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Synthesis and Characterization of Bis N & S-Protected Mannopyranosyl Isodithiobiurets

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ABSTRACT

Medicinal and Biological applications of various carbohydrates are studies earlier, in view of this application we have synthesized protected Mannopyranosyl isodithiobiurets by the interaction of N-tetra-O-acetyl-β-D-Mannopyranosyl isothiocyanate with 1-aryl-S-benzyl isothiocarbamides. The products were separated by column chromatography, melting points and specific rotations were measured by standard methods. The characterizations of these newly synthesized products were established on the basis of elemental analysis, UV, IR, ^{1}H NMR, ^{13}C NMR & Mass spectral studies.

Keywords: Synthesis, Mannopyranosyl isothiocyanate, Aryl isothicarbamides & isodithiobiurets

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INTRODUCTION

In important class of carbohydrate chemistry, synthesis of glucosylated[1-3], lacosylated[4-5], maltosylated[6], mannosylated[7, 8] and galactosyl[9] isothiocyanate and thiocarbamides are as an intermediate. Its derivatives show various medicinal and biological applications. In last few years we observed that, synthesis of glucosylated[10], lacosylated[11], maltosylated[6] isodithiobiurets have been reported. In view of this application of various carbohydrates and we have newly synthesized some protected mannopyranosyl isodithiobiurets.

Several 1-aryl-5-tetra-o-acetyl-□-D-mannopyranosyl-2-S-benzyl-2,4-isodithiobiurets (**3a-j**) have been synthesized first time in our laboratory by the interaction of N-tetra-O-acetyl-β-D-Mannopyranosyl isothiocyanate (**1**) with 1-aryl-S-benzyl isothiocarbamides (**2a-j**). The identities of these newly synthesized compounds were established on the basis of elemental analysis, UV, IR, ^{1}H NMR, ^{13}C NMR & Mass spectral studies.

MATERIALS AND METHODS:

Melting point of newly synthesized compounds were taken in open capillary method & are found uncorrected. Optical rotations $[\alpha]_D$ were measured on a EQUIP-TRONICS Digital Polarimeter model no. EQ 800 at 28 ^{0}C in $CHCl_3$. UV spectra were recorded on a UV-VIS Spectrophotometer (λmax 400-200 nm in $CHCl_3$). IR spectra were recorded on a Perkin Elmer spectrum RXI (4000-450 cm^{-1}) FTIR Spectrophotometer. ^{1}H NMR was obtained on a Bruker DRX-300 (300 MHz FT NMR) NMR Spectrometer in $CDCl_3$ with TMS as an internal reference. The FAB mass spectra were recorded on a JEOL SX 102/DA-6000 mass spectrometer / date system using argon / xenon (6Kv, 10 mA) as the FAB gas. The accelerating voltage was 10 Kv, and the spectra were recorded at room temperature. m-Nitrobenzyl alcohol (NBA) was used as matrix unless specified otherwise. TLC were performed with E. Merck precoated TLC plates, aluminium silica Gel_{60} $F_{254,}$ with visualization by UV cabinet, Iodine chamber and by charring with 10% H_2SO_4 & data was shown in Table 1.

The required N-tetra-O-acetyl-β-D-Mannopyranosyl isothiocyanate[7,8] (**1**) with 1-aryl-S-benzyl isothiocarbamides[12](**2a-j**).

N-Tetra-O-acetyl-β-D-Mannopyranosyl isothiocyanate[7,8]:

