

## ON THIOLACTOSIDES : SYNTHESIS OF S-HEPTA-O-ACETYL LACTOSYL ARYLDITHIOCARBAMATES

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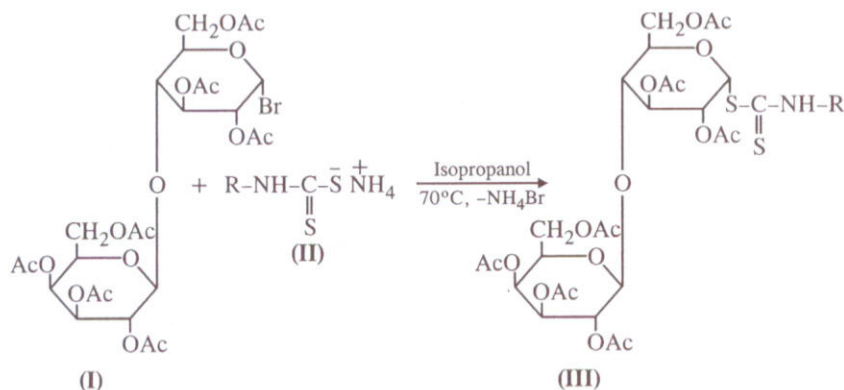
### ABSTRACT

Thiolactosides are those compounds in which lactosyl group or its derivatives are attached to the sulphur of the sulphur containing compounds. This class of compound is important and has several applications in industry and also in medicinal chemistry. Several S-hepta-O-acetyl lactosyl arylthiocarbamates have been prepared by the interaction of hepta-O-acetyl lactosyl bromide and ammonium arylthiocarbamates. The identities of these newly synthesized thiolactosides have been established on the basis of usual chemical transformations, IR, NMR and Mass spectral studies.

**Key words:** Lactosyl bromide, Ammonium arylthiocarbamates, Lactosyl arylthiocarbamates

### INTRODUCTION

Several methods of preparation of thioglucosides<sup>1</sup> have been well documented. But there is no report on thiolactosides of thioamido group containing compounds. Thiolactosides has several applications in industry, medicinal chemistry and in many other ways<sup>2,3</sup>. The present work deals with the synthesis of several S-hepta-O-acetyl lactosyl arylthiocarbamates (IIIa–III f). These were prepared by the interaction of hepta-O-acetyl lactosyl bromide (I) and ammonium arylthiocarbamates (II). The reaction scheme is as given below :



Where, R = (a) phenyl, (b) m-Cl-phenyl, (c) p-Cl-phenyl, (d) o-tolyl,  
(e) m-tolyl, f) p-tolyl, Ac = -COCH<sub>3</sub>

## EXPERIMENTAL -

The reagents used for the reaction were prepared as follows :

**Preparation of ammonium aryl dithiocarbamates :** Ammonium aryldithiocarbamates<sup>4</sup> were prepared by already known procedure i.e. by the interaction of ammonia, carbon disulphide and appropriate arylamines.

### Preparation of hepta-O-acetyl lactosyl bromide

(i) **Preparation of brominating reagent :** Glacial acetic acid (30 mL) was taken in a conical flask and red phosphorus (3 g) was added. To this mixture, molecular bromine (7 mL) was added gradually with constant shaking and cooling. The resultant mixture was allowed to stand at room temperature for about 30 min.

(ii) **Preparation of hepta-O-acetyl lactosyl bromide :** Finely powdered octa-O-acetyl lactose (0.03 M, 20.4 g) was added gradually to the brominating reagent. After the addition, the content of the flask was allowed to stand at room temperature for two hours. The reaction mixture was then mixed with chloroform (40 mL) and then mixture was shaken vigorously for about 15 min. The resultant mixture was poured into ice cold water. The chloroform layer was then separated. It was washed several times with aqueous sodium bicarbonate to remove excess of acetic acid followed by sodium metabisulphite to remove excess of bromine and finally 2-3 times with water. The chloroform layer on addition of petroleum ether afforded a white solid (16 g). This solid was expected hepta-O-acetyl lactosyl bromide<sup>5</sup>. It was crystallised from ethanol. m.p.<sup>6</sup>. 130°C.

