CHAPTER III

Synthesis of 1-Tetra-O-benzoyl-β-D-glucopyranosyl-5-aryl-2-S-benzyl-2,4-isothiobiurets and 1-Tetra-O-benzoyl-β-D-glucopyranosyl-5-Phenyl-2-S-benzyl-2-isothiobiuret along with their antimicrobial studies.

Abstract: Certain 1-tetra-O-benzoyl-β-D-glucopyranosyl-5-aryl-2-S-benzyl-2,4-isothiobiurets and only one 1-tetra-O-benzoyl-β-D-glucopyranosyl-5-Phenyl-2-S-benzyl-2-isothiobiuret have been synthesized by the interaction tetra-O-benzoyl-β-D-glucopyranosyl-5-benzyl isothiocarbamide and aryl isothiocyanates and phenyl isocyanate, respectively. All these products have been characterized through the usual chemical transformations and also IR, NMR and Mass spectral analysis and polarimetry. All compounds have been screened for their antimicrobial activities.

S-Alkyl isothiocarbamides and also S-alkyl-1-aryl isothiocarbamides because of their basic nature react with aryl/alkyl isothiocyanates and isocyanates and known to produce corresponding 2,4-isothiobiurets and 2-isothiobiurets.

\[
\begin{align*}
i) \quad & R' - \text{NH} - C = NH \quad + \quad R'' - N = C = S \quad \longrightarrow \quad R'NH - C = C - NHR'' \\
& \text{SR} \quad \text{Aryl/alkyl} \\
& \text{S-Alkyl-isothiocarbamide} \\
& \quad \text{isothiocyanates.} \\
& \text{SR} \quad \text{S} \\
& 1, 5 - \text{Disubstituted 2-S-alkyl-2,4-isothiobiuret.}
\end{align*}
\]

\[
\begin{align*}
ii) \quad & R' - \text{NH} - C = NH \quad + \quad R'' - N = C = O \quad \longrightarrow \quad R'NH - C = C - NHR'' \\
& \text{SR} \quad \text{Aryl/alkyl} \\
& \text{S-Alkyl-isothiocarbamide} \\
& \quad \text{isocyanates.} \\
& \text{SR} \quad \text{O} \\
& 1, 5 - \text{Disubstituted 2-S-alkyl-2,4-isothiobiuret.}
\end{align*}
\]

Where, \( R', R', R'' \) are suitable alkyl or aryl groups.

Therefore, it appeared sufficiently interesting to prepare the S-alkyl-tetra-O-benzoyl-β-D-glucopyranosyl isothiocarbamides and carry out the reaction of these isothiocarbamides with certain aryl isothiocyanates and phenyl isocyanate. With this end in view interaction of 1-tetra-O-benzoyl-β-D-glucopyranosyl-S-benzyl isothiocarbamide and certain aryl isothiocyanates and phenyl isocyanate have been carried out and the corresponding 2,4-isothiobiurets and 2-isothiobiuret have been realized for the first time the present chapter describes these syntheses.
Interaction of tetra- O - benzoyl-β- D - glucopyranosyl thiocarbamide with benzyl chloride has been carried out in boiling ethanol for 1½ hr. After cooling it was rendered basic with dilute ammonium hydroxide. A granular solid was isolated, crystallised from ethanol, m.p. 166°. The elemental analysis of this product indicated its molecular formula as C_{42}H_{36}O_{9}N_{7}S.

**Examination of the product with m.p. 166° (C_{42}H_{36}O_{9}N_{7}S).**

i) The product was moderately soluble in acetone, chloroform, benzene, carbon tetrachloride, Acetic acid while it was insoluble in water, alcohol and petroleum ether.

ii) When treated with alkali it was decomposed into benzyl mercaptan and other decomposition products.

iii) On thermal decomposition the smell of benzyl mercaptan was quite perceptible.

iv) The product was found non desulphurisable when boiled with alkaline plumbite solution. However, as expected a yellow lead mercaptide was formed.

v) When warmed with conc. sulphuric acid it gets charred.

The above observation have clearly indicated that the product with m.p. 166° was tetra- O - benzoyl-β- D - glucopyranosyl - S - benzyl isothiocarbamide (I).

