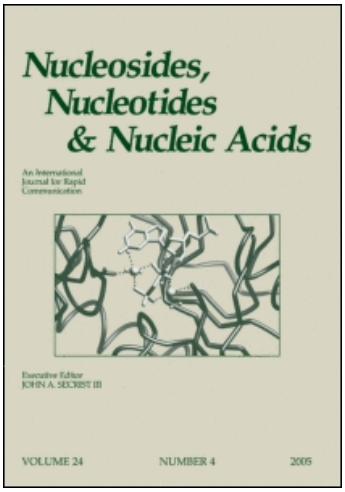

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Selective Synthesis and Structure of 6-Arylvinyl-2- and 4-Glucosyl-1,2,4-triazines of Expected Interesting Biological Activity

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Abstract: The 6-β-arylvinyl-2- and 4-glucosyl-3-thioxo-2,3-dihydro-1,2,4-triazin-5(4*H*)-ones were synthesized with high selectivity using the recently developed amino protecting group strategy. The structure of these new glucosides was established chemically and spectroscopically. Also, some interesting chemical transformations and rearrangements were observed.

Introduction

Many glycosides of 1,2,4-triazines have shown pronounced biological activity. Thus, some glycosyl derivatives of 1,2,4-triazine-3,5-diones (6-azauridine derivatives) and their 3-thiones possess cytotoxic, antiviral, enzyme inhibiting, immunosuppressive, antiphlogistic, antipsoriatic, bacteriostatic and antitumor activity.[1-7] Also, *N*-glycosyl derivatives of 3-amino- and 3-chloro-1,2,4-triazin-5(2*H*)-ones were reported to be useful as floor and wall disinfectants.[8] Moreover, the fact that some glycosides of 6-vinyl-1,2,4-triazines were shown to exhibit antiviral activity[9,10] prompted us to study the synthesis of the 2- and 4-glucosyl derivatives of certain 6-β-arylvinyl-1,2,4-triazines.

RESULTS AND DISCUSSION

In preliminary communications it has been shown that direct glycosidation of 3-thioxo-2,3-dihydro-4-amino-1,2,4-triazin-5(4*H*)-ones followed by deamination offers a convenient selective synthesis of the 2-glycosyl derivatives.[11,12] Also, glucosidation of unsubstituted 3-thioxo-2,3-dihydro-1,2,4-triazin-5(4*H*)-ones was shown to give the corresponding 4-glucosyl derivatives with high selectivity.[11-13] In the present investigation we applied these strategies

