SYNTHESIS OF SOME NEW -1, 2, 4-DITHIAZOLIDINE HYDROCHLORIDES

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ABSTRACT

Several 3-hepta-O-benzoyl-β-D-lactosyl-4-phenyl-5-arylimino-1, 2, 4-dithiazolidine hydrochlorides have been prepared by the interaction of 1-hepta-O-benzoyl-β-D-lactosyl-S-chloro isothiocarbamoyl chloride and 1-phenyl 3-aryl thiocarbamides. The structure of these new N-lactosylated -1,2,4-dithiazolidine hydrochlorides have been established on the basis of usual chemical transformations and IR, NMR, and Mass spectral analyses.

Key word: 1-Hepta-O-benzoyl-β-D-lactosyl-S-chloro isothiocarbamoyl chloride, 1-3-Diaryl thiocarbamides, 1,2,4-Dithiazolidine hydrochlorides, Synthesis.

INTRODUCTION

Very few compounds containing thioamido group and having lactosyl substituent on nitrogen have been reported and tested for their biological activity 1-3. Chemistry of N-phenyl-S-chloro isothiocarbamoyl chloride with special utility in the synthesis of nitrogen and sulphur containing five and six membered heterocyclic compounds have been exhaustively investigated by number of chemists 4-6. In view of our interest in the synthesis of newer types of 1,2,4-dithiazolidines; herein a simple method for the synthesis of 1,2,4-dithiazolidines has been reported.

EXPERIMENTAL

Melting points were taken in open capillary tubes and are uncorrected. Specific rotations were measured on Equip-Tronics Digital Polarimeter at 28°C in CHCl₃. IR spectra were recorded on Perkin-Elmer spectrum RXI FTIR spectrophotometer (4000-450 cm⁻¹). ¹H NMR were recorded in CDCl₃ on Bruker DRX-300 spectrometer operating at 300 MHz. The Mass spectra were recorded on Jeol-SX-102(FAB) instrument.

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Synthesis of 1-hepta-O-benzoyl-β-D-lactosyl-S-chloro isothiocarbamoyl chloride (1)

Chlorine gas (generated from 8 g KMnO₄ and 50 mL conc. HCl) was passed through a chloroform solution of 1-hepta–O-benzoyl-β-D-lactosyl isothiocyanate (0.005M, 5.5 g) maintaining the temperature below 10°C. Then the solvent was distilled off and the resulting syrupy mass was triturated several times with petroleum ether (60-80°C) to afford (1).

Preparation of 1- phenyl 3-aryl- thiocarbamide (2a-g)

1-Phenyl-3-aryl thiocarbamides (2a-g) were prepared by the interaction of phenyl isothiocyanate and appropriate aryl amines in benzene medium.

Synthesis of 3-hepta-O-benzoyl-β-D-lactosylimino-4-phenyl-5-arylimino-1,2,4-dithiazolidine hydrochlorides 3(a-g)

A mixture of 1-hepta-O-benzoyl-β-D-lactosyl-S-chloro isothiocarbamoyl chloride (1) (0.005 M) and 1-phenyl-3-aryl thiocarbamides (2a-g) (0.005 M) in chloroform was refluxed for 3 h. Then the solvent was distilled off and the resulting syrupy mass was triturated several times with petroleum ether (60-80°C) to afford a pale yellow solid (3a-g) (Table 1). The products were purified by chloroform – petroleum ether.

RESULTS AND DISCUSSION

The condensation of 1-hepta-O-benzoyl-β-D-lactosyl-S-chloro isothiocarbamoyl chloride (1) and 1-phenyl 3-aryl thiocarbamides (2a-g) in CHCl₃ was carried out for 3 h. After condensation, the solvent was distilled off and the resulting syrupy mass was triturated several times with petroleum ether (60-80°C) to afford a pale yellow solid of 3-hepta-O-benzoyl-β-D-lactosyl-4-phenyl-5arylimino-1,2,4-dithiazolidine hydrochlorides (3a-g) (Table 1). The products were purified by chloroform-petroleum ether. The structure of the products were confirmed by spectral analysis (IR, NMR and Mass). The specific rotation of the products were also recorded. All the compounds have been screened for both; antibacterial and antifungal activity.

