4. *O*-2-Propyl *N*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)thiocarbamate (2d)

White powder; yield 90%; mp 148.1–148.8 °C; $[\alpha]_D$ +9.71 (*c* 2.0, $CHCl_3$); IR (KBr) ν/cm^{-1}: 3338 (m, NH), 1746 (s, C=O), 1524 (m, NH(C=S)), 1239 and 1047 (s, C–O–C); ^1H NMR ($CDCl_3$, 500 MHz): δ 6.73 (d, 1H, *J* 8.5 Hz, NH), 5.62 (t, 1H, *J* 9.5, 9.5 Hz, H-1), 5.54 (m, 1H, $CH(CH_3)_2$), 5.40 (t, 1H, *J* 9.5, 9.5 Hz, H-2), 5.09 (t, 1H, *J* 9.5, 10.0 Hz, H-3), 4.99 (t, 1H, *J* 9.5, 9.0 Hz, H-4), 4.33 (dd, 1H, *J* 8.0, 7.5 Hz, H-6a), 4.11 (d, 1H, *J* 10.0 Hz, H-6b), 3.84 (m, 1H, H-5), 2.15, 2.14, 2.11, 2.07 (4s, 12H, $4CH_3CO$), 1.36 (m, 6H, $CH(CH_3)_2$); ^{13}C NMR (300 MHz, $CDCl_3$): δ 191.59 (C=S), 171.26, 170.87, 170.09, and 169.80 (4C, $4COCH_3$), 83.23 (C-1), 75.36 (C-5), 73.80 (C-3), 72.92 (C-2), 70.67 (C-4), 68.38 (OCH), 61.78 (C-6), 21.75 and 21.71 (2C, CH_3), 20.96, 20.87, and 20.81 (4C, $4COCH_3$). Anal. Calcd for $C_{18}H_{27}NO_{10}S$ (449.47): C, 48.10; H, 6.05; N, 3.12; S, 7.13. Found: C, 48.16; H, 6.11; N, 3.07; S, 7.19.

3.2.5. *O*-Butyl *N*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)thiocarbamate (2e)

Slightly yellow powder; yield 85%; mp 89.2–89.9 °C; $[\alpha]_D$ +8.01 (*c* 2.0, $CHCl_3$); IR (KBr) ν/cm^{-1}: 3385 (m, NH), 1744 (s, C=O), 1515 (m, NH(C=S)), 1229 and 1048 (s, C–O–C); ^1H NMR ($CDCl_3$, 500 MHz): δ 6.83 (d, 1H, *J* 9.0 Hz, NH), 5.60 (t, 1H, *J* 9.0, 9.0 Hz, H-1), 5.37 (t, 1H, *J* 9.5, 9.5 Hz, H-2), 5.08 (t, 1H, *J* 9.5, 10.0 Hz, H-3), 5.00 (t, 1H, *J* 9.5, 9.5 Hz, H-4), 4.46 (m, 2H, OCH_2), 4.33 (dd, 1H, *J* 4.0, 4.0 Hz, H-6a), 4.13 (d, 1H, *J* 12.5 Hz, H-6b), 3.86 (m, 1H, H-5), 1.98, 1.96, 1.93, 1.92 (4s, 12H, $4CH_3CO$), 1.71 (m, 2H, $CH_2CH_2CH_3$), 1.41 (m, 2H, $CH_2CH_2CH_3$), 0.94 (t, 3H, *J* 7.0, 7.5 Hz, $CH_2CH_2CH_3$); ^{13}C NMR (300 MHz, $CDCl_3$): δ 192.56 (C=S), 171.34, 170.84, 170.06, and 169.78 (4C, $4COCH_3$), 83.34 (C-1), 73.87 (C-5), 72.92 (C-3), 71.58 (C-2), 70.69 (C-4), 68.47 (OCH_2), 61.82 (C-6), 30.61 (CH_2), 20.94, 20.87, and 20.78 (4C, $4COCH_3$), 19.25 (CH_2), 13.92 (CH_3). Anal. Calcd for $C_{19}H_{29}NO_{10}S$ (463.50): C, 49.24; H, 6.31; N, 3.02; S, 6.92. Found: C, 49.20; H, 6.25; N, 3.07; S, 6.96.

3.2.6. *O*-Amyl *N*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)thiocarbamate (2f)

White powder; yield 84%; mp 106.2–106.7 °C; $[\alpha]_D$ +8.87 (*c* 2.0, $CHCl_3$); IR (KBr) ν/cm^{-1}: 3323 (m, NH), 1744 (s, C=O), 1523 (m, NH(C=S)), 1218 and 1039 (s, C–O–C); ^1H NMR ($CDCl_3$, 500 MHz): δ 6.83 (d, 1H, *J* 9.0 Hz, NH), 5.60 (t, 1H, *J* 9.0, 9.0 Hz, H-1), 5.36 (t, 1H, *J* 9.5, 9.5 Hz, H-2), 5.08 (t, 1H, *J* 9.5, 9.5 Hz, H-3), 5.00 (t, 1H, *J* 9.5, 9.5 Hz, H-4), 4.42 (m, 2H, OCH_2), 4.33 (dd, 1H, *J* 4.5, 4.5 Hz, H-6a), 4.13 (d, 1H, *J* 7.5 Hz, H-6b), 3.86 (m, 1H, H-5), 2.17, 2.16, 1.98, 1.92 (4s, 12H, $4CH_3CO$), 1.72 (t, 2H, *J* 6.5, 6.5 Hz, $CH_2(CH_2)_2CH_3$), 1.36 (m, 4H, $CH_2(CH_2)_2CH_3$), 0.94 (m, 3H, $CH_2(CH_2)_2CH_3$); ^{13}C NMR (300 MHz, $CDCl_3$): δ 192.55 (C=S), 171.32, 170.83, 170.05, and 169.77 (4C, $4COCH_3$), 83.37 (C-1), 73.87 (C-5), 72.93 (C-3), 71.85 (C-2), 70.68 (C-4), 68.46 (OCH_2), 61.81 (C-6), 28.26, 28.13, and 22.50 (3C, CH_2), 20.96, 20.87, and 20.81 (4C, $4COCH_3$), 14.14 (CH_3). Anal. Calcd for $C_{20}H_{31}NO_{10}S$ (477.53): C, 50.31; H, 6.54; N, 2.93; S, 6.71. Found: C, 50.36; H, 6.50; N, 2.99; S, 6.65.

3.2.7. *O*-Hexyl *N*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)thiocarbamate (2g)

White powder; yield 86%; mp 114.1–114.7 °C; $[\alpha]_D$ +8.35 (*c* 2.0, $CHCl_3$); IR (KBr) ν/cm^{-1}: 3311 (m, NH), 1742 (s, C=O), 1531 (m, NH(C=S)), 1218 and 1041 (s, C–O–C); ^1H NMR ($CDCl_3$, 500 MHz): δ 6.82 (d, 1H, *J* 9.0 Hz, NH), 5.60 (t, 1H, *J* 9.0, 9.0 Hz, H-1), 5.36 (t, 1H, *J* 9.5, 9.5 Hz, H-2), 5.08 (t, 1H, *J* 10.0, 9.5 Hz, H-3), 5.00 (t, 1H, *J* 9.5, 9.5 Hz, H-4), 4.42 (m, 2H, OCH_2), 4.33 (dd, 1H, *J* 4.5, 4.5 Hz, H-6a), 4.13 (d, 1H, *J* 12.0 Hz, H-6b), 3.86 (m, 1H, H-5), 2.18, 2.16, 2.13, 2.12 (4s, 12H, $4CH_3CO$), 1.69 (t, 2H, *J* 7.0, 7.0 Hz, $CH_2(CH_2)_3CH_3$), 1.33 (m, 6H, $CH_2(CH_2)_3CH_3$), 0.90 (t, 3H, *J* 7.0, 6.0 Hz, $CH_2(CH_2)_3CH_3$); ^{13}C NMR (300 MHz, $CDCl_3$): δ 192.52 (C=S), 171.16, 170.84, 170.07, and 169.78 (4C, $4COCH_3$), 83.25 (C-1), 73.73 (C-5), 72.93 (C-3), 71.71 (C-2), 70.57 (C-4), 68.32 (OCH_2), 61.80 (C-6), 31.56, 28.48, 25.61, and 22.70 (4C, $4CH_2$), 20.93, 20.88, and 20.78 (4C, $4COCH_3$), 14.20 (CH_3). Anal. Calcd for $C_{21}H_{33}NO_{10}S$ (491.55): C, 51.31; H, 6.77; N, 2.85; S, 6.52. Found: C, 51.36; H, 6.72; N, 2.89; S, 6.45.