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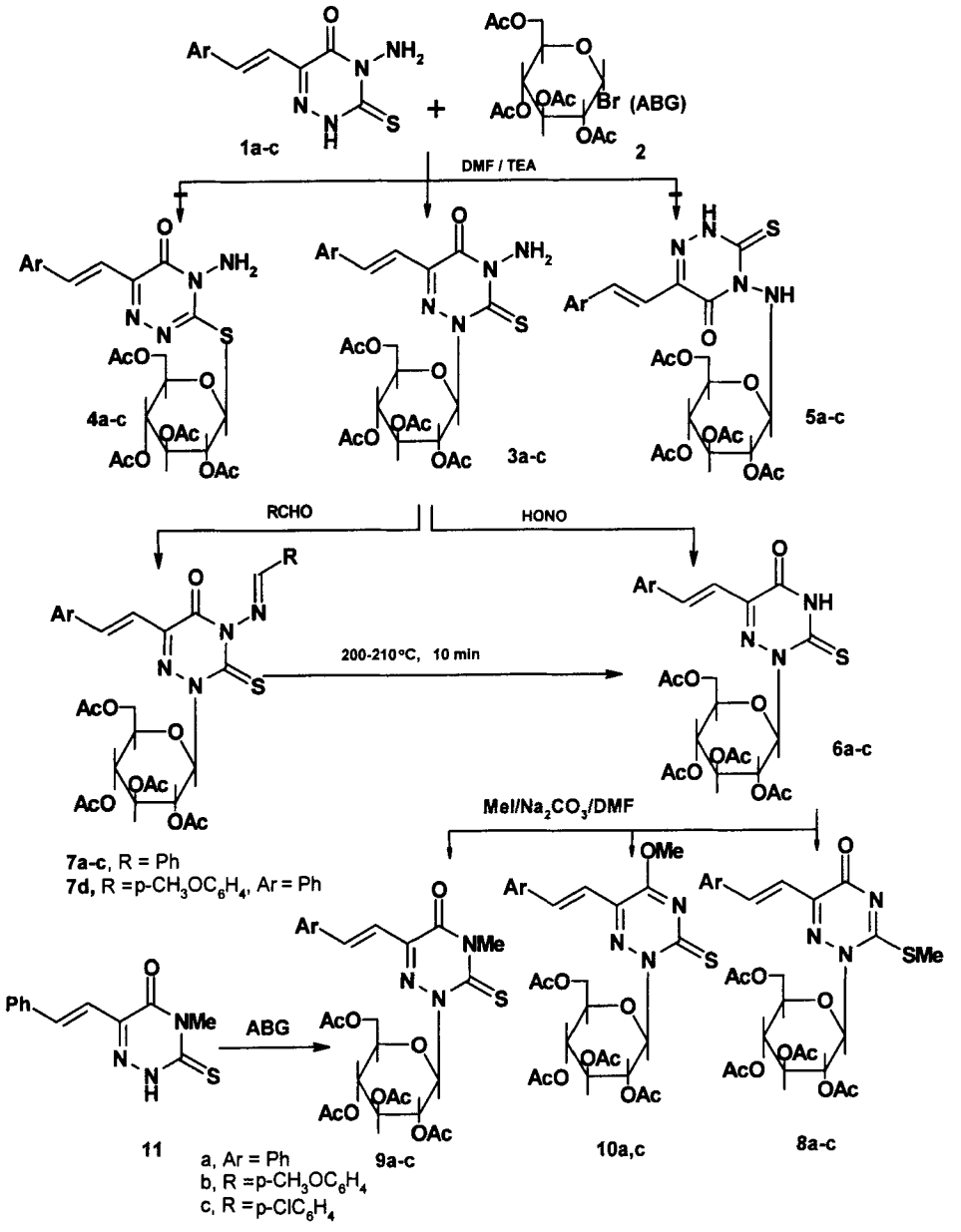
to selectively synthesize the 6-β-arylvinyl-2- and 4-glucosyl-3-thioxo-2,3-dihydro-1,2,4-triazin-5(4*H*)-ones and to study some of their chemical transformations. Thus, glucosidation of 4-amino-3-thioxo-2,3-dihydro-6-β-arylvinyl-1,2,4-triazin-5(4*H*)-ones (**1a-c**) with 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide (ABG) (**2**) in DMF in the presence of triethylamine afforded the corresponding 2-glucosyl derivatives **3a-c** (Scheme 1). Among the different possible monoglucosyl derivatives **3-5**, the structure of **3a-c** was established based on ^{1}H NMR data which show the position of the anomeric proton at δ = 6.7 (J = 9.4 Hz) and NH_2 protons at δ = 6.41-6.7 (s, 2H) consistent with similar reported data.[11] Moreover, the structure **3** was also chemically established as will be seen later.

Deamination of **3a-c** into the desired 2-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-6-β-arylvinyl-3-thioxo-2,3-dihydro-1,2,4-triazin-5(4*H*)-ones (**6a-c**) was achieved via two routes as outlined in Scheme 1. Thus, treatment of each of **3a-c** with nitrous acid in acetic acid gave directly the corresponding deaminated products **6a-c**, respectively. Alternatively, compounds **6a-c** were obtained by heating each of **3a-c** with benzaldehyde and/or *p*-anisaldehyde at 200-210°C for 10 minutes following a reported procedure.[11] The intermediate arylideneamino derivatives **7a-d** in the latter reaction, were isolated at lower temperature.