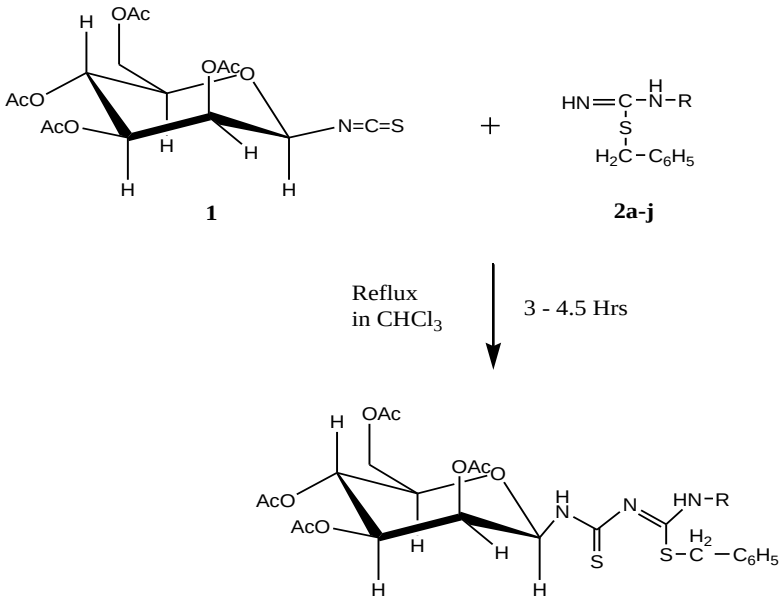
N-tetra-O-acetyl-β-D-Mannopyranosyl isothiocyanate was prepared by the condensation of N-tetra-O-acetyl-β-D-Mannopyranosyl Bromide (0.01M, 4.11g) and lead thiocyanate (0.005M, 1.615g) in boiling sodium dried xylene (20 mL) for 3h while reaction monitoring by TLC. Lead Bromide that formed was filtered and solvent was distilled off and the resultant sticky residue

triturated several times with petroleum ether to afford the syrupy semisolid mass. The products were separated as semisolid by column chromatography using 1:1 EtOAc/CCl_4.

Aryl-S-benzyl Isothiocarbamides[12] (2a-j):

Synthesis of various 1-aryl-S-benzyl isothiocarbamides were synthesized by the interaction of benzyl chloride with aryl thiocarbamides in ethanolic medium and reaction mixture were refluxed for 1.5 hrs. The products were basifying with cold ammonium hydroxide and recrystallised by ethanol. The whole reaction monitoring by TLC we got single spot.

1-Phenyl-5-tetra-o-acetyl- β -D-mannopyranosyl-2-S-benzyl-2,4-isodithiobiuret (3a): 1-Phenyl-5-tetra-o-acetyl-**β**-D-mannopyranosyl-2-S-benzyl-2,4-isodithiobiuret(**3a**) was synthesized by the interaction of N-Tetra-O-acetyl-β-D-Mannopyranosyl isothiocyanate (**1**, 2.03 g, 5 m mole) with 1-Phenyl-S-benzyl isothiocarbamide (**2a**, 1.21 g, 5 m mole) in boiling chloroform (15 mL) for 4 h while monitoring reaction by TLC. The product was separated as solid by column chromatography using 10% EtOAc/Hexane as elutent & the product was desulphurised by alkaline plumbite test.



1 **2a-j** **3a-j**

Where,

R= a) b) c) d) e) f) g) h) i) j)

Ac = CH_3-CO- (Acetyl Group)

Scheme -1

RESULT & DISCUSSION:

N-Tetra-O-acetyl-β-D-Mannopyranosyl isothiocyanate: The N-Tetra-O-acetyl-β-D-mannopyranosyl isothiocyanate was desulphurised by alkaline plumbite test & it also gives

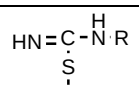
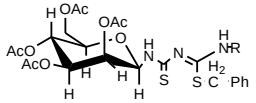
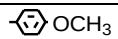
positive test of isothiocyanate. Yield, 2.25g (57.84%), mp 86-88^0(d), $[\alpha]_D^{29}$ -72^0 (c, 0.921 in $CHCl_3$), R_f, 0.66 (1:1; CCl_4: EtOAc). UV ($CHCl_3$), λmax, 264.5 nm. IR υmax cm^{-1} ($CHCl_3$), 2965, 2137, 2015, 1750, 1378, 1214, 1085. ^{1}H NMR ($CDCl_3$), δ= 5.69-4.14(m, 5H, Man. ring H_1-H_5), 4.07(s, 2H, O-CH_2-), 2.17(s, 12H, 4 –$COCH_3$). ^{13}C NMR ($CDCl_3$), δ= 171.3, 170.3, 169.0, 168.5(C=O), 146.2(S=C=N), 82.0(C-1), 75.1(C-5), 70.6(C-3), 69.3(C-2), 65.5(C-4), 62.5(C-4), 20.5($COCH_3$). FABMS (m/z), 389(M^+), 331(M – N=C=S). "Anal. Calcd. for $C_{15}H_{19}NO_9S$: C, 46.27; H, 4.88; N, 3.59; S, 8.22. Found: C, 46.03; H, 4.79; N, 3.42; S, 7.98".