3.2.8. *O*-Cyclohexyl *N*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)thiocarbamate (2h)

White powder; yield 92%; mp 119.0–119.9 °C; $[\alpha]_D$ +6.63 (*c* 2.0, $CHCl_3$); IR (KBr) ν/cm^{-1}: 3301 (m, NH), 1752 (s, C=O), 1536 (m, NH(C=S)), 1227 and 1049 (s, C–O–C); ^1H NMR ($CDCl_3$, 500 MHz): δ 6.75 (d, 1H, *J* 9.0 Hz, NH), 5.62 (t, 1H, *J* 9.5, 9.0 Hz, H-1), 5.36 (t, 1H, *J* 9.5, 9.5 Hz, H-2), 5.27 (m, 1H, $OCH(CH_2)_5$), 5.08 (t, 1H, *J* 9.5, 9.5 Hz, H-3), 5.00 (t, 1H, *J* 9.5, 10.0 Hz, H-4), 4.34 (dd, 1H, *J* 9.5, 9.5 Hz, H-6a), 4.10 (d, 1H, *J* 12.5 Hz, H-6b), 3.86 (m, 1H, H-5), 2.11, 2.08, 2.06, 2.05 (4s, 12H, $4CH_3CO$), 1.73, 1.55, 1.46, 1.36, 1.26 (5 m, 10H, $(CH_2)_5$); ^{13}C NMR (300 MHz, $CDCl_3$): δ 191.52 (C=S), 171.28, 170.90, 170.11, and 169.83 (4C, $4COCH_3$), 83.25 (C-1), 80.06 (OCH), 73.80 (C-5), 72.90 (C-3), 70.67 (C-2), 68.34 (C-4), 61.80 (C-6), 31.44, 25.43, 23.89, and 23.86 (5C, $5CH_2$), 20.93, 20.88, and 20.78 (4C, $4COCH_3$). Anal. Calcd for $C_{21}H_{31}NO_{10}S$ (489.54): C, 51.52; H, 6.38; N, 2.86; S, 6.55. Found: C, 51.57; H, 6.32; N, 2.81; S, 6.60.

3.2.9. *O*-Octyl *N*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)thiocarbamate (2i)

White powder; yield 83%; mp 75.0–76.1 °C; $[\alpha]_D$ +6.19 (*c* 2.0, $CHCl_3$); IR (KBr) ν/cm^{-1}: 3329 (m, NH), 1744 (s, C=O), 1517 (m, NH(C=S)), 1228 and 1035 (s, C–O–C); ^1H NMR ($CDCl_3$, 500 MHz): δ 6.82 (d, 1H, *J* 9.0 Hz, NH), 5.60 (t, 1H, *J* 8.5 9.0 Hz, H-1), 5.36 (t, 1H, *J* 9.5, 9.5 Hz, H-2), 5.08 (t, 1H, *J* 9.5, 10.0 Hz, H-3), 5.00 (t, 1H, *J* 9.5, 9.5 Hz, H-4), 4.41 (m, 2H, OCH_2), 4.33 (dd, 1H, *J* 4.5, 4.0 Hz, H-6a), 4.09 (d, 1H, *J* 7.5 Hz, H-6b), 3.86 (m, 1H, H-5), 2.11, 2.09, 2.06, 2.05 (4s, 12H, $4CH_3CO$), 1.69 (t, 2H, *J* 7.0, 6.5 Hz, $CH_2(CH_2)_5CH_3$), 1.30 (m, 10H, $CH_2(CH_2)_5CH_3$), 0.91 (t, 3H, *J* 7.0, 5.5 Hz, $CH_2(CH_2)_5CH_3$); ^{13}C NMR (300 MHz, $CDCl_3$): δ 192.55 (C=S), 171.41, 170.92, 170.13, and 169.84 (4C, $4COCH_3$), 83.37 (C-1), 73.82 (C-5), 72.87 (C-3), 71.93 (C-2), 70.61 (C-4), 68.37 (OCH_2), 61.77 (C-6), 32.00, 29.43, 29.40, 28.58, 26.02, and 22.88 (6C, $6CH_2$), 21.05, 20.96, and 20.85 (4C, $4COCH_3$), 14.36 (CH_3). Anal. Calcd for $C_{23}H_{37}NO_{10}S$ (519.61): C, 53.17; H, 7.18; N, 2.70; S, 6.17. Found: C, 53.13; H, 7.12; N, 2.78; S, 6.12.

3.2.10. *O*-Allyl *N*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)thiocarbamate (2j)

White powder; yield 89%; mp 122.4–123.1 °C; $[\alpha]_D$ +1.63 (*c* 2.0, $CHCl_3$); IR (KBr) ν/cm^{-1}: 3399 (m, NH), 1743 and 1701 (s, C=O),

1511 (m, NH(C=S)), 1230 and 1037 (s, C–O–C); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.15 (d, 1H, *J* 9.0 Hz, NH), 5.82 (m, 1H, CH=), 5.29 (t, 1H, *J* 9.5, 9.5 Hz, H-1), 5.24 (t, 1H, *J* 9.5, 9.5 Hz, H-2), 5.11 (m, 2H, =CH_2), 5.07 (t, 1H, *J* 9.5, 10.0 Hz, H-3), 4.91 (t, 1H, *J* 9.5, 9.5 Hz, H-4), 4.32 (dd, 1H, *J* 4.0, 4.0 Hz, H-6a), 4.10 (d, 1H, *J* 12.5 Hz, H-6b), 3.81 (m, 1H, H-5), 3.56 (d, 2H, *J* 6.5 Hz, OCH_2), 2.08, 2.05, 2.04, 2.01 (4s, 12H, 4CH_3CO); ^{13}C NMR (300 MHz, $CDCl_3$): δ 192.50 (C=S), 171.17, 170.89, 170.15, and 169.75 (4C, 4$COCH_3$), 133.44 (CH=), 118.31 (=CH_2), 83.35 (C-1), 73.74 (C-5), 72.79 (C-3), 70.53 (C-2), 68.21 (C-4), 61.74 (C-6), 33.07 (OCH_2), 20.98, 20.88, and 20.83 (4C, 4$COCH_3$). Anal. Calcd for $C_{18}H_{25}NO_{10}S$ (447.46): C, 48.32; H, 5.63; N, 3.13; S, 7.16. Found: C, 48.38; H, 5.59; N, 3.17; S, 7.21.