Table 1: Characterization data of the synthesized compounds

<table>
<thead>
<tr>
<th>Product</th>
<th>M.P. (°C)</th>
<th>Yield (%)</th>
<th>[α]D 28 (c, CHCl₃)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>155</td>
<td>83</td>
<td>+80° (0.156)</td>
</tr>
<tr>
<td>3b</td>
<td>146</td>
<td>87</td>
<td>+108° (0.157)</td>
</tr>
</tbody>
</table>

Cont...
<table>
<thead>
<tr>
<th>Product</th>
<th>M.P. (°C)</th>
<th>Yield (%)</th>
<th>$[\alpha]_{D}^{28}$ (c, CHCl₃)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3c</td>
<td>151</td>
<td>90</td>
<td>+120° (0.155)</td>
</tr>
<tr>
<td>3d</td>
<td>144</td>
<td>89</td>
<td>+95° (0.156)</td>
</tr>
<tr>
<td>3e</td>
<td>150</td>
<td>91</td>
<td>+148° (0.157)</td>
</tr>
<tr>
<td>3f</td>
<td>148</td>
<td>85</td>
<td>+134° (0.158)</td>
</tr>
<tr>
<td>3g</td>
<td>142</td>
<td>88</td>
<td>+110° (0.156)</td>
</tr>
</tbody>
</table>

Satisfactory C, H, N and S analysis were obtained in all cases.

Spectral data

3a. IR(KBr): 3065.4 cm⁻¹ (Ar-H stretching), 1728.2 cm⁻¹ (C=O), 1602.1 cm⁻¹ (C=N), 1269.5 cm⁻¹ (C-O), 850.5 cm⁻¹ (lactosyl C-H deformation), 765.8 cm⁻¹ (C-S) and 708.9 cm⁻¹ (C-H aromatic); $^1$H NMR (ppm) : δ 7.12-7.07 (10H, m, Ar-H) 7.14-5.73 (10H, m, lactosyl protons), 4.57-4.21(4H, d, -OCH₂) and 5.91-5.73 (35H, m,7-COCH₃); Mass (m/z) : 1411 (M⁺), 1412, 1337, 1052, 579, 391, 335 and 105.

3b. IR(KBr): 3064.5 cm⁻¹ (Ar-H stretching), 1728.8 cm⁻¹ (C=O), 1601.7 cm⁻¹ (C=N), 1269.8 cm⁻¹ (C-O), 854.4 cm⁻¹ (lactosyl C-H deformation), 765.3 cm⁻¹ (C-S) and 709.2 cm⁻¹
(C-H aromatic); $^1$H NMR (ppm) : $\delta$ 7.12-7.07 (9H, m, Ar-H) 7.14-5.73 (10H, m, lactosyl protons), 4.57-4.21 (4H,d,-OCH$_2$), 5.91-5.73 (35H, m, 7-COC$_6$H$_5$) and 4.57-4.21 (3H, S, -CH$_3$); Mass (m/z): 1424 (M$^+$), 1425, 1351, 1052, 579, 391, 335 and 105.

$3f$. IR (KBr): 3066 cm$^{-1}$ (Ar-H stretching), 1728.6 cm$^{-1}$ (C=O), 1601.1 cm$^{-1}$ (C=N), 1270.3 cm$^{-1}$ (C-O), 854.4 cm$^{-1}$ (lactosyl C-H deformation), 763.8 cm$^{-1}$ (C=S) and 709.7 cm$^{-1}$ (C-H aromatic); $^1$H NMR (ppm) : $\delta$ 7.12-7.07 (9H,m,Ar-H) 7.14-5.73 (10H,m, lactosyl protons), 4.57-4.21 (4H,d,-OCH$_2$) and 5.91-5.73(35H, m, 7-COC$_6$H$_5$) ; Mass (m/z): 1447 (M$^+$), 1448, 1372, 1052, 579, 391, 335 and 105.

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REFERENCES


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