1-Aryl-5-tetra-o-acetyl-β-D-mannopyranosyl-2-S-benzyl-2,4-isodithiobiurets (**3a-j**) were synthesized by the condensation of N-tetra-O-acetyl-β-D-Mannopyranosyl isothiocyanate (**1**) and Aryl-S-benzyl isothiocarbamides (**2a-j**) in boiling chloroform for 3.0-4.5 hrs while monitoring the reaction by TLC. The products were separated as solid by column chromatography using 10% EtOAc/Hexane as elutent. The characterizations of products (**3a-j**) were established on the basis of UV, IR, ^{1}H NMR, ^{13}C NMR & Mass spectral studies.

1-Phenyl-5-tetra-o-acetyl-β-D-mannopyranosyl-2-S-benzyl-2,4-isodithiobiuret (3a): Yield 2.76 g (87.52%), m.pt. 105^{0}C, $[\alpha]_D^{28}$ +112 (c, 0.567 in $CHCl_3$), UV ($CHCl_3$), λmax, 240 nm, IR υmax cm^{-1} ($CHCl_3$), 3351(N-H), 3087(Ar-H), 2890(C-H), 1757(C=O), 1592(S-C=N), 1200(C-O), 1100(C=S), 1032(Mannopyranosyl ring deformation), 740(C-S), 710, 690 cm^{-1}(Monosubstituted ring). ^{1}H NMR ($CDCl_3$), δ= 7.35-7.3 (m, 5H, Ar-H), 7.14-7.06(m, 5H, Ar-H), 5.25-4.65(m,5H, Man. ring), 4.52(s, 2H, O-CH_2-), 4.25-4.19(bs, 1H, NH), 4.13(s, 2H, CH_2-S), 4.0(s, 1H, NH), 2.01(s, 12H, 4 –$COCH_3$). ^{13}C NMR ($CDCl_3$), δ= 173.3, 169.5(C=O), 146.5(S-C=N), 130-125.5(Ar-C), 82.1(C-1), 75.0(C-5), 69.9(C-3), 68.5(C-2), 65.5(C-4), 20.9($COCH_3$). FABMS (m/z), 631(M^+), 389(Man-N=C=S), 331(Man). "Anal. Calcd. for $C_{29}H_{33}N_3O_9S_2$: C, 55.15; H, 5.22; N, 6.65; S, 10.14. Found: C, 55.55; H, 4.97; N, 6.24; S, 9.87".

1-o-Tolyl-5-tetra-o-acetyl-β-D-mannopyranosyl-2-S-benzyl-2,4-isodithiobiuret(3b): Yield 2.67 g (82.91%), m.pt. 165^{0}C, $[\alpha]_D^{28}$ + 256 (c, 0.323 in $CHCl_3$), UV ($CHCl_3$), λmax, 261 nm, IR υmax cm^{-1} ($CHCl_3$), 3389(N-H), 3065(Ar-H), 2945, 2885(C-H), 1735 (C=O), 1590(S-C=N), 1185(C-O), 1092(C=S), 1025(Mannopyranosyl ring deformation), 755(1,2-disubstituted ring), 745(C-S), 710, 690 cm^{-1}(Monosubstituted ring). ^{1}H NMR ($CDCl_3$), δ= 7.35-7.22(m, 4H, Ar-H),7.14-7.06(m, 5H, Ar-H), 5.32-4.65(m,5H, Man. ring), 4.21(s, 2H, O-CH_2-), 4.13(s, 2H, CH_2-S), 4.0 (s, 1H, NH), 2.35(s, 3H, CH_3-Ar), 2.01(s, 12H, 4 –$COCH_3$), 1.95(s, 1H, NH). ^{13}C NMR ($CDCl_3$), δ= 180.2, 172.5(C=O), 149.7(S-C=N), 131.7-126.4(Ar-C), 83.7(C-1), 76.2(C-5), 70.2(C-3), 69.7(C-2), 64.1(C-4), 20.2($COCH_3$). FAB MS (m/z), 645(M^+), 389(Man-N=C=S),

Table 1- Synthesis of 1-Aryl-5-tetra-O-acetyl-β-D-Mannopyranosyl-2-S-benzyl-2,4-isodithiobiurets (3a-j)

