

SYNTHESIS OF 2- *tert* BUTYLIMINO-3-ARYL-4-S- BENZYL-6-HEPTA-O-ACETYL-B-D-MALTOSYLIMINO-2, 3-DIHYDRO-1, 3, 5-THIADIAZINES (HYDROCHLORIDE)

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ABSTRACT

A series of 2-*tert*butylimino-3-aryl-4-S-benzyl-6-hepta-*O*-acetyl- β -D-maltosylimino-2, 3-dihydro-1, 3, 5-thiadiazines (hydrochloride) have been synthesized by the interaction of 1-Aryl-5-hepta-*O*-acetyl- β -D-maltosyl-2-*S*-benzyl-2, 4-isodithiobiurets and Tertiary butyl isocyanodichloride. All the newly synthesized N-maltosylated compounds characterized by elemental analysis, IR, ¹H-NMR and Mass spectral studies.

Keywords: Maltosyl isodithiobiurets, *tert* butyl isocyanodichloride, 1,3,5-thiadiazines.

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INTRODUCTION

Thiadiazine and its derivatives are found as an important pharmacologically¹ and biologically active precursor in the field of heterocyclic chemistry. Some amino derivatives prove useful as herbicides, insecticides, fungicides, diuretics and ant diabetics. Organic thiocyanates^{2,4} and sugar thiadiazines^{5,6} also posses great potential as carbonic anhydrase inhibitor, PET inhibitor, anti HIV agent, antitumor agent, psychotropic agent and used in treatment of breast cancer. In view of wide range of applications of N-maltosylated heterocyclic compounds, we herein planed to synthesize new class of N- maltosylated heterocyclic compounds by the interaction of 1-Aryl-5-hepta-*O*-acetyl- β -D-maltosyl-2-*S*-benzyl-2, 4-isodithiobiurets⁷ (I) and *tert* butyl isocyanodichloride (II).

EXPERIMENTAL

Melting points were taken in open capillary tubes and are found uncorrected. Optical rotations $[\alpha]_D^{32}$ were measured on Equip-Tronics EQ-800 Digital polarimeter in chloroform at 32°C. IR spectra⁸ were recorded on Perkin-Elmer RXI (4000-450 cm⁻¹) FTIR spectrometer. ¹HNMR⁹ were obtained on a Bruker DRX-300 NMR spectrometer at 300MHz. The samples were prepared in CDCl₃ with TMS as an internal reference. The mass spectra¹⁰ were recorded on Jeol SX-102 FAB Mass spectrometer.

