

## NOTE

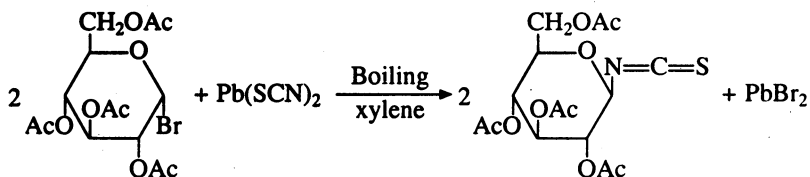
## N-Glucoylated Compounds: Synthesis of New 1-Tetra-O-acetyl- $\beta$ -D-glucopyranosyl-3-aryl Thiocarbamides

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Four new 1-tetra-O-acetyl- $\beta$ -D-glucopyranosyl-3-aryl thiocarbamides have been prepared by interaction of tetra-O-acetyl- $\beta$ -D-glucopyranosyl isothiocyanate and aryl amines. The identities of these compounds have been established on the basis of IR and NMR spectral analysis and usual chemical transformations. In view of our interest in carbohydrate chemistry we now report the synthesis of some new 1-tetra-O-acetyl- $\beta$ -D-glucopyranosyl-3-aryl thiocarbamides.

Tetra-O-acetyl- $\beta$ -D-glucopyranosyl isothiocyanate (I) have been prepared by the extension of an earlier known method<sup>1</sup> using lead thiocyanate in place of silver thiocyanate in boiling xylene medium.



where Ac = COCH<sub>3</sub>.

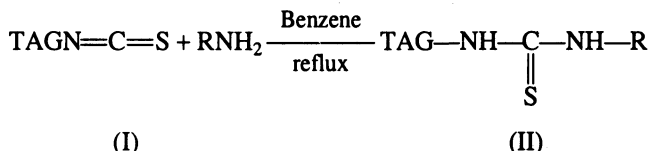
When the interaction of tetra-O-acetyl- $\beta$ -D-glucopyranosyl isothiocyanate and  $\alpha$ -naphthylamine has been carried out in boiling benzene medium a clear solution is obtained; this on mixing with petroleum ether deposits an oily liquid, which on trituration several times with petroleum ether gives a solid, m.p. 190°C.

The product is found desulphurisable when boiled with alkaline plumbite solution. The specific rotation was found to be +63.55° (0.944 in chloroform). The IR spectrum of the product showed bands due to  $\nu$ (NH) (3212 cm<sup>-1</sup>),  $\nu$ (C=O) (1744 cm<sup>-1</sup>),  $\nu$ (C—N) (1350 cm<sup>-1</sup>),  $\nu$ (C=S) (1004 cm<sup>-1</sup>),  $\nu$ ( $\beta$ -D-glucopyranosyl ring) (889 cm<sup>-1</sup>).<sup>2,3</sup> The NMR spectrum of the product distinctly displayed signals due to NH ( $\delta$  7.9 ppm), aromatic protons ( $\delta$  7.2–7.3 ppm). It also showed the signals due to protons of  $\beta$ -D-glucopyranosyl ring at ( $\delta$  4–4.3) and ( $\delta$  4.6–5.2 ppm).<sup>4,5</sup>

On the basis of all the above facts, the product with m.p. 190°C was assigned

the structure 1-tetra-O-acetyl- $\beta$ -D-glucopyransoyl-3- $\alpha$ -naphthyl thiocarbamide (Ia).

When the reaction of tetra-O-acetyl- $\beta$ -D-glucopyranosyl isothiocyanate TAGN=C=S is extended to three other aryl amines the related 1-tetra-O-acetyl- $\beta$ -D-glucopyranosyl-3-aryl thiocarbamides (IIb-IIId) have been isolated (Table-1).



where R = (a)  $\alpha$ -naphthyl, (b) *o*-anisyl, (c) *p*-anisyl, (d) benzyl.