S.N.	 **2a-j (g)**	Rea Time (h)	 **3a-j**	M.P. ^{O}C	Yield, (%)	$[\alpha]_D^{28}$ (C)	Rf (EtOAc / Hexane)
1.	2a, R =  (1.21)	4.0	3a, R= 	105	2.76 (87.52)	$+112^0$ (0.567)	0.46
2.	2b, R =  (1.28)	3.5	3b, R= 	165	2.67 (82.91)	$+256^0$ (0.323)	0.52
3.	2c, R =  (1.28)	4.5	3c, R= 	195	2.43 (75.37)	$+192^0$ (0.427)	0.57
4.	2d, R =  (1.28)	3.0	3d, R= 	172	2.87 (89.12)	-165^0 (0.572)	0.43
5.	2e, R=  (1.38)	3.0	3e, R= 	202	2.62 (77.17)	$+280^0$ (0.627)	0.62
6.	2f, R =  (1.38)	4.0	3f, R= 	178	2.07 (62.19)	$+302^0$ (0.397)	0.55
7.	2g, R =  (1.38)	3.0	3g, R= 	104	2.74 (82.57)	$+177^0$ (0.879)	0.42
8.	2h, R =  (1.36)	3.5	3h, R= 	95	2.81 (85.19)	$+44.7^0$ (0.937)	0.33
9.	2i, R =  (1.36)	4.5	3i, R= 	162	2.35 (71.17)	-12.3^0 (0.789)	0.39
10.	2j, R =  (1.36)	3.0	3j, R= 	184	2.93 (88.84)	$+113.7^0$ (0.657)	0.41

331(Man), 256(Tolyl isothiocarbamide). "Anal. Calcd. for $C_{30}H_{35}N_3O_9S_2$: C, 55.81; H, 5.42; N, 6.51; S, 9.92. Found: C, 55.45; H, 5.21; N, 6.47; S, 9.75".

1-m-Tolyl-5-tetra-o-acetyl-β-D-mannopyranosyl-2-S-benzyl-2,4-isodithiobiuret(3c): Yield 2.43 g (75.37%), m.pt. 195^{0}C, $[\alpha]_D^{28}$ + 192 (c, 0.427 in $CHCl_3$), UV ($CHCl_3$), λmax, 244 nm, IR υmax cm^{-1} ($CHCl_3$), 3367(N-H), 3080(Ar-H), 2965, 2890(C-H), 1750 (C=O), 1595(S-C=N), 1175(C-O), 1095(C=S), 1035(Mannopyranosyl ring deformation), 875, 830(1,2-disubstituted ring), 755(C-S), 710, 691 cm^{-1}(Monosubstituted ring). ^{1}H NMR ($CDCl_3$), δ= 7.14-7.06(m, 5H, Ar-H), 6.89-6.26(m, 4H, Ar-H), 5.25-4.65(m,5H, Man. ring), 4.24(s, 2H, O-CH_2-), 4.15(s, 2H, CH_2-S), 3.95(s, 1H, NH), 2.38(s, 3H, CH_3-Ar), 2.01(s, 12H, 4 –$COCH_3$), 1.90(s, 1H, NH). ^{13}C NMR ($CDCl_3$), δ= 182.3, 173.7(C=O), 148.9(S-C=N), 130.6-125.1(Ar-C), 83.9(C-1), 77.8(C-5), 71.4(C-3), 68.3(C-2), 65.6(C-4), 20.9($COCH_3$). FAB MS (m/z), 645(M^+), 405(Man-NH-C(=s)-NH), 331(Man). "Anal. Calcd. for $C_{30}H_{35}N_3O_9S_2$: C, 55.81; H, 5.42; N, 6.51; S, 9.92. Found: C, 55.49; H, 5.09; N, 6.03; S, 9.89".