Interaction of free base of tetra- O - benzoyl-β- D - glucopyranosyl - S - benzyl - isothiocarbamide and phenyl isothiocyanate have been carried out in refluxing dry benzene medium for 3 hr. After refluxing benzene was distilled off and sticky mass obtained as residue was triturated several times with petroleum ether(b.p. 60-80°) followed by ethanol, a white solid was isolated, crystallised from ethanol, m.p. 177°. The elemental analysis of the product indicated its molecular formula as C_{49}H_{41}O_{9}N_{7}S_{2}.

**Examination of the product with m.p. 177° (C_{49}H_{41}O_{9}N_{7}S_{2}).**

i) **Solubility**: The compound was insoluble in water, alcohol and petroleum ether. However, it was found highly soluble in acetone, chloroform, benzene, carbon tetrachloride and acetic acid.

ii) **Thermal decomposition**: On heating in a dry test tube odour of phenyl isothiocyanate was quite perceptible.

iii) **Action of conc. sulphuric acid**: The presence of glucosyl group was established on the basis of warming it with conc. sulphuric acid when product charred.
<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Aryl isothiocyanates</th>
<th>1-tetra-O-benzoyl-β-D-glucopyranosyl-5-aryl-2-S-benzyl-2,4-isodithiobiurets (III).</th>
<th>Yield %</th>
<th>M.P. °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Phenyl</td>
<td>5-Phenyl</td>
<td>(IIIa)</td>
<td>73.22</td>
</tr>
<tr>
<td>2</td>
<td>o-Tolyl</td>
<td>5-o-Tolyl</td>
<td>(IIIb)</td>
<td>62.5</td>
</tr>
<tr>
<td>3</td>
<td>m-Tolyl</td>
<td>5-m-Tolyl</td>
<td>(IIIc)</td>
<td>79.54</td>
</tr>
<tr>
<td>4</td>
<td>p-Tolyl</td>
<td>5-p-Tolyl</td>
<td>(IIIb)</td>
<td>67.56</td>
</tr>
<tr>
<td>5</td>
<td>o-Cl-Phenyl</td>
<td>5-o-Cl-Phenyl</td>
<td>(IIIe)</td>
<td>55.06</td>
</tr>
<tr>
<td>6</td>
<td>m-Cl-Phenyl</td>
<td>5-m-Cl-Phenyl</td>
<td>(IIIf)</td>
<td>50.66</td>
</tr>
</tbody>
</table>
iv) **Action of alkaline plumbite solution**: It was found desulphurisable when boiled with alkaline plumbite solution.

v) **Polarimetry**: The compound was optically active\(^1\) and its \([\alpha]_D\)^{35} was found in chloroform was -86.20\(^{op}\) (c, 0.464).

vi) **IR, NMR and Mass spectral analysis**: The infrared spectrum of the product clearly indicated the presence of \(\nu\text{NH}, \nu\text{C}^\equiv\text{N}, \nu\text{C}^=\text{O}, \nu\text{C} = \text{N}, \nu\text{S} - \text{Bz}, \nu\text{C} = \text{S}\) and band due to \(\beta - \text{D} - \text{glucopyranosyl ring deformation was also present}^{2-8}\) (Fig. 1).

The NMR spectrum displayed signals due to aromatic protons, N-H proton, and also protons of glucosyl ring\(^6-9,11\) (Fig. 2).

The Mass\(^{12-14}\) spectrum (Fig. 3) of IIIa was also recorded. The general fragmentation pattern has been shown in (scheme 1) while masses (m/z) of different fragments are tabulated in (Table- 2).

On the basis of all above facts the product with m.p. 177\(^o\) was assigned structure 1-tetra - O - benzoyl - \(\beta - \text{D} - \text{glucopyranosyl} - \text{S} - \text{phenyl} - \text{2} - \text{S} - \text{benzyl} - \text{2, 4} - \text{isodithioiubret (IIla).}

The reaction of tetra - O - benzoyl - \(\beta - \text{D} - \text{glucopyranosyl} - \text{S} - \text{benzyl}

isothiocarbamide was also found extendable to other aryl isothiocyanates and the corresponding 2, 4 - isodithioiubret (IIIb - IIIf) have been isolated (see Table-1).