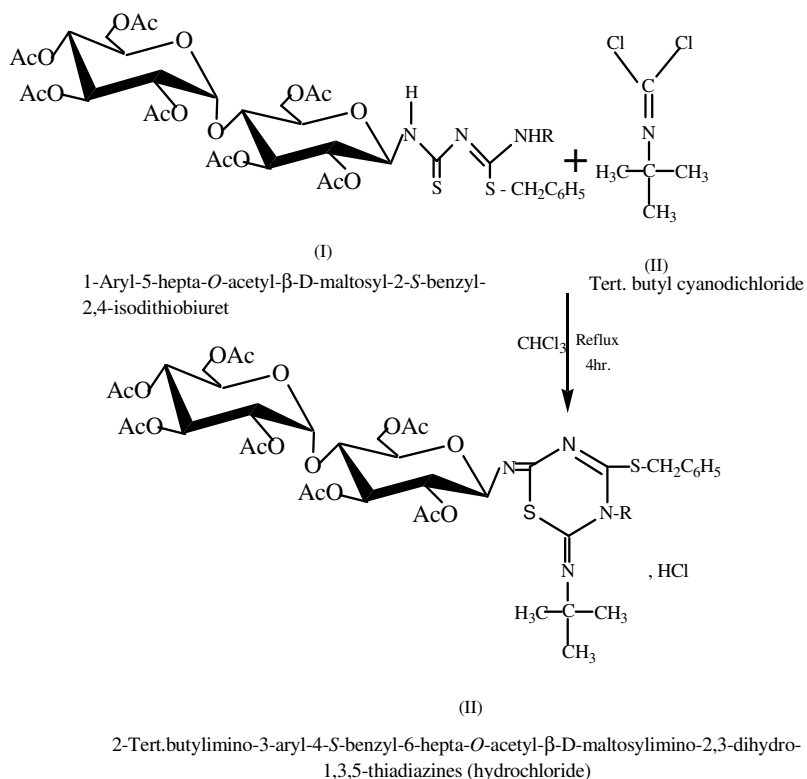
RESULTS AND DISCUSSION

General Procedures

(a.) The required 1-aryl-5-hepta-*O*-acetyl- β -D-maltosyl-2-*S*-benzyl-2,4-isodithiobiurets were prepared by the interaction of Hepta-*O*-acetyl- β -D-maltosyl isothiocyanate with various 1-Aryl-*S*-benzyl isothiocarbamides. The Tertiary butyl isocyanodichloride was prepared by passing chlorine gas through the chloroformic solution of *tert*butyl isothiocyanate.

(b.) Synthesis of 2-*tert*butylimino-3-phenyl-4-*S*-benzyl-6-hepta-*O*-acetyl- β -D-maltosylimino-2, 3-dihydro-1, 3, 5-thiadiazines (hydrochloride) (IIIa): A reaction mixture of tertiary butyl isocyanodichloride (0.47M, 0.46g in 5 mL CHCl₃) and of 1-phenyl-5-hepta-*O*-acetyl- β -D-maltosyl-2-*S*-benzyl-2, 4-isodithiobiuret (0.003 M, 2.75 g in 25 mL CHCl₃) was gently refluxed for 4 hr. evolution of hydrogen chloride was clearly noticed.

After completion of reaction, solvent was distilled off and sticky mass was isolated as residue. This when triturated several times with petroleum ether (60 –80°C) was converted to pale yellow granular solid (2.8 g) (III a).



Where, R=(a) phenyl, (b) *o*-Cl-phenyl, (c) *m*-Cl-phenyl, (d) *p*-Cl-phenyl, (e) *o*-tolyl, (f) *m*-tolyl, (g) *p*-tolyl and Ac = COCH₃
Scheme-1

Table-1: Characteristics of 2-*tert*butylimino-3-aryl-4-S-benzyl-6-hepta-O-acetyl-β-D-maltosylimino-2,3-dihydro-1,3,5-thiadiazines (hydrochloride) (III a-g).

S. No.	Products (III a-g)	Yield (%)	M.P. (°C)	[α] _D ³² (CHCl ₃) (c, 1.00)	Analysis		R _f (CCl ₄ : EtOAc) (3:2)
					Found (%)	Required (%)	
1	III a	87	141°C	+ 120°	N, 5.28 S, 6.0	N, 5.22 S, 5.97	0.39
2	III b	63	155°C	+ 100°	N, 5.1 S, 5.68	N, 5.06 S, 5.7	0.33
3	III c	69	130°C	+ 60°	N, 5.0 S, 5.60	N, 5.06 S, 5.7	0.46
4	III d	57	166°C	+ 130°	N, 5.16 S, 5.79	N, 5.06 S, 5.7	0.53
5	III e	62	114°C	+20°	N, 5.14 S, 5.89	N, 5.17 S, 5.19	0.62
6	III f	78	195°C	+55°	N, 5.18 S, 5.95	N, 5.17 S, 5.19	0.73
7	III g	75	124°C	+ 70°	N, 5.12 S, 5.91	N, 5.17 S, 5.19	0.57

*Satisfactory C & H analysis was found in all cases.

The crude product was purified from ethanol-water, m.p. 141°C. The purity of product checked by TLC. The product was found soluble in acetone, chloroform, benzene and DMSO while insoluble in ethanol, water and petroleum ether. It charred when warm with conc. sulphuric acid.

It was found non-desulphurisable when boiled with alkaline lead acetate solution. On extending this reaction to other 1-aryl-5-hepta-*O*-acetyl- β -D-maltosyl-2-*S*-benzyl-2, 4-isodithiobiurets, the related products (III b-g) were isolated. The % yield, M.P., optical rotation, R_f values and elemental analysis are shown in Table-1.