1-p-Tolyl-5-tetra-o-acetyl-β-D-mannopyranosyl-2-S-benzyl-2,4-isodithiobiuret(3d): Yield 2.87 g (89.12%), m.pt. 172^{0}C, $[\alpha]_D^{28}$ - 165 (c, 0.572 in $CHCl_3$), UV ($CHCl_3$), λmax, 256 nm, IR υmax cm^{-1} ($CHCl_3$), 3282(N-H), 3085(Ar-H), 2985, 2885(C-H), 1744(C=O), 1595(S-C=N), 1176(C-O), 1095(C=S), 1038(Mannopyranosyl ring deformation), 805(1,4-disubstituted ring), 755(C-S), 710, 690 cm^{-1}(Monosubstituted ring). ^{1}H NMR ($CDCl_3$), δ= 7.18-7.08(m, 5H, Ar-H), 7.01-6.89(m, 4H, Ar-H), 5.29-4.77(m,5H, Man. ring), 4.25(s, 2H, O-CH_2-), 4.10(s, 2H, CH_2-S), 4.0(s, 1H, NH), 2.38(s, 3H, CH_3-Ar), 2.04(s, 12H, 4 –$COCH_3$), 2.00(s, 1H, NH). ^{13}C NMR ($CDCl_3$), δ= 178.2, (C=O), 150.4(S-C=N), 133.7-127.0(Ar-C), 84.3(C-1), 77.7(C-5), 68.5(C-3), 67.2(C-2), 66.9(C-4), 21.1($COCH_3$). FAB MS (m/z), 645(M^+), 405(Man-NH-C(=s)-NH), 331(Man). "Anal. Calcd. for $C_{30}H_{35}N_3O_9S_2$: C, 55.81; H, 5.42; N, 6.51; S, 9.92. Found: C, 55.65; H, 5.11; N, 6.17; S, 9.54".

1-o-Chlorophenyl-5-tetra-o-acetyl-β-D-mannopyranosyl-2-S-benzyl-2,4-isodithiobiuret (3e): Yield 2.62 g (77.17%), m.pt. 202^{0}C, $[\alpha]_D^{28}$ +280 (c, 0.627 in $CHCl_3$), UV ($CHCl_3$), λmax, 215 nm, IR υmax cm^{-1} ($CHCl_3$), 3310(N-H), 3090(Ar-H), 2986, (C-H), 1750(C=O), 1590(S-C=N), 1172(C-O), 1094(C=S), 1035(Mannopyranosyl ring deformation), 760(1,2-disubstituted ring), 750(C-S), 710, 691 cm^{-1}(Monosubstituted ring). ^{1}H NMR ($CDCl_3$), δ= 7.15-7.06(m, 5H, Ar-H), 6.95-6.82(m, 4H, Ar-H), 5.30-4.80(m,5H, Man. ring), 4.30(s, 2H, O-CH_2-), 4.17(s, 2H, CH_2-S), 4.12(s, 1H, NH), 2.45(s, 1H,NH), 2.00(s, 12H, 4 –$COCH_3$), ^{13}C NMR ($CDCl_3$), δ= 171.5, (C=O), 152.4(S-C=N), 132.9-127.0 (Ar-C), 83.7(C-1), 77.9(C-5), 68.2(C-3), 68.7(C-2), 67.2(C-4), 20.9($COCH_3$). FAB MS (m/z), 665(M^+), 406(Man-NH-C(=s)-NH_2), 331(Man).

"Anal. Calcd. for $C_{29}H_{32}N_3O_9S_2Cl$: C, 52.33; H, 4.81; N, 6.31; S, 9.62; Cl,5.33. Found: C, 51.95; H, 4.51; N, 6.82; S, 9.24, Cl, 4.89".

1-m-Chlorophenyl-5-tetra-o-acetyl-β-D-mannopyranosyl-2-S-benzyl-2,4-isodithiobiuret (3f): Yield 2.07 g (62.19%), m.pt. 178^{0}C, $[\alpha]_D^{28}$ +302 (c, 0.397 in $CHCl_3$), UV ($CHCl_3$), λmax, 244 nm, IR υmax cm^{-1} ($CHCl_3$), 3305(N-H), 3090(Ar-H), 2985, (C-H), 1749(C=O), 1592(S-C=N), 1175(C-O), 1091(C=S), 1040(Mannopyranosyl ring deformation), 850, 760(1,3-disubstituted ring), 750(C-S), 710, 692 cm^{-1}(Monosubstituted ring). ^{1}H NMR ($CDCl_3$), δ= 7.25-7.16(m, 5H, Ar-H), 7.05-6.92(m, 4H, Ar-H), 5.30-5.05(m,5H, Man. ring), 4.20(s, 2H, O-CH_2-), 4.02(s, 2H, CH_2-S), 3.90(s, 1H, NH), 2.55(s, 1H,NH), 2.05(s, 12H, 4 –$COCH_3$), ^{13}C NMR ($CDCl_3$), δ= 180.2(C=O), 149.7(S-C=N), 134.7-126.2 (Ar-C), 84.0(C-1), 78.3(C-5), 69.2(C-3), 67.5(C-2), 65.8(C-4), 20.7($COCH_3$). FAB MS (m/z), 665(M^+), 405(Man-NH-C(=s)-NH), 331(Man). "Anal. Calcd. for $C_{29}H_{32}N_3O_9S_2Cl$: C, 52.33; H, 4.81; N, 6.31; S, 9.62; Cl,5.33. Found: C, 51.99; H, 4.67; N, 6.03; S, 9.18, Cl, 5.09".