The formation of 1-tetra - O - benzoyl - \(\beta - \text{D} - \text{glucopyranosyl} - \text{S} - \text{aryl}

- 2, 4 - isodithioiubret (III) may be represented as follows.

\[
\text{Tetra - O - benzoyl - } \beta - \text{D- glucopyranosyl thiocarbamide.}
\]

\[
\text{Tetra - O - benzoyl - } \beta - \text{D- glucopyranosyl thiocarbamide.}
\]

\[
\text{Tetra - O - benzoyl - } \beta - \text{D- glucopyranosyl - S - benzyl isothiocarbamide (hydrochloride)}
\]

\[
\text{Tetra - O - benzoyl - } \beta - \text{D- glucopyranosyl - S - benzyl isothiocarbamide (free base)}
\]
Where, R = a) Phenyl, b) o - tolyl, c) m - tolyl, d) p - tolyl, e) o - Cl - phenyl
f) m - Cl - phenyl.

1. Tetra - O - benzoyl - β - D - glucopyranosyl - 5 - phenyl - 2 - S - benzyl - 2
isothiobiuret (IV).

When interaction of tetra - O - benzoyl - β - D - glucopyranosyl - S
benzyl isothiocarbamide and phenyl isocyanate has been carried out in dry
benzene medium for 24 hr. at room temperature a clear solution was obtained. On
mixing this clear solution with petroleum ether a white solid was isolated. The
product was crystallised from ethanol, m.p. 140°. The elemental analysis
indicated the molecular formula of the product as C_{49}H_{41}O_{10}N_{5}S.

Examination of the product with m.p. 140° (C_{49}H_{41}O_{10}N_{5}S)

i) Solubility: It was soluble in acetone, chloroform, benzene and acetic acid
while insoluble in petroleum ether, alcohol and water.

ii) Action of alkaline plumbite solution: The product was found
nondesulphurisable when boiled with alkaline plumbite solution.

iii) Action of conc. sulphuric acid: On warming with conc. sulphuric acid it
charred.

iv) Thermal decomposition: On thermal decomposition smell of phenyl isocy-
anate was quite perceptible.

v) Polarimetry: The compound was optically active and its [α]_D^{25} = -80.01°
(c, 0.892 in chloroform).
vi) **IR spectrum**: Its IR spectrum showed the presence of bands due to νNH, νC = O, νC = N, νS - Bz and band due to β - D - glucopyranose ring (deformation) was also noticed (Fig. 8). Its NMR spectrum displayed signals due to aromatic protons, NH proton and signals due to protons of glucopyranosyl ring (Fig. 9).

These observations indicated the structure of the product with m.p. 140° as 1 - tetra - O - benzoyl - β - D - glucopyranosyl - 5 - phenyl - 2 - S - benzyl - 2 - isothiobiuret (IV).

The formation of (IV) may be represented as follows:

![Diagram](image)

Where Bz = benzoyl, Ph = phenyl.

This reaction of 1 - tetra - O - benzoyl - β - D - glucopyranosyl - S - benzyl isothiocarbamide could not be extended to other isocyanate because of non-availability.
Antimicrobial activity

Antibacterial activity:

All the compounds were screened for their antibacterial activity against various pathogenic bacteria. Such as S. aureus, E. coli, P. vulgaris, Pseudomonas, Bacillus, and Salmonella Sp. by cup plate method\textsuperscript{15,16} at a concentration 100 $\mu$g/ml$^{-1}$ in DMF by using the standard Co-Trimazine (25 $\mu$g ml$^{-1}$) for bacteria.

Amongst the compounds tested for their antibacterial activity compounds IIIa, IIIb and IIId showed good activity against S. aureus. Compounds IIIb, IIIc, IIIe showed good activity against E. coli, P. vulgaris while all compounds showed moderate activities against Bacillus, Pseudomonas and Salmonella Sp.