Spectral Analysis

2-tert butylimino-3-phenyl-4-*S*-benzyl-6-hepta-*O*-acetyl- β -D-maltosylimino-2,3-dihydro-1, 3, 5-thiadiazines (hydrochloride) (III a)

IR (KBr) : 3343 cm^{-1} (N-H str.), 3062 (Aromatic C-H str.), 2951.09 (Aliphatic C-H str.), 1764.87 (C=O str.), 1556.5 (C=N str.), 1371.39 (C-N str.), 1056.99,939.33 and 902 (Characteristic of maltose), 756.10 (C-S str.), 702.10 (monosubstituted benzene); $^1\text{HNMR}$ (ppm) : δ 6.24 ppm (s, 1H, N-H protons) , δ 8.03-7.26 (m, 11H, aromatic protons), δ 5.64-3.84 (m,14H, maltosyl protons), δ 2.1-1.7 (m, 21H, acetyl protons), δ 1.56-1.15 (t, 9H, *tert* butyl protons); Mass(m/z): 1072, 1052, 992, 917, 828, 786, 784, 619, 559, 391, 168.8 and 109. The analysis calcd. for $\text{C}_{46}\text{H}_{56}\text{O}_{17}\text{N}_4\text{S}_2 \cdot 2\text{HCl}$. [Found :C,51.47;H,5.21 ; N,5.28; S,6.0; requires : C, 51.49; H, 5.22; N, 5. 22; S, 5.97%.].

2-tert butylimino-3-*p*-Cl-phenyl-4-*S*-benzyl-6-hepta-*O*-acetyl- β -D-maltosylimino-2,3-dihydro-1, 3, 5-thiadiazines (hydrochloride) (III d)

IR(KBr): 3343 cm^{-1} (N-H str.) ,3062 (Aromatic C-H str.), 2951.09 (Aliphatic C-H str.), 1745.58 (C=O str.), 1556.5 (C=N str.), 1371.39 (C-N str.), 1037.70 , 935.48 and 906.4 (Characteristic of maltose), 758.2 (C-S str.), 603.09 (disubstituted benzene)

$^1\text{HNMR}$ (ppm): δ 5.56 ppm (s, 1H, N-H protons), δ 8.55-7.26, (m, 9H, aromatic protons), δ 5.6-3.55 (m, 14H, maltosyl protons), δ 2.07-1.8 (m, 21H, acetyl protons), δ 1.56-1.43 (m, 9H, *tert* butyl protons)

Mass (m/z): 1105, 1066, 1006, 917, 828, 786, 784, 619, 559, 391, 168.8 and 109.

The analysis Calculated for $\text{C}_{46}\text{H}_{54}\text{O}_{17}\text{N}_4\text{S}_2 \text{Cl}_2\text{HCl}$. [Found : C, 49.95; H,4.87; N, 5.16; S, 5.79; requires : C, 49.95; H, 4.88; N, 5.06; S, 5.79 %.]

2-tert butylimino-3-*m*-tolyl-4-*S*-benzyl-6-hepta-*O*-acetyl- β -D-maltosylimino-2,3-dihydro-1, 3, 5-thiadiazines (hydrochloride) (III f):

IR(KBr): 3481 cm^{-1} (N-H str.),3079 (Aromatic C-H str.),2960(Aliphatic C-H str.), 1745.58 (C=O str.), 1556.5 (C=N str.), 1371.39 (C-N str.), 1041.56, 937.40 and 898.83 (Characteristic of maltose), 756.10(C-S str.), 601.79 (disubstituted benzene)

$^1\text{HNMR}$ (ppm): δ 6.23 ppm (t,1H, N-H protons), δ 7.89 (m,13H, aromatic protons), δ 5.61-3.7 (m,14H, maltosyl protons), δ 2.21-1.84 (m, 21H, acetyl protons), δ 1.56-1.43 (m, 9H, *tert*butyl protons)

Mass (m/z):1082, 828, 786, 784, 619, 559, 391, 168.8 and 109.

The analysis Calculated for $\text{C}_{47}\text{H}_{57}\text{O}_{17}\text{N}_4\text{S}_2 \cdot 2\text{HCl}$. [Found: C, 52.10; H, 5.26; N, 5.18; S, 5.95; requires : C, 52.12; H, 5.26; N, 5.17; S,5.91 %.]

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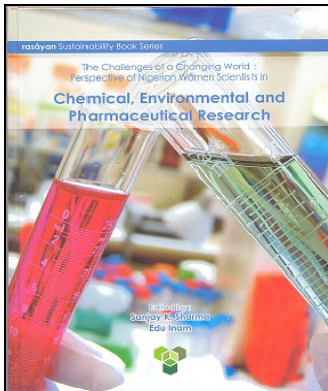
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