1-p-Chlorophenyl-5-tetra-o-acetyl-β-D-mannopyranosyl-2-S-benzyl-2,4-isodithiobiuret (3g): Yield 2.74 g (82.57%), m.pt. 104^{0}C, $[\alpha]_D^{28}$ +177 (c, 0.879 in $CHCl_3$), UV ($CHCl_3$), λmax, 232 nm, IR υmax cm^{-1} ($CHCl_3$), 3284(N-H), 3065(Ar-H), 2989, (C-H), 1729(C=O), 1587(S-C=N), 1165(C-O), 1084(C=S), 1026(Mannopyranosyl ring deformation), 814(1,4-disubstituted ring), 751(C-S), 710, 690 cm^{-1}(Monosubstituted ring). ^{1}H NMR ($CDCl_3$), δ= 7.50-7.41(m, 5H, Ar-H), 6.98-6.87(m, 4H, Ar-H), 5.35-5.16(m,5H, Man. ring), 4.12(s, 2H, O-CH_2-), 4.00(s, 2H, CH_2-S), 3.79(s, 1H, NH), 2.75(s, 1H,NH), 2.10(s, 12H, 4 –$COCH_3$), ^{13}C NMR ($CDCl_3$), δ= 182.9(C=O), 151.4(S-C=N), 133.2-129.7 (Ar-C), 88.1(C-1), 77.7(C-5), 69.9(C-3), 67.3(C-2), 66.4(C-4), 21.1($COCH_3$). FAB MS (m/z), 665(M^+), 406(Man-NH-C(=s)-NH_2), 331(Man). "Anal. Calcd. for $C_{29}H_{32}N_3O_9S_2Cl$: C, 52.33; H, 4.81; N, 6.31; S, 9.62; Cl,5.33. Found: C, 52.00; H, 4.48; N, 5.89; S, 9.38; Cl, 5.15".

1-o-Methoxyphenyl-5-tetra-o-acetyl-β-D-mannopyranosyl-2-S-benzyl-2,4-isodithiobiuret(3h): Yield 2.81 g (85.19%), m.pt. 95^{0}C, $[\alpha]_D^{28}$ +44.7 (c, 0.937 in $CHCl_3$), UV ($CHCl_3$), λmax, 262 nm, IR υmax cm^{-1} ($CHCl_3$), 3387(N-H), 3099(Ar-H), 2967, (C-H), 1756(C=O), 1593(S-C=N), 1187(C-O), 1070(C=S), 1038(Mannopyranosyl ring deformation), 765(1,2-disubstituted ring), 760(C-S), 710, 688 cm^{-1}(Monosubstituted ring). ^{1}H NMR ($CDCl_3$), δ= 7.14-7.06(m, 5H, Ar-H), 6.68-6.56(m, 4H, Ar-H), 5.12-5.06(m,5H, Man. ring), 4.17(s, 2H, O-CH_2-), 4.03(s, 2H, CH_2-S), 3.84(s, 1H, NH), 3.43(s, 3H, CH_3), 2.15(s, 1H,NH), 2.02(s, 12H, 4 –$COCH_3$), ^{13}C NMR ($CDCl_3$), δ= 178.7(C=O), 152.2(S-C=N), 135.7-127.3 (Ar-C), 85.0(C-1), 78.9(C-5), 68.3(C-3), 66.4(C-2), 65.9(C-4), 20.8($COCH_3$). FAB MS (m/z), 661.2(M^+),

331.3(Man). "Anal. Calcd. for $C_{30}H_{35}N_3O_{10}S_2$: C, 54.46; H, 5.29; N, 6.35; S, 9.68. Found: C, 54.07; H, 5.18; N, 5.95; S, 9.02".