Antifungal activity:

The compounds were screened for their antifungal activity against Fusarium and A. niger by cup plate method at a concentration of 100 $\mu$g/ml in DMF and using the standard griseofulvin (10 $\mu$g/ml). Amongst the compounds tested, compounds IIIe and IIIf showed good activity against Fusarium while other compounds found resistant against A. niger.
EXPERIMENTAL PART

The reagents required for the reactions described in this chapter were prepared as follows.

a) Tetra- O - benzoyl - β - D - glucopyranosyl isothiocyanate:

It was prepared as described earlier (See chapter I, Page 44) by the interaction of lead thiocy anate and tetra- O - benzoyl - α - D - glucopyranosyl bromide in xylene medium.

b) Tetra- O - benzoyl - β - D - glucopyranosyl thiocarbamide:

It was prepared by the interaction of tetra- O - benzoyl - β - D - glucopyranosyl isothiocyanate and ammonia in a benzene medium. (See also chapter I, Page 52).

c) The phenyl isocyanate used was of commercial grade.

d) Aryl isothiocyanates:

The required aryl isothiocyanates were prepared as usual, by the oxidative decomposition of ammonium aryl dithiocarbamates with the help of lead nitrate.

e) 1-tetra- O - benzoyl - β - D - glucopyranosyl - S - benzyl isothiocarbamide:

It was prepared by the interaction of tetra- O - benzoyl - β - D - glucopyranosyl thiocarbamide and benzyl chloride. Details of a typical experiment are as follows:

A mixture of tetra- O - benzoyl - β - D - glucopyranosyl thiocarbamide (0.01 M, 6.5g), benzyl chloride (0.01M, 1.2g) and ethanol 20 ml were heated under gentle reflux for 90 min. The resultant acidic solution when rendered basic with dilute ammonium hydroxide a granular solid (6g) was obtained. Crystallised from ethanol, m.p. 166°. [Found : N, 3.69, S, 4.24 C₄H₆O₅N₂S. requires ; N, 3.76, S, 4.30 %].

The product was found non-desulphurisable when boiled with an alkaline plumbite solution.
FIG. 1: INFRARED SPECTRUM OF Illa.
1) Synthesis of 1-tetra-O-benzoyl-β-D-glucopyranosyl-5-aryl-2-S-benzyl-2,4-isodithioiurets (III).


A benzene solution of phenyl isothiocyanate (0.01M, 1.3g in 10 ml) was added to a benzene solution of 1-tetra-O-benzoyl-β-D-glucopyranosyl-S-benzyl isothiocarbamide (0.01 M, 7.4 g in 30 ml) and the reaction mixture was refluxed over a boiling water bath for 3 hr. Afterwards, the solvent benzene was removed by distillation and the resultant syrupy mass was triturated several times with petroleum ether to remove unreacted phenyl isothiocyanate a white solid (6.4g) was obtained. It was crystallised from ethanol, m.p. 177°. [Found: C, 66.29, H, 4.26, N, 4.67, S, 7.30 C_{4g}H_{51}O_{4}N_{3}S_{2} requires; C, 66.89, H, 4.66, N, 4.77, S, 7.28%].

The product was soluble in acetone, chloroform, benzene, carbon tetrachloride and acetic acid and insoluble in water, alcohol and petroleum ether. It charred on heating with sulphuric acid. It was found desulphurisable when boiled with alkaline plumbite solution. On heating in a dry test tube the characteristic smell of benzyl mercaptan and phenyl isothiocyanate were quite perceptible. Its specific rotation [α]_{D}^{25} -86.20° (c, 0.464 in chloroform).

The main absorption bands observed in the IR spectrum of IIla (Fig. 1) are listed below.

<table>
<thead>
<tr>
<th>Absorption observed (cm⁻¹)</th>
<th>Assignment</th>
<th>Absorption expected (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3557</td>
<td>N-H-stretching.</td>
<td>3500-3100²a, 3a, 6, 8a</td>
</tr>
<tr>
<td>1728</td>
<td>C=O stretching.</td>
<td>1730-1715²b, 3b, 5, 6</td>
</tr>
<tr>
<td>1591</td>
<td>C = N stretching.</td>
<td>1689-1471³c, 5</td>
</tr>
<tr>
<td>1097</td>
<td>C = S stretching.</td>
<td>1200-1050⁴d, 4a</td>
</tr>
<tr>
<td>854</td>
<td>Glycosidic C - H deformation.</td>
<td>844 ± 8¹⁰</td>
</tr>
<tr>
<td>767</td>
<td>C - S stretching.</td>
<td>800-600²c, 3d</td>
</tr>
<tr>
<td>709</td>
<td>C - H aromatic.</td>
<td>900-675³c, 3c, 7</td>
</tr>
</tbody>
</table>
FIG. 2: NMR SPECTRUM OF Illa.
FIG. 3: MASS SPECTRUM OF IIa.