3.2.11. *O*-Phenyl *N*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)thiocarbamate (2k)

2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl isothiocyanate (2 g, 0.005 mol), phenol (1 g, 0.01 mol), and toluene (20 mL) were added to a flask. Then the flask was put into a microwave reactor. The solution was heated to 80 °C and stirred for 0.5 h. A white solid was obtained after removal of the solvent. Recrystallization from 1:2 toluene–EtOAc gave a pure white solid. Yield 91%; mp 107.1–107.9 °C; $[\alpha]_D$ +2.87 (*c* 2.0, $CHCl_3$); IR (KBr) *ν*/cm^{-1}: 3316 (m, NH), 1752 and 1727 (s, C=O), 1529 (m, NH(C=S)), 1209 and 1046 (s, C–O–C); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.28–7.08 (m, 5H, aromatics), 6.85 (d, 1H, *J* 8.0 Hz, NH), 5.60 (t, 1H, *J* 9.0, 9.0 Hz, H-1), 5.40 (t, 1H, *J* 9.5, 9.5 Hz, H-2), 5.12 (t, 1H, *J* 11.5, 9.5 Hz, H-3), 5.06 (t, 1H, *J* 9.5, 9.5 Hz, H-4), 4.37 (dd, 1H, *J* 4.5, 4.5 Hz, H-6a), 4.16 (d, 1H, *J* 11.0 Hz, H-6b), 3.88 (ddd, 1H, *J* 2.0, 2.5, 2.5 Hz, H-5), 2.13, 2.10, 2.09, 2.07 (4s, 12H, 4CH_3CO); ^{13}C NMR (300 MHz, $CDCl_3$): δ 191.52 (C=S), 171.42, 170.89, 170.10, 169.81 (4C, 4$COCH_3$), 153.03, 129.85, 129.52, 129.25, 128.44, 126.71, 125.51, 122.72, and 122.85 (Ph), 83.91 (C-1), 74.08 (C-5), 72.88 (C-3), 70.88 (C-2), 68.42 (C-4), 61.80 (C-6), 20.79, 20.92, and 20.96 (4C, 4$COCH_3$). Anal. Calcd for $C_{21}H_{25}NO_{10}S$ (483.49): C, 52.17; H, 5.21; N, 2.90; S, 6.63. Found: C, 52.12; H, 5.25; N, 2.85; S, 6.59.

3.2.12. *O*-Benzyl *N*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)thiocarbamate (2l)

Compound **2l** was prepared in a similar manner to that used for **2k**, replacing phenol with benzyl alcohol. White powder; yield 77%; mp 158.9–159.6 °C; $[\alpha]_D$ +3.19 (*c* 2.0, $CHCl_3$); IR (KBr) *ν*/cm^{-1}: 3311 (m, NH), 1739 (s, C=O), 1520 (m, NH(C=S)), 1243 and 1036 (s, C–O–C); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.38–7.28 (m, 5H, aromatics), 6.93 (d, 1H, *J* 8.5 Hz, NH), 5.58 (t, 1H, *J* 9.0, 9.0 Hz, H-1), 5.39 (t, 1H, *J* 9.5, 9.5 Hz, H-2), 5.22 (s, 2H, OCH_2), 5.11 (t, 1H, *J* 7.0, 7.5 Hz, H-3), 5.03 (t, 1H, *J* 6.5. 6.5 Hz, H-4), 4.33 (dd, 1H, *J* 5.5, 5.0 Hz, H-6a), 4.13 (d, 1H, *J* 11.5 Hz, H-6b), 3.86 (m, 1H, H-5), 2.13, 2.10, 2.05, 2.04 (4s, 12H, 4CH_3CO); ^{13}C NMR (300 MHz, $CDCl_3$): δ 192.05 (C=S), 171.20, 170.81, 170.11, 169.70 (4C, 4$COCH_3$), 155.62, 137.65, 135.89, 135.21, 129.07, 128.77, 128.63, 126.59, 128.39, and 127.60 (Ph), 83.51 (C-1), 73.61 (C-5), 73.02 (C-3), 70.48 (C-2), 68.36 (C-4), 61.81 (C-6), 34.47 (OCH_2), 20.91 and 20.77 (4C, 4$COCH_3$). Anal. Calcd for $C_{22}H_{27}NO_{10}S$ (497.52): C, 53.11; H, 5.47; N, 2.82; S, 6.44. Found: C, 53.16; H, 5.42; N, 2.79; S, 6.41.

3.2.13. *O*-(Tetrahydrofurfuryl-2′-ylmethyl) *N*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)thiocarbamate (2m)

White powder; yield 79%; mp 132.2–133.4 °C; $[\alpha]_D$ +12.37 (*c* 2.0, $CHCl_3$); IR (KBr) *ν*/cm^{-1}: 3379 (m, NH), 1742 (s, C=O), 1516 (m, NH(C=S)), 1226 and 1049 (s, C–O–C); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.92 (d, 1H, *J* 9.0 Hz, NH), 5.59 (t, 1H, *J* 9.5, 9.0 Hz, H-1), 5.35 (t, 1H, *J* 9.5, 9.5 Hz, H-2), 5.08 (t, 1H, *J* 9.5, 9.5 Hz, H-3), 5.00 (t, 1H, *J* 9.5, 9.0 Hz, H-4), 4.53 (m, 2H, OCH_2), 4.36 (dd, 1H, *J* 3.5, 3.0 Hz, H-6a), 4.19 (m, 1H, H-2′), 4.13 (d, 1H, *J* 12.0 Hz, H-6b), 3.91 (m, 2H, H-5′), 3.82 (m, 1H, H-5), 2.11, 2.08, 2.06, 2.04 (4s, 12H, 4CH_3CO), 1.93 (m, 2H, H-3′), 1.65 (m, 2H, H-4′); ^{13}C NMR (300 MHz, $CDCl_3$): δ 192.34 (C=S), 171.13, 170.91, 170.15, and 169.80 (4C, 4$COCH_3$), 83.37 (C-1), 76.42 (OCH_2), 73.83 (C-5), 73.28 (C-2′), 73.02 (C-3), 70.50 (C-2), 68.68 (C-5′), 68.34 (C-4), 61.77 (C-6), 28.20 (C-4′), 25.80 (C-3′), 21.00, 20.95, and 20.83 (4C, 4$COCH_3$). Anal. Calcd for $C_{20}H_{29}NO_{11}S$ (491.51): C, 48.87; H, 5.95; N, 2.85; S, 6.52. Found: C, 48.82; H, 5.92; N, 2.91; S, 6.56.

3.2.14. Preparation of *O*-(1*H*-1,2,4-triazole-1-ylmethyl) *N*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)thiocarbamate (2n)

The preparation of 1-(hydroxymethyl)-1*H*-1,2,4-triazole followed the literature procedure.[33] 1-(Hydroxymethyl)-1*H*-1,2,4-triazole (2 g, 10 mmol) was added to acetone (15 mL), and Et_3N (0.15 g, 1.5 mmol) was dripped to the solution. Then 2,3,4,6-tetra-*O*-acetyl-β-D-glucosyl isothiocyanate (**1**, 2 g, 5 mmol) was added to the solution, and the mixture was stirred until the TLC showed that the glucosyl isothiocyanate disappeared. After removing the solvent, the product was separated from the excess 1-(hydroxymethyl)-1*H*-1,2,4-triazole by silica gel column chromatography. Recrystallization from ether yielded 87% of a white solid. Mp 61.2–62.5 °C; $[\alpha]_D$ +11.99 (*c* 2.0, $CHCl_3$); IR (KBr) *ν*/cm^{-1}: 3499 (m, NH of triazole), 3312 (m, NH), 1741 (s, C=O), 1646 (s, C=N of triazole), 1530 (m, NH(C=S)), 1240 and 1034 (s, C–O–C); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.65 (s, 1H, Tr-H), 8.07 (s, 1H, Tr-H), 6.91 (d, 1H, *J* 9.0 Hz NH), 5.57 (t, 1H, *J* 9.0, 9.5 Hz, H-1), 5.37 (t, 1H, *J* 9.5, 9.5 Hz, H-2), 5.12 (t, 1H, *J* 10.0, 9.5 Hz, H-3), 5.02 (t, 1H, *J* 9.5, 9.5 Hz, H-4), 4.32 (dd, 1H, *J* 4.5, 4.0 Hz, H-6a), 4.10 (d, 1H, *J* 12.5 Hz, H-6b), 4.01 (s, 2H, OCH_2), 3.86 (m, 1H, H-5), 2.11, 2.09, 2.06, 2.05 (4s, 12H, 4CH_3CO); ^{13}C NMR (300 MHz, $CDCl_3$): δ 190.01 (C=S), 170.77, 170.08, and 169.75 (4C, 4$COCH_3$), 152.83, 146.05 (2C, Tr), 83.53 (C-1), 74.05 (OCH_2), 73.50 (C-5), 72.96 (C-3), 70.61 (C-2), 68.19 (C-4), 61.73 (C-6), 20.88 and 20.74 (4C, 4$COCH_3$). Anal. Calcd for $C_{18}H_{24}N_4O_{10}S$ (488.47): C, 44.26; H, 4.95; N, 11.47; S, 6.56. Found: C, 44.22; H, 4.89; N, 11.51; S, 6.58.