Methylation of compounds **6a-c** with methyl iodide in dimethylformamide and sodium carbonate gave a mixture of the 3-SCH_3 **8a-c** as the major product and 4-NCH_3 **9a-c** and the 5-OCH_3 **10a,c** as minor products. Only the methylthio derivatives **8a-c** were isolated in pure state. The structure of these products and their ratios were deduced from their ^{1}H NMR by comparing the relative integration of SCH_3, NCH_3, OCH_3 proton signals at near δ 2.6, 3.7, 3.4, respectively. Thus, ^{1}H NMR of the methylation products from compound **6a** revealed the presence of compounds **8a**, **9a** and **10a** in a ratio of 77.5:13.5:9.0, respectively. The structure of the 4-NCH_3 derivative **9a** was distinguished by an authentic synthesis by the action of ABG (**2**) on 4-methyl-6-styryl-3-thioxo-2,3-dihydro-1,2,4-triazin-5(4*H*)-one (**11**). Similarly, the products from compound **6b** were **8b**, **9b** in a ratio of 90:10, respectively, and from **6c** were **8c**, **9c** and **10c** in a ratio of 65.5:21.7:12.8, respectively.

Following reported methods for the conversion of 6-β-arylvinyl-1,2,4-triazin-5-ones into thieno[2,3-e][1,2,4]triazines by the action of phosphorus pentasulfide in pyridine,[14-18] we studied the action of the same reagent on the 2-glucosyl derivatives **3a-c**, **6a-c** in an attempt to prepare the 5-glucosylthieno[2,3-e][1,2,4]triazine-6(5*H*)-thiones (**12a-c**). In the present investigation we found that the action of phosphorus pentasulfide in pyridine on either of compounds **3a-c** or **6a-c** leads only to the formation of the corresponding 2-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-6-β-arylvinyl-1,2,4-triazine-3,5(2*H*,4*H*)-dithiones (**13a-c**). Increasing



Scheme 1

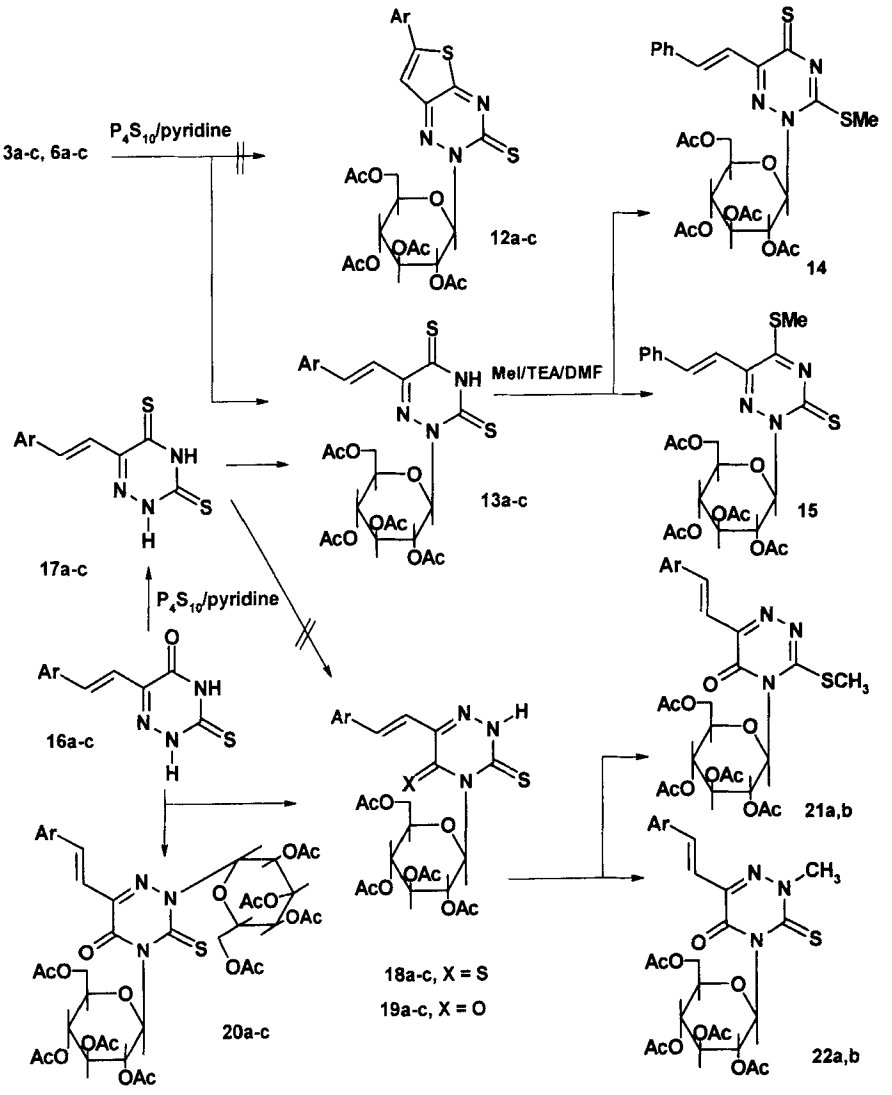
the reaction time or the molar ratio of phosphorus pentasulfide did not affect the formation of the target glucosylthienotriazines **12a-c**. In the present reaction only thiation and deamination took place. Assignment of the structure of compounds **13a-c** was based on chemical reactions, analytical and spectral data. Thus, methylation of compound **13a** with methyl iodide in