MASS SPECTRUM
Data File: ÆEDC01F
Sample: CVK-5 PRINCIPAL, AKOLA #2811
RT: 0.24" FAB(Pos.) GC 1.4c BP: m/z 154.0000 Int. 50.2794 LV 0.10
Scan# (2 to 4)
Scheme - 1

Probable fragmentation pattern of 1-tetra-O-benzoyl-β-D-glucopyranosyl-5-phenyl-2-S-benzyl-2,4-isodithiobiuret (IIa).

(M+ 879)

(M/z 787)

(M/z 743)

(M/z 307)

(M/z 578)

(M/z 289)

(M/z 136)

(M/z 105)

Where, Bz = Benzoyl = COC₈H₈
The NMR spectrum of IIIa (Fig. 2) distinctly displayed signals due to aromatic protons at δ8.0 - 7.8 and δ7.6 - 7.1 ppm, NH proton at δ6.0 ppm, and signals in the form of multiplets characteristic of the pyranosyl ring were located at δ5.9 - 5.1 and δ4.6 - 4.2 ppm.

Its Mass spectrum\(^{12,13,14}\) (Fig. 3) showed molecular ion peak at m/z 879. Some important fragment peaks with their relative abundances are listed in Table - 2. The probable fragmentation pattern are shown in Scheme - 1.

<table>
<thead>
<tr>
<th>Ion</th>
<th>M/z</th>
</tr>
</thead>
<tbody>
<tr>
<td>M(^+)</td>
<td>879</td>
</tr>
<tr>
<td>[ M - C(_6)H(_5)-NH ]</td>
<td>787</td>
</tr>
<tr>
<td>[ M - C(_6)H(_5)-NH, CS]</td>
<td>743</td>
</tr>
<tr>
<td>[ M - C(_6)H(_5)-NH, CS,C(_8)H(_9)N(_2)S]</td>
<td>578</td>
</tr>
<tr>
<td>[ TBG - C(<em>{15})H(</em>{11})O(_3) ]</td>
<td>307</td>
</tr>
<tr>
<td>[ TBG - C(<em>{15})H(</em>{11})O(_3),H(_2)O ]</td>
<td>289</td>
</tr>
<tr>
<td>[2C(_6)H(_3) ](^+) Base peak(^*)</td>
<td>154</td>
</tr>
<tr>
<td>[ C(_8)H(_8)O(_2) ](^+)</td>
<td>136</td>
</tr>
<tr>
<td>[ C(_7)H(_3)O ](^+)</td>
<td>105</td>
</tr>
</tbody>
</table>

TBG - tetra - O - benzoyl - β - D - glucopyranosyl, Bz = Benzoyl.

\(^*\) Relative abundance of the base peak has been arbitrarily taken to be 100%.

**Experiment No. 2 : 1 - tetra - O - benzoyl - β - D - glucopyranosyl - 5 - o - tolyl - 2 - S - benzyl - 2,4 - isodithiobiuret (IIIb).**

The benzene solution of 1 - tetra - O - benzoyl - β - D - glucopyranosyl - S - benzyl isothiocarbamide (0.01 M, 7.4 g in 30 ml) was mixed with a solution of o - tolyl isothiocyanate (0.01 M, 1.4 g in 10 ml). Benzene and the reaction mixture was refluxed over a boiling water bath for 3 hr. After heating, solvent benzene was distilled off and the sticky mass obtained as residue was triturated several times with ethanol a white product separated out (5.4 g). Crystallised from ethanol, m.p. 114\(^0\). [Found : C, 66.98 H, 4.29N, 4.65, S, 7.10 C\(_{15}\)H\(_{11}\)O\(_3\)N\(_2\)S\(_2\); requires : C, 67.18, H, 4.81, N, 4.70, S, 7.16 %].
It charred on heating with sulphuric acid. It was desulphurisable when boiled with alkaline plumbite solution. On thermal decomposition the smell of o-tolyl isothiocyanate was quite perceptible. Its $[\alpha]_D^{25}$ was found to be -66.96° (c, 0.448) in chloroform.