3.2.15. *O*-2-Propylimino *N*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)thiocarbamate (2o)

The preparation of acetoxime followed the literature procedure.[34] Compound **2o** was prepared in a similar manner of **2n**, replacing 1-(hydroxymethyl)-1*H*-1,2,4-triazole with acetoxime. White powder; yield 40%; mp 78.2–79.1 °C; $[\alpha]_D$ +8.87 (*c* 2.0, $CHCl_3$); IR (KBr) *ν*/cm^{-1}: 3342 (m, NH), 1752 (s, C=O), 1611 (s, C=N), 1546 (m, NH(C=S)), 1279 and 1037 (s, C–O–C); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.30 (d, 1H, *J* 7.5 Hz, NH), 5.85 (t, 1H, *J* 9.5, 7.0 Hz, H-1), 5.39 (t, 1H, *J* 9.5, 9.0 Hz, H-2), 5.09 (t, 1H, *J* 9.5, 9.5 Hz, H-3), 5.02 (t, 1H, *J* 9.5, 9.5 Hz, H-4), 4.35 (dd, 1H, *J* 4.0, 4.0 Hz, H-6a), 4.13 (d, 1H, *J* 12.5 Hz, H-6b), 3.88 (m, 1H, H-5), 2.09, 2.07, 2.06, 2.05 (4s, 12H, 4CH_3CO), 1.23 (m, 6H, C(CH_3)$_2$); ^{13}C NMR (300 MHz, $CDCl_3$): δ 189.41 (C=S), 170.94, 170.13, 169.85, and 169.03 (4C, 4$COCH_3$), 162.98 (C=N), 83.52 (C-1), 74.09 (C-5), 72.81 (C-3), 70.59 (C-2), 68.35 (C-4), 61.80 (C-6), 22.05, 21.01, and 20.85 (4C, 4$COCH_3$), 17.92 (2C, 2CCH_3). Anal. Calcd for $C_{18}H_{26}N_2O_{10}S$ (462.47): C, 46.75; H, 5.67; N, 6.06; S, 6.93. Found: C, 46.79; H, 5.60; N, 6.08; S, 6.97.

3.2.16. *O*-(2′-Hydroxylethyl) *N*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)thiocarbamate (2p)

White powder; yield 87%; mp 158.9–159.8 °C; $[\alpha]_D$ +9.44 (*c* 2.0, $CHCl_3$); IR (KBr) *ν*/cm^{-1}: 3503 (m, OH), 3319 (m, NH), 1742 (s, C=O), 1523 (m, NH(C=S)), 1241 and 1037 (s, C–O–C); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.03 (d, 1H, *J* 9.0 Hz, NH), 5.60 (t, 1H, *J* 8.5, 8.5 Hz, H-1), 5.40 (t, 1H, *J* 9.5, 9.5 Hz, H-2), 5.11 (t, 1H, *J* 9.0, 9.5 Hz, H-3), 5.03 (t, 1H, *J* 9.0, 9.0 Hz, H-4), 4.60 (m, 2H, C$H_2$$CH_2$OH), 4.35 (dd, 1H, *J* 5.0, 5.0 Hz, H-6a), 4.14 (d, 1H, *J* 11.5 Hz, H-6b), 3.92 (m, 2H, CH_2OH), 3.87 (m, 1H, H-5), 2.12.

2.10, 2.08, 2.07 (4s, 12H, $4CH_3CO$), 1.73 (s, 1H, OH); ^{13}C NMR (300 MHz, $CDCl_3$): δ 191.51 (C=S), 171.04, 170.20, 169.93, and 169.79 (4C, $4COCH_3$), 83.24 (C-1), 73.70 (C-5), 73.16 (C-3), 72.42 (C-2), 70.62 (C-4), 68.28 (C-1′), 63.67 (C-2′), 61.78 (C-6), 21.75, 20.96, 20.87, and 20.81 (4C, $4COCH_3$). Anal. Calcd for $C_{17}H_{25}NO_{11}S$ (451.45): C, 45.23; H, 5.58; N, 3.10; S, 7.10. Found: C, 45.19; H, 5.62; N, 3.06; S, 7.07.

3.2.17. *O*-(2′-Hydroxylbutyl) *N*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)thiocarbamate (2q)

White powder; yield 50%; mp 206.6–207.5 °C; $[\alpha]_D$ +7.56 (*c* 2.0, $CHCl_3$); IR (KBr) ν/cm^{-1}: 3541 (m, OH), 3331 (m, NH), 1744 (s, C=O), 1519 (m, NH(C=S)), 1226 and 1036 (s, C–O–C); ^1H NMR ($CDCl_3$, 500 MHz): δ 6.90 (d, 1H, *J* 8.0 Hz, NH), 5.60 (t, 1H, *J* 9.0, 9.0 Hz, H-1), 5.38 (t, 1H, *J* 9.5, 9.0 Hz, H-2), 5.10 (t, 1H, *J* 9.0, 9.5 Hz, H-3), 5.01 (t, 1H, *J* 9.5, 9.5 Hz, H-4), 4.44 (m, 2H, OCH_2CHOH), 4.33 (dd, 1H, *J* 4.5, 4.0 Hz, H-6a), 4.13 (d, 1H, *J* 11.5 Hz, H-6b), 3.86 (m, 1H, H-5), 3.70 (m, 1H, CHOH), 2.11, 2.10, 2.06, 2.05 (4s, 12H, $4CH_3CO$), 1.83 (m, 2H, CH_2CH_3), 1.66 (t, 3H, *J* 7.5, 6.5 Hz, CH_2CH_3), 1.55 (s, 1H, OH); ^{13}C NMR (300 MHz, $CDCl_3$): δ 192.51 (C=S), 171.07, 170.95, 170.15, and 169.88 (4C, $4COCH_3$), 83.20 (C-1), 73.67 (C-5), 73.05 (C-3), 71.24 (C-2), 70.61 (C-4), 68.31 (C-1′), 62.05 (C-2′), 61.87 (C-6), 29.00 (C-3′), 25.03 (C-4′), 20.91, 20.88 and 20.78 (4C, $4COCH_3$). Anal. Calcd for $C_{19}H_{29}NO_{11}S$ (479.50): C, 47.59; H, 6.10; N, 2.92; S, 6.69. Found: C, 47.54; H, 6.16; N, 2.88; S, 6.62.

