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SYNTHESIS AND SPECTRAL STUDIES OF NOVEL THIOAMIDO LINKED GLYCOSYL HETEROCYCLES

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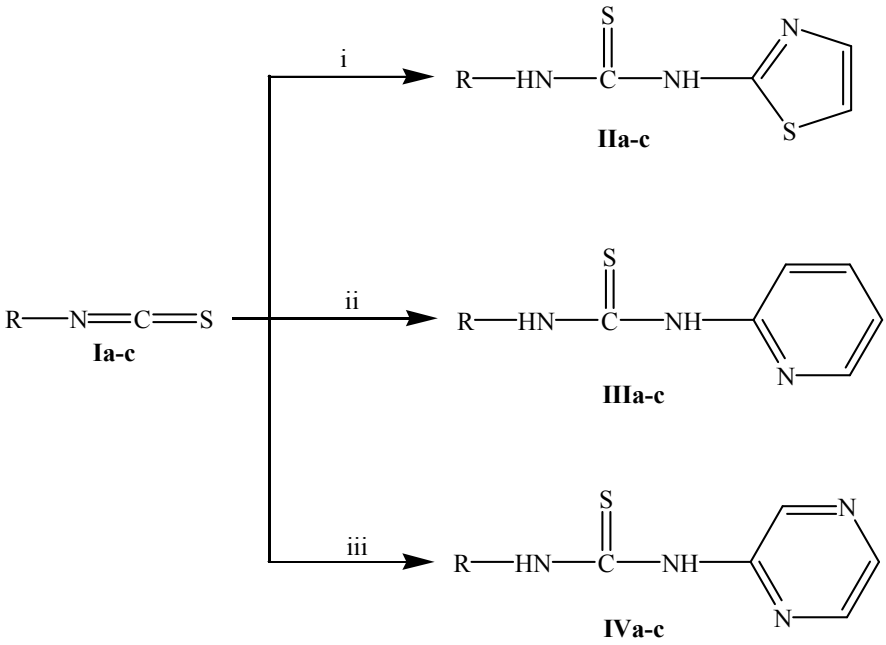
ABSTRACT
Glycosyl isothiocyanates being a versatile reagent in carbohydrate chemistry is widely used in the synthesis of glycosyl heterocycles. Several thioamido linked glycosyl thiazole **II**, glycosyl pyridine **III** and glycosyl pyrazine **IV** has been synthesised by the condensation of glycosyl isothiocyanate **Ia-c** with amino thiazole, amino pyridine and amino pyrazine respectively. Structures of these compounds were confirmed on the basis of IR, ^{1}HNMR and mass spectral study.

KEYWORDS
Glycosyl isothiocyanates, thioamido glycosyl thiazole, glycosyl pyridine and glycosyl pyrazine.

INTRODUCTION
Isothiocyanates are precursors of a wide range of *N*-thiocarbamoyl derivatives; their tendency to undergo nucleophilic additions and cycloadditions make them highly important intermediates in organic synthesis[i] for the preparation of thioureas and heterocyclic compounds[ii,iii].
In particular, sugar isothiocyanates[iv-vii] have been used extensively in the preparation of compounds with synthetic, biological and pharmacological interest; among them, noteworthy are thioureas[viii,ix] , glycosyl amines[x], *N*-glycopeptides[xi], and glycosyl guanidines[xii]. The preparation of antitumor agents obtained by reaction of glycosyl isothiocyanates with 5-aminopyrimidine derivatives have also been reported[xiii]. Recently, sugar isothiocyanates have been used for obtaining glycoclusters bearing a thioureido tether[xiv,xv] and calyx-sugars[xvi] in the field of supramolecular chemistry.

EXPERIMENTAL
All reactions are monitored on Merck silica gel plates. Melting points were recorded on electro thermal melting point apparatus without correction. IR spectra were recorded on a Perkin–Elmer spectrum RXI (4000-450cm^{-1}) FTIR spectrometer. ^{1}HNMR spectrum were obtained on a Bruker DRX-300 (300 MHz FT NMR) NMR spectrometer in $CDCl_3$ solution with TMS as an internal reference. The mass spectra were recorded on a Jeol SX−102 mass spectrometer.