dimethylformamide containing triethylamine gave a mixture of the 3-methylthio **14** and the 5-methylthio **15** derivatives in a ratio of 57:43 [as identified from the ^{1}H NMR where the 3-methylthio derivative **14** showed the SCH_3 at δ 2.67 and the 5-methylthio derivative **15** showed the SCH_3 at δ 2.73. The mass spectrum of compound **13a** showed the parent ion peak at m/z 577 (M^+, 13.6%). The ^{1}H NMR and ^{13}C NMR of compounds **13a-c** showed signals consistent with their structure (*cf.* Experimental).

Further evidence for the structure of the dithioxo derivatives comes from study of the glucosidation of the 3,5-dithioxo-1,2,4-triazines **17a-c** (Scheme 2). The latter were synthesized by thiation of corresponding 3-thioxo-1,2,4-triazin-5(4*H*)-ones **16a-c** with phosphorus pentasulfide in pyridine. Interestingly we found that whereas glucosidation of **17a-c** with ABG in DMF and triethylamine or in acetone and KOH (one equivalent) led only to the formation of the corresponding 2-glucosyl derivatives **13a-c** (identical with those obtained previously) but none of the expected 4-glucosyl derivatives **18a-c.** Similar treatment of the 5-oxo derivatives **16a-c** gave a mixture of the 4-glucosyl derivatives **19a-c** and the 2,4-diglucosyl derivatives **20a-c**. When the reactions of **16a,c** were carried out in acetone with two equivalent of each of ABG and KOH the diglucosyl derivatives **20a,c** respectively were obtained as the major product along with the 4-glucosyl derivatives **19a,c** as minor products. The structure of the glucosyl derivatives was assigned based on spectral data and chemical evidence. Thus, whereas the ^{1}H NMR spectra of compounds **19a-c** showed signals at δ 13.78-10.35 (s, 1H, NH) and 7.04-6.88 (d, J = 9.0 - 9.2 Hz, H-1) and ^{13}C NMR of compounds **19a** showed signal at δ 85.25 (C-1), the ^{1}H NMR of **20a,c** showed signals at δ 7.04 (d, 1H, H-1 of the 4-glucosyl moiety) and 6.65 (d, J = 9.4-9.6 Hz, H-1 of the 2-glucosyl moiety) and ^{13}C NMR of compounds **20a** showed signals at δ 86.29, 88.32 (C-1 of both 2 and 4 glucosyl groups).

Methylation of the 4-glucosyl derivatives **19a,b** in dimethylformamide and sodium carbonate or triethylamine afforded a mixture of the corresponding 3-methylmercapto derivatives **21a,b** and the 2-methyl derivatives **22a,b** in a ratio of ca. 80:20. The composition of these mixtures was determined from the ^{1}H NMR. Thus, the ^{1}H NMR of **21a,b** showed the SCH_3 signal at δ 2.7, 2.76 and that of **22a,b** showed the NCH_3 signal at δ 3.95, 4.0, respectively.