3.2.18. *O*-(2′-Hydroxylamyl) *N*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)thiocarbamate (2r)

White powder; yield 44%; mp 192.5–193.7 °C; $[\alpha]_D$ +7.03 (*c* 2.0, $CHCl_3$); IR (KBr) ν/cm^{-1}: 3477 (m, OH), 3323 (m, NH), 1745 (s, C=O), 1520 (m, NH(C=S)), 1228 and 1035 (s, C–O–C); ^1H NMR ($CDCl_3$, 500 MHz): δ 7.06 (d, 1H, *J* 9.0 Hz, NH), 5.58 (t, 1H, *J* 9.0, 9.0 Hz, H-1), 5.36 (t, 1H, *J* 9.5, 9.5 Hz, H-2), 5.08 (t, 1H, *J* 10.0, 9.5 Hz, H-3), 4.99 (t, 1H, *J* 9.5, 9.5 Hz, H-4), 4.52 (m, 1H, OCH_2-CHOH), 4.27 (dd, 1H, *J* 8.0, 7.5 Hz, H-6a), 4.14 (d, 1H, *J* 14.5 Hz, H-6b), 3.95 (m, 1H, CHOH), 3.86 (m, 1H, H-5), 2.10, 2.09, 2.06, 2.05 (4s, 12H, $4CH_3CO$), 1.93 (s, 1H, OH), 1.46 (m, 4H, $CH_2CH_2CH_3$), 0.95 (t, 3H, *J* 7.0, 6.5 Hz, $CH_2CH_2CH_3$); ^{13}C NMR (300 MHz, $CDCl_3$): δ 192.29 (C=S), 171.37, 170.87, 170.08, and 169.80 (4C, $4COCH_3$), 83.47 (C-1), 75.30 (C-5), 73.91 (C-3), 72.92 (C-2), 70.75 (C-4), 69.62 (C-1′), 68.41 (C-2′), 61.82 (C-6), 35.44 (C-3′), 20.92 and 20.78 (4C, $4COCH_3$), 18.79 (C-4′), 14.19 (C-5′). Anal. Calcd for $C_{20}H_{31}NO_{11}S$ (493.53): C, 48.67; H, 6.33; N, 2.84; S, 6.50. Found: C, 48.61; H, 6.39; N, 2.78; S, 6.56.

3.2.19. *O,O′*-Ethyl 1,2-di[*N*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)thiocarbamate] (2s)

White powder; yield 25%; mp 165.1–166.3 °C; $[\alpha]_D$ +10.11 (*c* 2.0, $CHCl_3$); IR (KBr) ν/cm^{-1}: 3327 (m, NH), 1745 (s, C=O), 1523 (m, NH(C=S)), 1227 and 1037 (s, C–O–C): ^1H NMR ($CDCl_3$, 500 MHz): δ 7.08 (br, 2H, 2NH), 5.61 (t, 2H, *J* 8.5, 8.5 Hz, 2H-1), 5.35 (t, 2H, *J* 9.0, 9.0 Hz, 2H-2), 5.15 (t, 2H, *J* 9.5, 9.0 Hz, 2H-3), 4.95 (t, 2H, *J* 9.0, 9.5 Hz, 2H-4), 4.31 (dd, 2H, *J* 9.5, 12.5 Hz, 2H-6a), 4.15 (d, 2H, *J* 11.0 Hz, 2H-6b), 3.92 (m, 4H, CH_2CH_2), 3.84 (m, 2H, 2H-5), 2.12–2.06 (m, 24H, $8CH_3CO$); ^{13}C NMR (300 MHz, $CDCl_3$): δ 185.67 (2C, C=S), 171.89, 170.83, 170.00, and 169.85 (8C, $8COCH_3$), 83.01 (2C, 2C-1), 73.63 (2C, 2C-5), 72.85 (2C, 2C-3), 71.09 (2C, 2C-2), 68.57 (2C, 2C-4), 61.96 (2C, 2C-6), 60.35 (2C, $2OCH_2$), 21.09, 20.95, 20.88, and 20.72 (8C, $8COCH_3$). Anal. Calcd for $C_{32}H_{44}N_2O_{20}S_2$ (840.82): C, 45.71; H, 5.27; N, 3.33; S, 7.63. Found: C, 45.77; H, 5.22; N, 3.38; S, 7.60.

3.2.20. *O,O′*-Propyl 1,2-di[*N*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)thiocarbamate] (2t)

White powder; yield 40%; mp 117.6–118.4 °C; $[\alpha]_D$ +9.23 (*c* 2.0, $CHCl_3$); IR (KBr) ν/cm^{-1}: 3327 (m, NH), 1745 (s, C=O), 1523 (m, NH(C=S)), 1226 and 1038 (s, C–O–C); ^1H NMR ($CDCl_3$, 500 MHz): δ 7.08 (br, 2H, 2NH), 5.65 (t, 2H, *J* 8.5, 8.5 Hz, 2H-1), 5.37 (t, 2H, *J* 9.0, 9.5 Hz, 2H-2), 5.13 (t, 2H, *J* 9.0, 9.0 Hz, 2H-3), 4.99 (t, 2H, *J* 9.5, 9.5 Hz, 2H-4), 4.33 (dd, 2H, *J* 8.0, 12.0 Hz, 2H-6a), 4.14 (d, 2H, *J* 12.0 Hz, 2H-6b), 3.92 (m, 3H, CH_2CH), 3.87 (m, 2H, 2H-5), 2.04–2.26 (m, 24H, $8CH_3CO$), 1.28 (m, 3H, CH_2CHCH_3); ^{13}C NMR (300 MHz, $CDCl_3$): δ 185.50 (2C, C=S), 171.83, 170.80, 170.08, and 169.85 (8C, $8COCH_3$), 82.82 (2C, 2C-1), 73.52 (2C, 2C-5), 72.79 (2C, 2C-3), 71.06 (2C, 2C-2), 68.50 (2C, 2C-4), 61.93 (2C, 2C-6), 60.64 (2C, $2OCH_2$), 21.04, 20.98, 20.81, and 20.78 (8C, $8COCH_3$), 14.41 (CH_3). Anal. Calcd for $C_{33}H_{46}N_2O_{20}S_2$ (854.85): C, 46.37; H, 5.42; N, 3.28; S, 7.50. Found: C, 46.33; H, 5.46; N, 3.24; S, 7.55.

3.3. General reaction of glucosyl thiocarbamates with $HgCl_2$

Glucosyl thiocarbamates **2a**–**2i** (1 mmol) were dissolved in DMF (20 mL) at room temperature, Et_3N (0.15 g, 1.5 mmol) was dripped into the solution, and the mixture was stirred for 20 min. Then to the reaction mixture $HgCl_2$ (0.14 g, 0.5 mmol) was slowly added with stirring for 2–5 h at 0–35 °C. After purification by silica gel column chromatography and crystallization from ethanol, compounds **3a**–**3i** were obtained.

3.3.1. Bis[*O*-methyl *N*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)thiocarbamato]mercury (3a)

White powder; yield 90%; decomposition temperature (dt) 202.5 °C; $[\alpha]_D$ +53.45 (*c* 2.0, $CHCl_3$); IR (KBr) ν/cm^{-1}: 1746 (s, C=O), 1647 (m, C=N), 1225 and 1037 (s, C–O–C); ^1H NMR ($CDCl_3$, 500 MHz): δ 5.30 (t, 2H, *J* 9.5, 9.5 Hz, 2H-2), 5.13–5.18 (m, 4H, 2H-3, 2H-4), 4.80 (d, 2H, *J* 8.5 Hz, 2H-1), 4.27 (dd, 2H, *J* 5.0, 5.0 Hz, 2H-6a), 4.15 (dd, 2H, *J* 1.5, 1.5 Hz, 2H-6b), 3.84 (m, 2H, 2H-5), 3.81 (s, 6H, $2OCH_3$), 2.09, 2.04, 2.03, 2.02 (4s, 24H, $8CH_3CO$); ^{13}C NMR (300 MHz, $CDCl_3$): δ 170.87, 170.52, 169.68, and 169.42 (8C, $8COCH_3$), 163.46 (2C, 2C-S), 90.48 (2C, 2C-1), 73.87 (2C, 2C-5), 73.33 (2C, 2C-3), 72.87 (2C, 2C-2), 68.67 (2C, 2C-4), 62.37 (2C, 2C-6), 56.80 (2C, $2OCH_3$), 21.09, 21.01, 20.89, and 20.86 (8C, $8COCH_3$). Anal. Calcd for $C_{32}H_{44}HgN_2O_{20}S_2$ (1041.41): C, 36.91; H, 4.26; N, 2.69; S, 6.16; Hg, 19.26. Found: C, 36.96; H, 4.21; N, 2.63; S, 6.12; Hg, 19.13.