Scheme-I

Where, R= a) Per-*O*-acetyl glucosyl, b) Per-*O*-acetyl lactosyl, c) Per-*O*-acetyl maltosyl
i) 2-Amino thiazole, toluene, reflux, 3-4 hr, ii) 2-amino Pyridine, toluene, reflux, 3-4 hr, iii) 2-Amino pyrazine, toluene, reflux, 3-4 hr

General Procedure A solution of Per-*O*-acetyl glycosyl isothiocyanate **1a-c** (1 mmol) and aryl amines (1 mmol) are refluxed in toluene (50ml) for 3-4 hr. Progress of reaction is monitored by TLC (Ethyl acetate: petroleum ether 1:1). Toluene is distilled off under reduced pressure, sticky mass obtained was triturated with petroleum ether (60-80^{o}). The granular solid obtained is purified on silica gel chromatography.

RESULTS AND DISCUSSION

Tetra-*O*-acetyl-β-D-glucosyl-3-*N*-thiazol-2-yl isothiocarbamide (2a)

^{1}HNMR ($CDCl_3$) δ: 7.7-7.1 (2H, Ar−H), 5.65-3.81 (7H, glucose unit), 2.12-1.97 (12H, $4COCH_3$). IR(KBr)cm^{-1}: 3345(N−H),1762(C=O), 1607(C=N), 1360(C−N), 1228 (C−O), 1045 (C=S). FAB-MS *m/z*: 489.5 (M^+).

Hepta-*O*-acetyl-β-D-lactosyl-3-*N*-thiazol-2-yl isothiocarbamide (2b)

^{1}HNMR ($CDCl_3$) δ: 7.27-7.01 (2H, Ar−H), 5.45-3.48 (14H, lactose unit), 2.19-2.00 (21H, $7COCH_3$). IR (KBr) cm^{-1}: 3350(N−H), 1760(C=O), 1600(C=N), 1435(C−N), 1228(C−O), 1037(C=S), 1045 & 910 (Lactose unit). FAB-MS *m/z*: 778.1 (M^++1), 619, 559, 331, 169, 109.

Hepta-*O*-acetyl-β-D-maltosyl-3-*N*-thiazol-2-yl isothiocarbamide (2c)

^{1}HNMR ($CDCl_3$) δ: 7.33−7.12 (2H, Ar−H), 5.6−3.9 (14H, maltose unit), 2.3-1.9 (21H, $7COCH_3$). IR (KBr) cm^{-1}: 3350(N−H), 1760(C=O), 1620(C=N), 1440(C−N), 1240(C−O), 1060(C=S), 1037, 937, 901 (maltose unit). FAB-MS *m/z*: 778.1 (M^++1), 619, 559, 331, 169, 109.

Tetra-*O*-acetyl-β-D-glucosyl-3-*N*-pyridin-2-yl isothiocarbamide (3a)
^{1}HNMR ($CDCl_3$) δ: 8.25-8.1 (4H, Ar−H), 5.62-3.75 (7H, glucose unit), 2.17-1.92 (12H, $4COCH_3$). IR (KBr) cm^{-1}: 3355(N−H),1758(C=O), 1615(C=N), 1365(C−N), 1228 (C−O), 1036 (C=S). FAB-MS *m/z*: 483.5 (M^++1)

Hepta-*O*-acetyl-β-D-lactosyl-3-*N*-pyridin-2-yl isothiocarbamide (3b)
^{1}HNMR ($CDCl_3$) δ: 7.27−7.12 (4H, Ar−H), 5.11−3.77 (14H, lactose unit), 2.01−1.95 (21H, $7COCH_3$). IR(KBr)cm^{-1}: 3350(N−H),1760(C=O), 1608(C=N), 1440(C−N), 1228 (C−O), 1037(C=S), 1045 & 910 (Lactose unit). FAB-MS *m/z*: 771.2 (M^++1), 619, 559, 331, 169, 109.