**Experiment No. 3**: 1-tetra-O-benzoyl-β-D-glucopyranosyl-5-m-tolyl-2-S-benzyl-2,4-isodithiobiuret (IIIc).

The solution of m-tolyl isothiocyanate in benzene (0.01 M, 1.4 g in 10 ml) was added to a benzene solution of 1-tetra-O-benzoyl-β-D-glucopyranosyl-S-benzyl isothiocarbamide (0.01 M, 7.4 g in 30 ml) and the mixture was refluxed over a boiling water bath for 3 hr. Solvent benzene was removed by distillation and sticky mass obtained as residue. This when tritiated several times with petroleum ether, a white solid was obtained (7 g). Crystallised from ethanol, m.p. 118° (d). [Found: C, 66.95 H, 4.21 N, 4.63, S, 7.08 C$_{50}$H$_{4}$O$_{5}$N$_{2}$S$_{2}$ requires; C, 67.18, H, 4.81, N, 4.70, S, 7.16%].

It was found desulphurisable when boiled with an alkaline plumbite solution. On thermal decomposition smell of m-tolyl isothiocyanate was quite perceptible. Its $[\alpha]_D^{25}$ in chloroform was found to be -38.16° (c, 0.524).

**Experiment No. 4**: 1-tetra-O-benzoyl-β-D-glucopyranosyl-5-p-tolyl-2-S-benzyl-2,4-isodithiobiuret (IIIc).

The benzene solution of 1-tetra-O-benzoyl-β-D-glucopyranosyl-S-benzyl isothiocarbamide (0.01 M, 7.4 g in 30 ml) was mixed with p-tolyl isothiocyanate (0.01 M, 1.4 g in 10 ml) in benzene and the mixture was refluxed over a boiling water bath for 3 hr. Benzene was removed by distillation and sticky mass obtained as the residue was trituated with petroleum ether several times to remove unreacted isothiocyanate. On treatment with ethanol a pale yellow solid was separated out (6 g) Crystallised from ethanol, m.p 122° [Found: C, 66.98 H, 4.32 N, 4.66, S, 7.12 C$_{50}$H$_{4}$O$_{5}$N$_{2}$S$_{2}$ requires; C, 67.18, H, 4.81, N, 4.70, S, 7.16%].

It was soluble in acetone, chloroform, benzene, carbon tetrachloride and acetic acid and insoluble in water, alcohol. It charred on heating with sulphuric acid. On boiling with an alkaline plumbite solution desulphurisation was observed. On thermal decomposition the smell of p-tolyl isothiocyanate was quite perceptible. Its $[\alpha]_D^{25}$ was found to be -68.96° (c, 0.580 in chloroform).
Figure 5: NMR Spectrum of IIId.
The following absorption bands were located in its IR spectrum (Fig. 4)

<table>
<thead>
<tr>
<th>Absorption observed (cm⁻¹)</th>
<th>Assignment</th>
<th>Absorption expected (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3368</td>
<td>N-H stretching.</td>
<td>3500-3100²a, ³a, ⁸a, ⁶</td>
</tr>
<tr>
<td>1730</td>
<td>C = O stretching.</td>
<td>1730-1715²b, ³b, ⁵, ⁶</td>
</tr>
<tr>
<td>1585</td>
<td>C = N stretching.</td>
<td>1680-1471³c, ⁵</td>
</tr>
<tr>
<td>1092</td>
<td>C = S stretching.</td>
<td>1200-1050³d, ⁴a</td>
</tr>
<tr>
<td>852</td>
<td>Glycosidic C - H deformation.</td>
<td>844 + 8¹⁰</td>
</tr>
<tr>
<td>766</td>
<td>C - S stretching.</td>
<td>800-600²c, ³d</td>
</tr>
<tr>
<td>1316</td>
<td>C - N stretching.</td>
<td>1350-1280⁸b</td>
</tr>
<tr>
<td>709</td>
<td>C - H aromatic.</td>
<td>900-675³e, ⁷</td>
</tr>
</tbody>
</table>