3.3.2. Bis[*O*-ethyl *N*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl) thiocarbamato]mercury (3b)

White powder; yield 90%; dt 96.8 °C; $[\alpha]_D$ +43.63 (*c* 2.0, $CHCl_3$); IR (KBr) ν/cm^{-1}: 1752 (s, C=O), 1626 (m, C=N), 1229 and 1042 (s, C–O–C); ^1H NMR ($CDCl_3$, 500 MHz): δ 5.29 (t, 2H, *J* 9.5, 9.5 Hz, 2H-2), 5.11–5.16 (m, 4H, 2H-3, 2H-4), 4.79 (d, 2H, *J* 8.5 Hz, 2H-1), 4.26 (dd, 2H, *J* 6.0, 4.5 Hz, 2H-6a), 4.25 (m, 4H, $2OCH_2$), 4.14 (d, 2H, *J* 12.0 Hz, 2H-6b), 3.84 (m, 2H, 2H-5), 2.08, 2.06, 2.02, 2.01 (4s, 24H, $8CH_3CO$), 1.21 (t, 6H, *J* 3.5, 5.0 Hz, $2OCH_2CH_3$); ^{13}C NMR (300 MHz, $CDCl_3$): δ 170.96, 170.58, 169.71, and 169.42 (8C, $8COCH_3$), 162.76 (2C, 2C-S), 90.53 (2C, 2C-1), 73.81 (2C, 2C-5), 73.40 (2C, 2C-3), 72.86 (2C, 2C-2), 68.70 (2C, 2C-4), 66.05 (2C, $2OCH_2$), 62.37 (2C, 2C-6), 21.08, 20.96, 20.91, and 20.87 (8C, $8COCH_3$), 14.47 (2C, $2CH_3$). Anal. Calcd for $C_{34}H_{48}HgN_2O_{20}S_2$ (1069.47): C, 38.18; H, 4.52; N, 2.62; S, 6.00; Hg, 18.76. Found: C, 38.22; H, 4.57; N, 2.67; S, 6.05; Hg, 18.69.

3.3.3. Bis[*O*-propyl *N*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)thiocarbamato]mercury (3c)

White powder; yield 86%; dt 92.5 °C; $[\alpha]_D$ +45.32 (*c* 2.0, $CHCl_3$); IR (KBr) ν/cm^{-1}: 1755 (s, C=O), 1616 (m, C=N), 1228 and 1045 (s, C–O–C); ^1H NMR ($CDCl_3$, 500 MHz): δ 5.31 (t, 2H, *J* 9.5, 9.5 Hz, 2H-2), 5.11–5.16 (m, 4H, 2H-3, 2H-4), 4.81 (d, 2H, *J* 8.0 Hz, 2H-1), 4.28 (dd, 2H, *J* 5.0, 5.0 Hz, 2H-6a), 4.20 (m, 4H, $2OCH_2$), 4.16 (dd, 2H, *J* 3.5, 2.0 Hz, 2H-6b), 3.87 (m, 2H, 2H-5), 2.10, 2.05, 2.04, 2.03 (4s,

24H, 8CH_3CO), 1.62 (m, 4H, 2CH_2CH_3), 0.95 (t, 6H, *J* 7.5, 7.5 Hz, 2CH_2CH_3); ^{13}C NMR (300 MHz, $CDCl_3$): δ 170.84, 170.48, 169.66, and 169.28 (8C, 8$COCH_3$), 163.15 (2C, 2C-S), 90.53 (2C, 2C-1), 73.76 (2C, 2C-5), 73.32 (2C, 2C-3), 72.80 (2C, 2C-2), 71.56 (2C, 2OCH_2), 68.66 (2C, 2C-4), 62.32 (2C, 2C-6), 22.07 (2C, 2CH_2), 21.02, 20.84, and 20.81 (8C, 8$COCH_3$), 10.80 (2C, 2CH_3). Anal. Calcd for $C_{36}H_{52}HgN_2O_{20}S_2$ (1097.52): C, 39.40; H, 4.78; N, 2.55; S, 5.84; Hg, 18.28. Found: C, 39.46; H, 4.73; N, 2.59; S, 5.81; Hg, 18.20.

3.3.4. Bis[*O*-2-propyl *N*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)thiocarbamato]mercury (3d)

White powder; yield 82%; dt 103.4 °C; $[\alpha]_D$ +40.92 (*c* 2.0, $CHCl_3$); IR (KBr) ν/cm^{-1}: 1755 (s, C=O), 1620 (m, C=N), 1228 and 1044 (s, C–O–C); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.32 (t, 2H, *J* 9.5, 9.5 Hz, 2H-2), 5.25 (m, 2H, 2OCH), 5.12–5.17 (m, 4H, 2H-3, 2H-4), 4.82 (d, 2H, *J* 6.5 Hz, 2H-1), 4.32 (dd, 2H, *J* 5.5, 5.5 Hz, 2H-6a), 4.18 (d, 2H, *J* 9.5 Hz, 2H-6b), 3.87 (m, 2H, 2H-5), 2.10, 2.08, 2.05, 2.03 (4s, 24H, 8CH_3CO), 1.24 (m, 12H, 2CH(CH_3)$_2$); ^{13}C NMR (300 MHz, $CDCl_3$): δ 171.01, 170.61, 169.71, and 169.36 (8C, 8$COCH_3$), 162.00 (2C, 2C-S), 90.62 (2C, 2C-1), 73.82 (2C, 2C-5), 73.75 (2C, 2C-3), 73.53 (2C, 2C-2), 72.82 (2C, 2OCH), 68.78 (2C, 2C-4), 62.39 (2C, 2C-6), 22.38 and 21.68 (2C, 2CH_3), 21.07, 20.91, and 20.87 (8C, 8COCH_3). Anal. Calcd for $C_{36}H_{52}HgN_2O_{20}S_2$ (1097.52): C, 39.40; H, 4.78; N, 2.55; S, 5.84; Hg, 18.28. Found: C, 39.44; H, 4.82; N, 2.50; S, 5.89; Hg, 18.19.