Deacetylation of the previously synthesized acetylated glucosyl derivatives was accomplished by leaving the appropriate acetyl derivative in methanolic solution saturated with dry ammonia gas at 0°C for overnight. Scheme 3 illustrates the different reaction products obtained. Thus, deacetylation of **3a, 6a-c** led to the formation of the corresponding expected deacetylated derivatives **23**, **24a-c**. On the other hand, deacetylation of the 4-benzylideneamino derivative **7a** gave the 3-hydrazono derivative **26**, which showed an NH signal in its ^{1}H NMR at δ = 11.79.

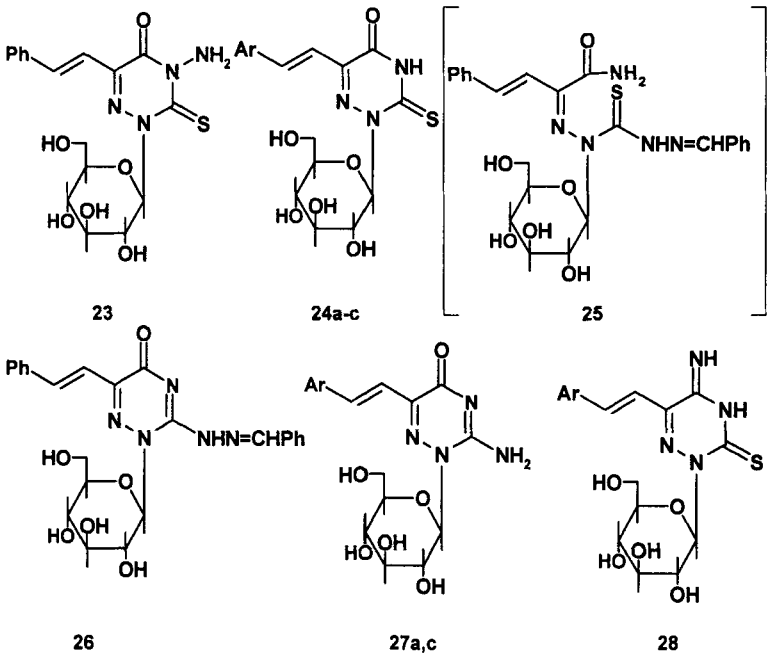


Scheme 2

The reaction presumably proceeds via ANRORG mechanism to give the intermediate **25** followed by ring closure with elimination of H_2S and rearrangement leading to the 3-benzylidenehydrazono derivative **26** (similar nucleophilic ring opening and rearrangement for some 4-substituted triazine derivatives has been reported).[19,20] Interestingly, deacetylation of **8a,c** is accompanied by ammoniolysis of the 3-methylthio group leading to the corresponding 3-amino derivatives **27a,c**. Similar ammoniolysis of the 5-thioxo group in compound **13b** led to the formation of the 5-imino derivative **28**. Finally, when the 4-tetraacetylglucosyl derivative

19b was subjected to this deacetylation reaction the glucosyl group was eliminated and 6-β-(*p*-methoxyphenyl)vinyl-3-thioxo-2,3-dihydro-1,2,4-triazin-5(4*H*)-one (**16b**) was formed. Similar deglycosylations of the 4-glycosyl derivatives have been reported.[21]

The structures of the deactylated derivatives were confirmed by analytical data, NMR and mass spectra. The ^{1}H NMR spectra were performed in DMSO-d_6 followed by D_2O to establish the exchangeable protons in each product. The biological screening of the new compounds obtained in this work is under investigation.