The NMR spectrum of IIId (Fig. 5) distinctly displayed signals due to aromatic protons at δ8.30 - 7.84 and δ7.62 - 6.93 ppm⁸,⁹,¹¹. NH proton at δ6.02 ppm, Methyl protons of p-tolyl at δ2.40 ppm and multiplies characteristics of the glucopyranosyl ring protons were also located at δ5.99 - 5.37 and δ4.62 - 4.28 ppm⁶,⁹,¹¹.

**Experiment No. 5 : 1 - tetra - O - benzoyl - β - D - glucopyranosyl - 5 - o - Cl - phenyl - 2 - S - benzyl - 2,4 - isodithiobiuret (IIIe).**

The benzene solution of 1 - tetra - O - benzoyl - β - D - glucopyranosyl - S - benzyl isothiocarbamide (0.01 M, 7.4 g in 30 ml) was mixed with o - Cl - phenyl isothiocyanate (0.01 M, 1.6 g in 10 ml). in benzene and the mixture was refluxed over a boiling water bath for 3 hr. Benzene was removed by distillation and sticky mass obtained as the residue was triturated several times with petroleum ether to remove unreacted isothiocyanate. On treatment with ethanol a pale yellow solid was separated out (5 g) Crystallised from ethanol, m.p. 65⁰ (d). [Found : C, 64.01 H, 4.19 N, 4.56, S, 6.72 C₄₉H₄₆O₅N₃S₂Cl, requires ; C, 64.40, H, 4.38, N, 4.59, S, 7.00 %].

It was soluble in acetone, chloroform, carbon tetrachloride, benzene and acetic acid and insoluble in water, alcohol. It charred on heating with sulphuric acid. On boiling with an alkaline plumbite solution desulphurisation was observed. On thermal decomposition the smell of o - Cl - phenyl isothiocyanate was quite perceptible. Its [α]d,³⁵ was found to be -189.87⁰ (c, 0.316 in chloroform).
Experiment No. 6: 1-tetra-O-benzoyl-β-D-glucopyranosyl-S-m-Cl-phenyl-2-S-benzyl-2,4-isodithiobiuret (IIIf).

The benzene solution of m-Cl-phenyl isothiocyanate (0.01 M, 1.6 g in 10 ml) was mixed with 1-tetra-O-benzoyl-β-D-glucopyranosyl-S-benzyl isothiocarbamide (0.01 M, 7.4 g in 30 ml) in benzene and the mixture was refluxed over a boiling water bath for 3 hr. Benzene was removed by distillation and sticky mass obtained as the residue was triturated several times with petroleum ether to remove unreacted isothiocyanate. On treatment with ethanol a pale yellow solid was separated out (4.6 g). Crystallised from ethanol, m.p. 88º(d). [Found: C, 64.12 H, 4.20 N, 4.53 S, 6.97 C_{60}H_{46}O_{5}N_{3}S_{2}Cl, requires: C, 64.40, H, 4.38, N, 4.59, S, 7.00 %].

The compound was soluble in acetone, chloroform, carbon tetrachloride, benzene and acetic acid and was insoluble in alcohol and water. It charred on heating with sulphuric acid. On boiling with an alkaline plumbite solution desulphurisation was observed. On thermal decomposition the smell of m-Cl-phenyl isothiocyanate was quite perceptible. Its [α]_{D}^{20} was found to be -83.89º (c, 0.596 in chloroform).

The main absorption bands observed in the IR spectrum of IIIf (Fig. 6) are listed below.