**Synthesis of S-hepta-O-acetyl lactosyl phenyldithiocarbamate :** A suspension of hepta-O-acetyl lactosyl bromide (0.01 M, 6.98 g in 20 mL isopropanol) was mixed with a suspension of ammonium phenyldithiocarbamate (0.01 M, 1.8 g in 20 mL isopropanol). The resultant mixture was shaken and heated on a water bath at 70°C till the suspension gets clear. The clear solution was kept at room temperature for 18 hrs, and then a solid was obtained. The solid was identified as ammonium bromide. The clear filtrate was mixed with 100 mL distilled water where a semisolid mass separated out. This semisolid mass was not solidified after standing for several hours. The semisolid mass failed to afford solid, even when triturated several times with petroleum ether. The sticky mass was purified with ethanol-water and the crystals were obtained (4.2 g) m. p. 115° - 118°C. (Found : N, 1.76; S, 8.08; C<sub>33</sub>H<sub>41</sub>O<sub>17</sub>NS<sub>2</sub>, requires : N, 1.77; S, 8.13%). The specific rotation was found  $[\alpha]_{D23} - 98.52^{\circ}$  (C, 1.015 in CHCl<sub>3</sub>). It gave charring test and was desulphurisable, when boiled with alkaline plumbite solution. All these observations clearly indicated the product as S-hepta-O-acetyl lactosyl phenyldithiocarbamate.

## RESULTS AND DISCUSSION

A suspension of hepta-O-acetyl lactosyl bromide in isopropanol was mixed with a suspension of ammonium phenyldithiocarbamate in isopropanol. The resultant mixture was heated on a water bath at 70°C till the suspension gets clear. This clear solution was kept at room temperature for 18 hrs, a solid was obtained. The solid was identified as ammonium bromide. The clear filtrate was mixed with 100 mL distilled water, and then a semisolid separated out. This semisolid mass was not solidified even after standing for several hours. It failed to afford solid, when triturated several times with petroleum ether. The semisolid mass was purified by ethanol-water and the crystals were obtained m.p. 115<sup>o</sup>-118<sup>o</sup>C. It gave charring test and was desulphurible, when boiled with alkaline plumbite solution. The specific rotation was found  $[\alpha]_D^{23} - 98.52^{\circ}(\text{C}, 1.015 \text{ in } \text{CHCl}_3)$ .

**Table 1. Interaction of hepta-O-acetyl lactosyl bromide (0.01 M, 6.98 g) and ammonium aryldithiocarbamates (0.01 M)**

Sr. No.	Ammonium aryldithiocarbamate (g)		S-hepta-O-acetyl lactosyl aryl dithiocarbamate yield (g)		M.P. °C	% Yield	Analysis		[ $\alpha$ ] <sub>D</sub> <sup>23</sup> C in CHCl <sub>3</sub>
							Found %	Required %	
1.	-phenyl-	(1.8)	-phenyl-	(4.2)	115-118	53.23	N, 1.76 S, 8.08	N, 1.77 S, 8.13	-98.52 <sup>o</sup> (1.015)
2.	-m-Cl-phenyl-	(2.2)	-m-Cl-phenyl-	(4.1)	85-87	49.81	N, 1.66 S, 7.89	N, 1.70 S, 7.79	19.90 <sup>o</sup> (1.005)
3.	-p-Cl-phenyl-	(2.2)	-p-Cl-phenyl-	(4.3)	145-147	52.24	N, 1.59 S, 7.85	N, 1.70 S, 7.79	76.92 <sup>o</sup> (1.040)
4.	-o-tolyl-	(2.0)	-o-tolyl-	(3.5)	122-123	43.58	N, 1.61 S, 8.20	N, 1.74 S, 7.99	87.80 <sup>o</sup> (1.025)
5.	-m-tolyl-	(2.0)	-m-tolyl-	(4.4)	109-110	54.79	N, 1.52 S, 7.72	N, 1.74 S, 7.99	9.85 <sup>o</sup> (1.015)
6.	-p-tolyl-	(2.0)	-p-tolyl-	(4.1)	136-138	51.05	N, 1.44 S, 7.87	N, 1.74 S, 7.99	69.30 <sup>o</sup> (1.010)

Satisfactory C and H analysis were obtained for all the compounds.