TABLE-1  
1-TETRA-O-ACETYL- $\beta$ -D-GLUCOPYRANOSYL-3-ARYL-THIOCARBAMIDES (II)  
TETRA-O-ACETYL- $\beta$ -D-GLUCOPYRANOSYL ISOTHIOCYANATE USED  
(0.01 M, 3.8 g) (I) SOLVENT-BENZENE

S.No.	Amines used (g)	1-tetra-O-acetyl- $\beta$ -D-glucopyranosyl-3-substituted thiocarbamides (g)	Yield % (m.p. °C)	Analysis, Found (Required)	$[\alpha]_D^{33}$ in chloroform
1.	$\alpha$ -Naphthyl (1.4)	-3- $\alpha$ -Naphthyl thiocarbamide (IIa) (2.5)	39.2 (190)	N; 5.50 (N; 5.25) S; 6.60 (S; 6.02)	+63.55 (c, 0.944)
2.	<i>o</i> -Anisidine (1.2)	-3- <i>o</i> -Anisyl thiocarbamide (IIb) (3.8)	67.97 (58)	N; 5.45 (N; 5.46) S; 6.32 (S; 6.24)	+118.53 (c, 0.928)
3.	<i>p</i> -Anisidine (1.2)	-3- <i>p</i> -Anisyl thiocarbamide (IIc) (3.1)	61.97 (67)	N; 5.48 (N; 5.46) S; 6.42 (S; 6.24)	+98.22 (c, 0.966)
4.	Benzyl (1.0)	-3-Benzyl thiocarbamide (IIId) (2.9)	83 (137)	N; 5.71 (N; 5.71) S; 6.53 (S; 6.44)	-28.95 (c, 1.036)

Satisfactory C and H analysis found in all cases.

The required tetra-O-acetyl- $\alpha$ -D-glucopyranosyl bromide has been prepared by the known method<sup>6</sup>.

### (1) Tetra-O-acetyl- $\beta$ -D-glucopyranosyl isothiocyanate (I)

Details of a typical experiment are as follows:

A solution of tetra-O-acetyl- $\alpha$ -D-glucopyranosyl bromide (5 g) in sodium dried xylene (30 mL) is treated with anhydrous lead thiocyanate (4 g); the mixture is refluxed gently for 3 h. The solution is then allowed to cool and is filtered from lead salts and then treated with petroleum ether (70 mL) with stirring. Tetra-O-

acetyl- $\beta$ -D-glucopyranosyl isothiocyanate precipitates out; yield is 3.5 g, 74%. The crude isothiocyanate is crystallised from ethanol-water, m.p. 112–114°C. (Found: C, 45.87; H, 4.32; N, 3.59; S, 8.22%.  $C_{15}H_{19}O_9NS$  requires C, 46.28; H, 4.88; N, 3.59; S, 8.22%).

The product has specific rotation  $(\alpha)_D^{35} = +4.160^\circ$  (ca. 2.2552, chloroform). The IR spectrum of the product exhibits a very strong and broad band at 2090  $cm^{-1}$  and also a band at 1090  $cm^{-1}$ , characteristic of isothiocyanate.

## (2) 1-Tetra-O-acetyl- $\beta$ -D-glucopyranosyl-3-aryl-thiocarbamide (II)

$\alpha$ -Naphthylamine (0.01 M, 1.4 g) was added to the benzene solution of tetra-O-acetyl- $\beta$ -D-glucopyranosyl isothiocyanate (0.01 M, 3.8 g in 50 mL) and the reaction mixture is refluxed over a water bath for 3 h.

After cooling it is mixed with petroleum ether when an oily liquid is separated out. This on trituration several times with petroleum ether gives a solid (2.5 g). Crystallised from ethanol, m.p. 190°C (Found: C, 54.30; H, 4.20; N, 5.50; S, 6.60%;  $C_{25}H_{28}O_9N_2S$  requires: C, 56.34; H, 5.25; N, 5.25; S, 6.02%).

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