3.3.5. Bis[*O*-butyl *N*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl) thiocarbamato]mercury (3e)

White powder; yield 84%; dt 86.3 °C; $[\alpha]_D$ +37.47 (*c* 2.0, $CHCl_3$); IR (KBr) ν/cm^{-1}: 1752 (s, C=O), 1611 (m, C=N), 1227 and 1043 (s, C–O–C); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.31 (t, 2H, *J* 9.5, 9.5 Hz, 2H-2), 5.12–5.18 (m, 4H, 2H-3, 2H-4), 4.81 (d, 2H, *J* 8.5 Hz, 2H-1), 4.28 (dd, 2H, *J* 4.5, 5.0 Hz, 2H-6a), 4.24 (m, 4H, 2OCH_2), 4.16 (d, 2H, *J* 6.5 Hz, 2H-6b), 3.85 (m, 2H, 2H-5), 2.08, 2.05, 2.04, 2.03 (4s, 24H, 8CH_3CO), 1.58 (m, 4H, 2$CH_2CH_2CH_3$), 1.35 (m, 4H, 2$CH_2CH_2CH_3$), 0.92 (t, 6H, *J* 7.5, 7.0 Hz, 2$CH_2CH_2CH_3$); ^{13}C NMR (300 MHz, $CDCl_3$): δ 170.96, 170.59, 169.70, and 169.39 (8C, 8$COCH_3$), 162.72 (2C, 2C-S), 90.56 (2C, 2C-1), 73.86 (2C, 2C-5), 73.50 (2C, 2C-3), 72.90 (2C, 2C-2), 70.05 (2C, 2OCH_2), 68.76 (2C, 2C-4), 62.40 (2C, 2C-6), 30.80 (2C, 2CH_2), 21.05, 20.96, 20.90, and 20.86 (8C, 8COCH_3), 19.62 (2C, 2CH_2), 14.18 (2C, 2CH_3). Anal. Calcd for $C_{38}H_{56}HgN_2O_{20}S_2$ (1125.57): C, 40.55; H, 5.01; N, 2.49; S, 5.70; Hg, 17.82. Found: C, 40.61; H, 5.05; N, 2.44; S, 5.74; Hg, 17.75.

3.3.6. Bis[*O*-amyl *N*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl) thiocarbamato]mercury (3f)

White powder; yield 85%; dt 89.8 °C; $[\alpha]_D$ +34.02 (*c* 2.0, $CHCl_3$); IR (KBr) ν/cm^{-1}: 1754 (s, C=O), 1614 (m, C=N), 1223 and 1042 (s, C–O–C); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.31 (t, 2H, *J* 9.5, 9.5 Hz, 2H-2), 5.12–5.18 (m, 4H, 2H-3, 2H-4), 4.81 (d, 2H, *J* 8.5 Hz, 2H-1), 4.28 (dd, 2H, *J* 5.0, 5.0 Hz, 2H-6a), 4.22 (m, 4H, 2OCH_2), 4.15 (d, 2H, *J* 8.0 Hz, 2H-6b), 3.83 (m, 2H, 2H-5), 2.10, 2.05, 2.04, 2.03 (4s, 24H, 8CH_3CO), 1.60 (m, 4H, 2$CH_2(CH_2)_2CH_3$), 1.32 (m, 8H, 2$CH_2(CH_2)_2CH_3$), 0.90 (t, 6H, *J* 6.0, 6.5 Hz, 2$CH_2(CH_2)_2CH_3$); ^{13}C NMR (300 MHz, $CDCl_3$): δ 170.91, 170.55, 169.64, and 169.33 (8C, 8$COCH_3$), 162.59 (2C, 2C-S), 90.54 (2C, 2C-1), 73.92 (2C, 2C-5), 73.58 (2C, 2C-3), 72.96 (2C, 2C-2), 70.37 (2C, 2OCH_2), 68.86 (2C, 2C-4), 62.44 (2C, 2C-6), 28.61, 28.50 and 22.56 (6C, 6CH_2), 21.00, 20.93, 20.86, and 20.81 (8C, 8COCH_3), 14.18 (2C, 2CH_3). Anal. Calcd for $C_{40}H_{60}HgN_2O_{20}S_2$ (1153.63): C, 41.65; H, 5.24; N, 2.43; S, 5.56; Hg, 17.39. Found: C, 41.62; H, 5.20; N, 2.48; S, 5.59; Hg, 17.31.

3.3.7. Bis[*O*-hexyl *N*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)thiocarbamato]mercury (3g)

White powder; yield 89%; dt 74.6 °C; $[\alpha]_D$ +40.92 (*c* 2.0, $CHCl_3$); IR (KBr) ν/cm^{-1}: 1754 (s, C=O), 1613 (m, C=N), 1224 and 1042 (s, C–O–C); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.30 (t, 2H, *J* 9.5, 9.5 Hz, 2H-2), 5.12–5.18 (m, 4H, 2H-3, 2H-4), 4.80 (d, 2H, *J* 8.0 Hz, 2H-1), 4.28 (dd, 2H, *J* 5.0, 4.5 Hz, 2H-6a), 4.24 (t, 4H, *J* 12.0, 11.5 Hz, 2OCH_2), 4.15 (d, 2H, *J* 6.5 Hz, 2H-6b), 3.85 (m, 2H, 2H-5), 2.10, 2.07, 2.05, 2.03 (4s, 24H, 8CH_3CO), 1.60 (m, 4H, 2$CH_2(CH_2)_3CH_3$), 1.30 (m, 12H, 2$CH_2(CH_2)_3CH_3$), 0.89 (t, 6H, *J* 7.0, 6.5 Hz, 2$CH_2(CH_2)_3CH_3$); ^{13}C NMR (300 MHz, $CDCl_3$): δ 171.00, 170.62, 169.71, and 169.39 (8C, 8$COCH_3$), 162.59 (2C, 2C-S), 90.57 (2C, 2C-1), 73.86 (2C, 2C-5), 73.48 (2C, 2C-3), 72.86 (2C, 2C-2), 70.42 (2C, 2OCH_2), 68.70 (2C, 2C-4), 62.36 (2C, 2C-6), 31.65, 28.74, 26.10, and 22.78 (8C, 8CH_2), 21.08, 21.00, 20.93, and 20.88 (8C, 8COCH_3), 14.29 (2C, 2CH_3). Anal. Calcd for $C_{42}H_{64}HgN_2O_{20}S_2$ (1181.69): C, 42.69; H, 5.46; N, 2.37; S, 5.43; Hg, 16.97. Found: C, 42.63; H, 5.41; N, 2.43; S, 5.46; Hg, 16.88.

3.3.8. Bis[*O*-cyclohexyl *N*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)thiocarbamato]mercury (3h)

White powder; yield 87%; dt 78.5 °C; $[\alpha]_D$ +36.36 (*c* 2.0, $CHCl_3$); IR (KBr) ν/cm^{-1}: 1753 (s, C=O), 1617 (m, C=N), 1224 and 1041 (s, C–O–C); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.30 (t, 2H, *J* 9.5, 9.5 Hz, 2H-2), 5.13–5.16 (m, 4H, 2H-3, 2H-4), 5.08 (m, 2H, 2OCH), 4.81 (d, 2H, *J* 8.5 Hz, 2H-1), 4.30 (dd, 2H, *J* 5.0, 5.5 Hz, 2H-6a), 4.17 (d, 2H, *J* 9.5 Hz, 2H-6b), 3.87 (m, 2H, 2H-5), 2.10, 2.05, 2.03, 2.02 (4s, 24H, 8CH_3CO), 1.31–1.70 (m, 20H, 2$(CH_2)_5$); ^{13}C NMR (300 MHz, $CDCl_3$): δ 171.02, 170.62, 169.72, and 169.31 (8C, 8$COCH_3$), 161.89 (2C, 2C-S), 90.67 (2C, 2C-1), 77.87 (2C, 2OCH), 73.79 (2C, 2C-5), 73.49 (2C, 2C-3), 72.78 (2C, 2C-2), 68.73 (2C, 2C-4), 62.36 (2C, 2C-6), 31.67, 30.82, 25.57, 23.60, and 23.39 (10C, 10CH_2), 21.06, 20.91, 20.86 and 20.84 (8C, 8COCH_3). Anal. Calcd for $C_{42}H_{60}HgN_2O_{20}S_2$ (1177.65): C, 42.84; H, 5.14; N, 2.38; S, 5.44; Hg, 17.03. Found: C, 42.80; H, 5.19; N, 2.33; S, 5.48; Hg, 16.94.