<table>
<thead>
<tr>
<th>Absorption observed (cm⁻¹)</th>
<th>Assignment</th>
<th>Absorption expected (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3334</td>
<td>N-H-stretching.</td>
<td>3500-3100²ᵃ, 3ᵃ, 8ᵃ, 6ⁿ</td>
</tr>
<tr>
<td>1729</td>
<td>C = O stretching.</td>
<td>1730-1715²ᵇ, 3ᵇ, 5, 6ⁿ</td>
</tr>
<tr>
<td>1583</td>
<td>C = N stretching.</td>
<td>1689-1471³ᵇ, 5</td>
</tr>
<tr>
<td>1091</td>
<td>C = S stretching.</td>
<td>1200-1050³ᵈ, 4ᵃ</td>
</tr>
<tr>
<td>857</td>
<td>Glycosidic C-H deformation.</td>
<td>844 ± 8¹⁰</td>
</tr>
<tr>
<td>774</td>
<td>C = S stretching.</td>
<td>800-600²ᶜ, 3ᵈ</td>
</tr>
<tr>
<td>1355</td>
<td>C = N stretching.</td>
<td>1350-1280⁸ᵇ</td>
</tr>
<tr>
<td>708</td>
<td>C = H aromatic.</td>
<td>900-675⁵, 3ᶜ, 7</td>
</tr>
</tbody>
</table>

The NMR spectrum of IIIf (Fig. 7) distinctly displayed signals due to aromatic protons at δ8.07 - 7.80 and δ7.65 - 7.04 ppm⁸, ⁹, ¹¹. NH proton at δ6.06 - 6.03 ppm⁸, and multiplates characteristics of the glucopyranosyl ring protons were also located at δ5.99 - 5.67 and δ5.40 - 4.48 ppm⁶, ⁹, ¹¹.
FIG. 9: NMR SPECTRUM OF IV.

Interaction of 1-tetra-O-benzoyl-β-D-glucopyranosyl-S-benzyl isothiocarbamide and phenyl isocyanate.

The benzene solution of 1-tetra-O-benzoyl-β-D-glucopyranosyl-S-benzyl isothiocarbamide (0.01 M, 7.4 g in 40 ml) was mixed with phenyl isocyanate (0.01 M, 1.1 g), and the mixture was shaken for a few minutes. The clear solution kept for 24 hr at room temperature. Afterwards it was mixed with petroleum ether when a white solid (6 g) was separated out. It was crystallised from ethanol, m.p. 140⁰C. [Found: C, 67.81; H, 4.21; N, 4.39; S, 3.36. C₄₉H₄₁O₁₀N₃S. requires: C, 68.13; H, 4.75; N, 4.86; S, 3.70%].

The product was soluble in alcohol, acetone, chloroform, benzene, carbon tetrachloride and acetic acid. It charred on heating with sulphuric acid which indicated the presence of glucosyl group. The product was found non-desulphurisable when boiled with alkaline plumbite solution. On thermal decomposition the smell of phenyl isocyanate was quite perceptible. Its [α]₀ was found to be -80.01⁰ (c, 0.892 in chloroform).

In its IR spectrum (Fig. 8) following important bands were located:

<table>
<thead>
<tr>
<th>Absorption observed (cm⁻¹)</th>
<th>Assignment</th>
<th>Absorption expected (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3377</td>
<td>N-H-stretching.</td>
<td>3500-3100²a, 3a, 8a, 6</td>
</tr>
<tr>
<td>1729</td>
<td>C = O stretching.</td>
<td>1730-1715²b, 3b, 5, 6</td>
</tr>
<tr>
<td>1586</td>
<td>C = N stretching.</td>
<td>1689-1471³c, 5</td>
</tr>
<tr>
<td>756</td>
<td>C - S stretching.</td>
<td>800-600²c, 3d</td>
</tr>
<tr>
<td>854</td>
<td>Glycosidic C - H deformation.</td>
<td>844 ± 8¹⁰</td>
</tr>
<tr>
<td>707</td>
<td>C - H aromatic.</td>
<td>900-675³e, 3e, 7</td>
</tr>
</tbody>
</table>

The NMR spectrum of IV (fig. 9) distinctly displayed signals due to aromatic protons at δ8.04 - 7.83 and δ7.81 - 7.05 ppm⁶,⁹,¹¹. NH proton at δ7.02 - 6.00 ppm⁸, and multiplates characteristics of the glucopyranosyl ring protons were also located at δ5.70 - 5.60 and δ4.62 - 5.60 ppm⁶,⁹,¹¹.
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