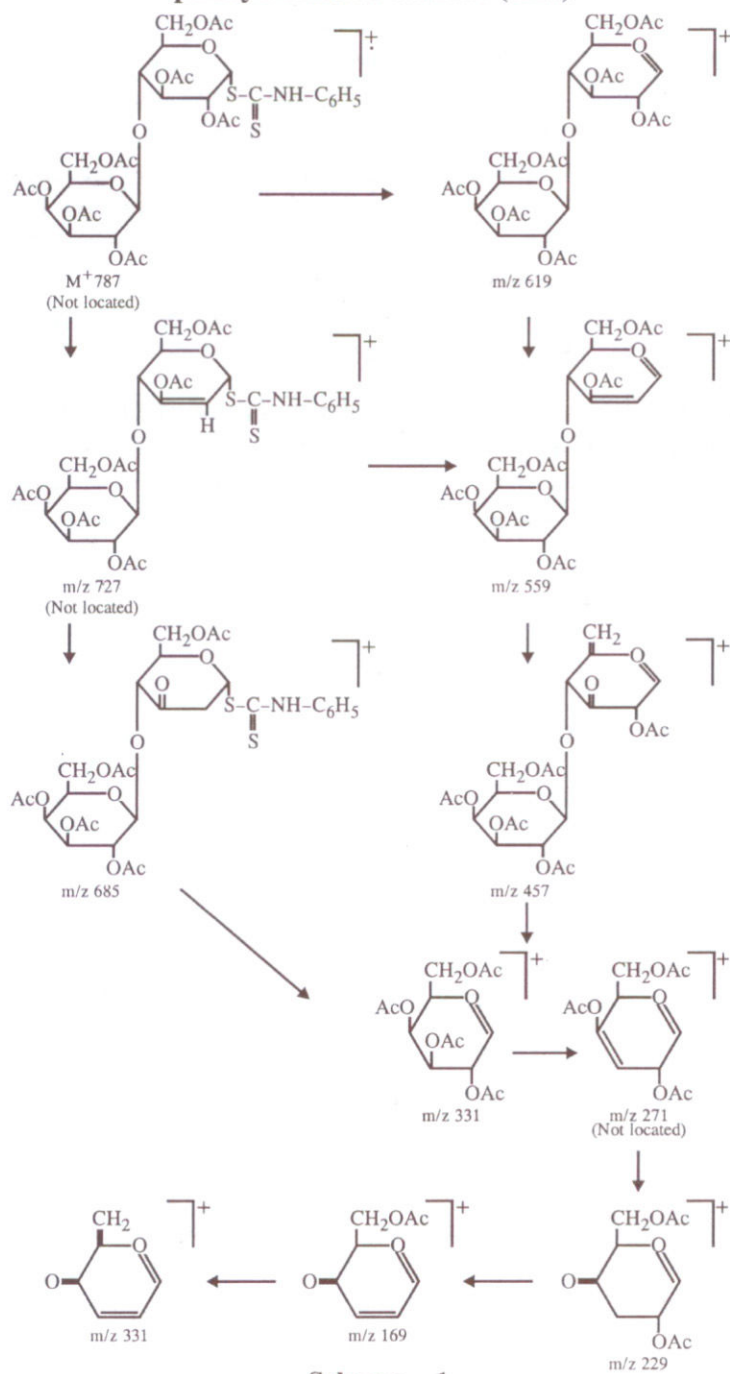
The IR spectrum<sup>7-10</sup> shows bands due to N-H (3408 cm<sup>-1</sup>), C=O (1753 cm<sup>-1</sup>), C-S (604 cm<sup>-1</sup>), C=S (1172 cm<sup>-1</sup>), C-O (1229 cm<sup>-1</sup>) and Ar-H (2964 cm<sup>-1</sup>).

The NMR spectrum<sup>7-10</sup> distinctly displayed signals due to N-H proton at  $\delta$  7.9 ppm, Ar-H at  $\delta$  7.3-6.6 ppm and acetyl proton at  $\delta$  2.1 - 1.1 ppm.

In the mass spectrum<sup>11</sup>, the molecular ion peak was not located. The probable fragmentation pattern alongwith their masses (m/z) are shown in Scheme - 1. All the above facts clearly indicated that the product is S-hepta-O-acetyl lactosyl phenyldithiocarbamate (IIIa).



**Probable fragmentation pattern of S-hepta-O-acetyl-lactosyl phenyldithiocarbamate (IIIa)**



Scheme - 1

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