3.3.9. Bis[*O*-octyl *N*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl) thiocarbamato]mercury (3i)

White powder; yield 84%; dt 64.9 °C; $[\alpha]_D$ +31.67 (*c* 2.0, $CHCl_3$); IR (KBr) ν/cm^{-1}: 1745 (s, C=O), 1641 (m, C=N), 1228 and 1038 (s, C–O–C); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.31 (t, 2H, *J* 9.5, 9.5 Hz, 2H-2), 5.15–5.20 (m, 4H, 2H-3, 2H-4), 4.80 (d, 2H, *J* 8.5 Hz, 2H-1), 4.30 (dd, 2H, *J* 4.5, 4.5 Hz, 2H-6a), 4.25 (m, 4H, 2OCH_2), 4.18 (d, 2H, *J* 8.5 Hz, 2H-6b), 3.87 (m, 2H, 2H-5), 2.09, 2.00, 1.99, 1.97 (4s, 24H, 8CH_3CO), 1.60 (m, 8H, 2$(CH_2)_2(CH_2)_5CH_3$), 1.17 (m, 20H, 2$(CH_2)_2(CH_2)_5CH_3$), 0.90 (t, 6H, *J* 7.0, 6.0 Hz, 2$(CH_2)_2(CH_2)_5CH_3$); ^{13}C NMR (300 MHz, $CDCl_3$): δ 171.00, 170.61, 169.70, and 169.38 (8C, 8$COCH_3$), 162.62 (2C, 2C-S), 90.60 (2C, 2C-1), 73.86 (2C, 2C-5), 73.49 (2C, 2C-3), 72.87 (2C, 2C-2), 70.37 (2C, 2OCH_2), 68.70 (2C, 2C-4), 62.35 (2C, 2C-6), 29.44, 28.77, and 26.40 (12C, 12CH_2), 21.08, 21.01, 20.93, and 20.88 (8C, 8COCH_3), 14.36 (2C, 2CH_3). Anal. Calcd for $C_{46}H_{72}HgN_2O_{20}S_2$ (1237.79): C, 44.64; H, 5.86; N, 2.26; S, 5.18; Hg, 16.21. Found: C, 44.68; H, 5.81; N, 2.21; S, 5.14; Hg, 16.13.

Acknowledgments

This work was supported by the Natural Science Foundation of Jiangsu Province, China (No. BK2005094) and the Science & Technology Development Foundation of Nanjing Agricultural University, China (No. 0506F0005).

References

1. Goel, A.; Mazur, S. J.; Fattah, R. J.; Hartman, T. L.; Turpin, J. A.; Huang, M.; Rice, W. G.; Appella, E.; Inman, J. K. *Bioorg. Med. Chem. Lett.* **2002**, *12*, 767–770.
2. Ryder, N. S.; Frank, I.; Dupont, M. C. *Antimicrob. Agents Chemother.* **1986**, *29*, 858–860.
3. Beji, M.; Sbihi, H.; Baklouti, A.; Cambon, A. *J. Fluorine Chem.* **1999**, *99*, 17–24.
4. Breiter, W. A.; Baker, J. M.; Koskinen, W. C. *J. Agric. Food Chem.* **1998**, *46*, 1624–1629.

5. Lee, S. J.; Caboni, P.; Tomizawa, M.; Casida, J. E. *J. Agric. Food Chem.* **2004**, *52*, 95–98.
6. Chen, Y. S.; Schuphan, I.; Casida, J. E. *J. Agric. Food Chem.* **1979**, *27*, 709–712.
7. Chen-Hsien, W. *Synthesis* **1981**, 622–623.
8. Chai, C.; Ye, F. *World Pestic.* **2004**, *26*, 33–36.
9. Mizuno, T.; Takahashi, J.; Ogawa, A. *Tetrahedron* **2003**, *59*, 1327–1331.
10. Zhang, X. P.; Jing, H. Z.; Miao, J. H.; Lu, S. W. *J. Prog. Chem.* **2008**, *7/8*, 1102–1106.
11. Liu, A. P.; Yu, Z. Y.; Li, Z. L. *J. Pestic.* **1997**, *36*, 8–12.
12. Zhang, S. S.; Wang, Z. W.; Li, M.; Jiao, K.; Razak, I. A.; Sundara Raj, S. S.; Fun, H. K. *Acta Crystallogr., Sect. C* **2001**, *57*, 566–568.
13. Prata, C.; Mora, N.; Lacombe, J. M.; Maurizis, J. C.; Pucci, B. *Carbohydr. Res.* **1999**, *321*, 4–14.
14. Avalos, M.; Babiano, R.; Cintas, P.; Jiménez, J. L.; Palacios, J. C. *J. Chem. Soc., Perkin Trans. 1* **1990**, 495–501.
15. Reitz, A. B.; Tuman, R. W.; Marchione, C. S.; Jordan, A. D., Jr.; Bowden, C. R.; Maryanoff, B. E. *J. Med. Chem.* **1989**, *32*, 2110–2116.
16. Parrot-Lopez, H.; Galons, H.; Coleman, A. W.; Mahnteau, J.; Miocque, M. *Tetrahedron Lett.* **1992**, *33*, 209–212.
17. Mukerjee, A. K.; Ashare, R. *Chem. Rev.* **1991**, *91*, 1–24.
18. Pill, T.; Beck, W. *Z. Naturforsch. B: Chem. Sci.* **1993**, *48*, 1461–1469.
19. Chen, Q.; Lu, Q. C. *Microelement and Human Health*; Perking University Press: Perking, 1989.
20. Shagun, V. A.; Smirnov, V. I.; Shagun, L. G.; Shevchenko, S. G.; Frolov, Yu. L. *J. Struct. Chem.* **2006**, *47*, 831–838.
21. Gutiérrez, A. J.; Lozano, G.; González, T.; Reguera, J. I.; Hardisson, A. *J. Food Prott.* **2006**, *69*, 2237–2240.
22. Liu, G. Y.; Zhong, H.; Dai, T. G.; Xia, L. Y. *Miner. Eng.* **2008**, *21*, 1050–1054.
23. Seryakova, I. V.; Vorobiova, G. A.; Glembotskii, A. V. *Anal. Chim. Acta* **1975**, *77*, 183–190.
24. Cao, L. H.; Zhou, C. J.; Gao, H. Y.; Liu, Y. T. *J. Chin. Chem. Soc.* **2001**, *48*, 207–210.
25. Kühne, M.; Györgydeák, Z.; Lindhorst, T. K. *Synthesis* **2006**, 949–951.
26. Lindhorst, T. K.; Kiebury, C. *Synthesis* **1995**, 1228–1230.
27. Deng, X. J.; Wan, Q. H. *Fine Chem.* **2005**, *22*, 308–310.
28. Jian, F. F.; Wen, L. R.; Li, X. M.; Zhang, S. S.; Jiao, K. *Chem. J. Chin. Univ.* **2003**, 58–60.
29. Martos, M. B. *Nature* **1950**, *165*, 369.
30. Li, Y. W.; Li, Y. X.; Zhang, W.; Guan, H. S. *Chin. J. Org. Chem.* **2004**, *24*, 438–439.
31. Yang, L. P.; Li, S. Z.; Li, Y. C.; Gao, R. Y. *Chin. J. Pestic. Sci.* **2002**, *4*, 67–70.
32. Li, M.; Wen, L. R.; Jing, S. X.; Zhang, Y. B.; Yang, W. Z.; Zhang, S. S. *Chin. J. Org. Chem.* **2001**, *21*, 1137–1141.
33. Tang, Z. L.; Liu, H. W.; Wang, X. G.; Ou, X. M.; Tang, R. H.; Chen, Y. B. *Chin. J. Org. Chem.* **2007**, *27*, 999–1006.
34. Wang, Y. G.; Yuan, L. P.; Chen, L.; Cao, J.; Guo, Q. M.; Zhang, Y. B. *Chin. J. Pestic. Sci.* **2005**, *7*, 114–118.