1-m-Methoxyphenyl-5-tetra-o-acetyl-β-D-mannopyranosyl-2-S-benzyl-2,4-isodithiobiuret(3i): Yield 2.35 g (71.17%), m.pt. 162^0C, $[\alpha]_D^{28}$ -12.3 (c, 0.789 in $CHCl_3$), UV ($CHCl_3$), λmax, 247 nm, IR υmax cm^{-1} ($CHCl_3$), 3309(N-H), 3083(Ar-H), 2977, (C-H), 1750(C=O), 1590(S-C=N), 1181(C-O), 1077(C=S), 1032(Mannopyranosyl ring deformation), 845, 775(1,3-disubstituted ring), 750(C-S), 710, 690 cm^{-1}(Monosubstituted ring). ^{1}H NMR ($CDCl_3$), δ= 7.34-7.22(m, 5H, Ar-H), 7.11-7.01(m, 4H, Ar-H), 5.62-5.33(m,5H, Man. ring), 4.22(s, 2H, O-CH_2-), 4.09(s, 2H, CH_2-S), 3.97(s, 1H, NH), 3.57(s, 3H, CH_3), 3.03(s, 1H,NH), 2.07(s, 12H, 4 –$COCH_3$), ^{13}C NMR ($CDCl_3$), δ= 183.9(C=O), 160.0(S-C=N), 133.5-129.8(Ar-C), 88.0(C-1), 79.1(C-5), 69.2(C-3), 65.7(C-2), 62.0(C-4), 20.0($COCH_3$). FAB MS (m/z), 661(M^+), 390(Man-NH-C=S), 331(Man), 271(Chloro isothiocarbamide). "Anal. Calcd. for $C_{30}H_{35}N_3O_{10}S_2$: C, 54.46; H, 5.29; N, 6.35; S, 9.68. Found: C, 54.89; H, 5.00; N, 6.45; S, 9.14".

1-p-Methoxyphenyl-5-tetra-o-acetyl-β -D-mannopyranosyl-2-S-benzyl-2,4-isodithiobiuret(3j): Yield 2.93 g (88.84%), m.pt. 184^0C, $[\alpha]_D^{28}$+113.7 (c, 0.657 in $CHCl_3$), UV ($CHCl_3$), λmax, 214.7 nm, IR υmax cm^{-1} ($CHCl_3$), 3329(N-H), 3095(Ar-H), 2997, (C-H), 1752(C=O), 1592(S-C=N), 1178(C-O), 1072(C=S), 1039(Mannopyranosyl ring deformation), 820 (1,4-disubstituted ring), 759(C-S), 710, 687 cm^{-1}(Monosubstituted ring). ^{1}H NMR ($CDCl_3$), δ= 7.24-7.09(m, 5H, Ar-H), 7.01-6.93(m, 4H, Ar-H), 5.35-5.21(m,5H, Man. ring), 4.13(s, 2H, O-CH_2-), 4.01(s, 2H, CH_2-S), 3.62(s, 1H, NH), 3.19(s, 3H, CH_3), 2.67(s, 1H,NH), 2.01(s, 12H, 4 –$COCH_3$). ^{13}C NMR ($CDCl_3$), δ= 189.5(C=O), 171.1(S-C=N), 131.7-127.5(Ar-C), 89.2(C-1), 77.3(C-5), 70.4(C-3), 67.9(C-2), 64.7(C-4), 20.9($COCH_3$). FAB MS (m/z), 661(M^+), 390(Man-NH-C=S), 331(Man). "Anal. Calcd. for $C_{30}H_{35}N_3O_{10}S_2$: C, 54.46; H, 5.29; N, 6.35; S, 9.68. Found: C, 54.13; H, 4.87; N, 6.05; S, 9.29".

CONCLUSION:

In this research work, various 1-Aryl-5-tetra-o-acetyl- **β** -D-mannopyranosyl-2-S-benzyl-2,4-isodithiobiurets were synthesized and yield of product ranged from 62-89%. The characterizations of newly synthesized products were established on the basis of UV, IR, ^{1}H NMR, ^{13}C NMR & Mass spectral studies.

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