Hepta-*O*-acetyl-β-D-maltosyl-3-*N*-pyridin-2-yl isothiocarbamide (3c)
^{1}HNMR ($CDCl_3$) δ: 8.33-7.56 (4H, Ar−H), 5.46-3.98 (14H, maltose unit), 2.11−1.96 (21H, $7COCH_3$). IR(KBr)cm^{-1}: 3370(N−H),1760(C=O), 1600(C=N), 1430(C−N), 1060(C=S), 1240 (C−O), 1037, 937, 901 (maltose unit). FAB-MS *m/z*: 771.2 (M^++1), 619, 559, 331, 169, 109.

Tetra-*O*-acetyl-β-D-glucosyl-3-*N*-pyrazin-2-yl isothiocarbamide (4a)
^{1}HNMR ($CDCl_3$) δ: 8.3-8.2 (3H, Ar−H), 5.8-3.9 (7H, glucose unit), 2.1-2.01 (12H, $4COCH_3$). IR(KBr)cm^{-1}: 3350(N−H),1760(C=O), 1610(C=N), 1371(C−N), 1228 (C−O), 1037 (C=S). FAB-MS *m/z*: 485.19 (M^++1).

Hepta-*O*-acetyl-β-D-lactosyl-3-*N*-pyrazin-2-yl isothiocarbamide (4b)
^{1}HNMR ($CDCl_3$) δ: 8.0-7.94 (3H, Ar−H), 5.5−3.7 (14H, lactose unit), 2.16−1.97 (21H, $7COCH_3$). IR (KBr) cm^{-1}: 3380 (N−H),1755 (C=O), 1640(C=N), 1360(C−N), 1210 (C−O), 1040 (C-S), 1060 & 920 (Lactose unit). FAB-MS *m/z*: 773.2 (M^++1), 619, 559, 331, 169, 109.

Hepta-*O*-acetyl-β-D-maltosyl-3-*N*-pyrazin-2-yl isothiocarbamide (4c)
^{1}HNMR ($CDCl_3$) δ: 7.94-7.28 (3H, Ar−H), 5.6−3.9 (14H, maltose unit), 2.4-1.9 (21H, $7COCH_3$). IR(KBr)cm^{-1}: 3400(N−H),1755(C=O), 1635(C=N), 1361(C−N), 1228 (C−O), 1037 (C-S), 1040, 941, 905 (maltose unit). FAB-MS *m/z*: 773.2 (M^++1), 619, 559, 331, 169, 109.

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REFERENCES

i. Braverman S., Cherkinsky M. and Birsa M. L., Sci. Synth., 18, (2005), 65
ii. Mukerjee A. K. and Ashare R., Chem. Rev., 91, (1991), 196
iii. Fernández-Bolaños J. G., López Ó. and Brandsma L., Eur. J. Org. Chem., (2001) 4569
iv. García Fernández J. And Ortiz Mellet C., Adv. Carbohydr. Chem. Biochem., 55, (2000), 35
v. Witczak Z. J., Adv. Carbohydr. Chem. Biochem., 44, (1986), 91
vi. García Fernández J. M. and Ortiz Mellet C., Sulfur Rep. 19, (1996),61
vii. Goodman I., Adv. Carbohydr. Chem., 13, (1958), 215
viii. López Ó., Maya I., Fuentes J. and Fernández-Bolaños J. G., Tetrahedron, 60, (2004), 61
ix. Fuentes J., Angulo M. and Pradera M. A., J. Org. Chem., 67, (2002), 2577
x. Isac-García J., Calvo-Flores F. G., Hernández-Mateo F. and Santoyo-González F. Eur.

J. Org. Chem., (2001), 383
xi. Taylor C. M., Tetrahedron 54, (1998), 11317
xii. Shi H. F. and Cao L. H., Youji Huaxue, 25, (2005),1066
xiii. Machón Z., Mielczarek I., Wieczorek J. and Mordarski M., Arch. Immunol. Ther. Exp.35, (1987), 609
xiv. Benito J. M., Gómez-García M., Ortiz Mellet C., Baussanne I., Defaye J. and García Fernández J. M., J. Am. Chem. Soc., 126, (2004), 10355
xv. Patel A. and Lindhorst T. K., Eur. J. Org. Chem., (2002), 79
xvi. Saitz-Barrie C., Torres-Pinedo A. and Santoyo-González F., Synlett, (1999), 1891

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