23 24a-c 25

26 27a,c 28

Conclusion:

From this study the following important findings were observed:

1. Applying the recently developed technique of selective reversible protection with *N*-amino group it was possible to selectively synthesize the 2- and 4-glucosyl derivatives **6**, **19**.
2. The 3-thioxo-5-oxo-1,2,4-triazines **16** and the corresponding 3,5-dithioxo derivatives **17** underwent monoglucosidation to give the 4-glucosyl **19** and the 2-glucosyl **13**. That difference in regioselectivity is presumably due to the steric effect of the sulfur atom.
3. An interesting rearrangement reaction was observed during deacetylation of the 4-benzylideneamino derivative **7a**. This leads to a new class of substituted glucosyl derivatives **26**, which constitute a subject of interesting future investigation.

EXPERIMENTAL

All melting points are uncorrected. IR (KBr pellets) spectra were recorded on a Perkin-Elmer 1430 spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were measured with a Varian GEMINI 200 spectrometer (200 MHz ^{1}H NMR; 50 MHz ^{13}C NMR). ^{13}C NMR spectra were recorded using the APT pulse sequence. Mass spectra were recorded on a GCMS-QP 1000 EX (70 EV) spectrometer. Elemental analyses were carried out at the Microanalytical Centre, Cairo University. The starting 4-amino-6-β-arylvinyl-3-thioxo-2,3-dihydro-1,2,4-triazin-5(4H)-ones (**1a-c**),[14] 6-β-arylvinyl-3-thioxo-2,3-dihydro-1,2,4-triazin-5(4*H*)-ones (**16a-c**),[23-26] 4-methyl-6-styryl-3-thioxo-2,3-dihydro-1,2,4-triazin-5(4*H*)-one (**11**),[22] were prepared as reported.

6-β-Arylvinyl-1,2,4-triazine-3,5(2*H*,4*H*)-dithiones (**17a-c**)

General Procedure: To a solution of each of **16a-c** (1 mmol) in dry pyridine (5 ml) was added phosphorus pentasulfide (4.44 g, 2 mmol). The reaction mixture was then heated under reflux for 6 hr., cooled and the product was extracted from the oily materials with ethanol (10 ml). The precipitate obtained on acidification with acetic acid (0.5 ml) was recrystallized from ethanol/water as yellow crystals.

6-Styryl-1,2,4-triazine-3,5(2*H*,4*H*)-dithione (**17a**)

From **16a** (50%), mp. 238°C; ^{1}H NMR (DMSO-d_6) δ = 14 (brs, 1H, NH), 7.37, 7.68 (2d, 2H, J = 16.4 Hz, trans CH=CH), 7.33-7.62 (m, 5H, ArH's), 3.5 (brs, overlapped with H_2O in the NMR solvent); ^{13}C NMR δ = 119.65, 127.57, 129.14, 129.41, 133.99 (ArCH's and CH=CH), 135.69 147.68, 168.93, 175.88 (ArC's, C=N, C=S).

Anal. for $C_{11}H_9N_3S_2$ Calcd.: C, 53.42; H, 3.67. Found: C, 53.29; H, 3.60.

6-β-(4-Methoxyphenyl)vinyl-1,2,4-triazine-3,5(2*H*,4*H*)-dithione (**17b**)

From **16b** (60%), mp. 242°C.

Anal. for $C_{12}H_{11}N_3OS_2$ Calcd.: C, 51.96; H, 4.00. Found: C, 52.01; H, 3.90.

6-β-(4-Chlorophenyl)vinyl-1,2,4-triazine-3,5(2*H*,4*H*)-dithione (**17c**)

From **16c** (50%), mp. 250°C.

Anal. for $C_{11}H_8ClN_3S_2$ Calcd.: C, 46.89; H, 2.86. Found: C, 47.01; H, 2.90.

4-Amino-2-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-6-β-arylvinyl-3-thioxo-2,3-dihydro-1,2,4-triazin-5(4*H*)-ones (**3a-c**)

General Procedure: To a solution of each of **1a-c** (7 mmol) in DMF (7 ml), triethylamine (2 ml, 14 mmol) was added followed by tetra-*O*-acetyl-α-D-glucopyranosyl bromide (**2**) (6.2 g, 15 mmol). The reaction mixture was stirred for 20 min. and then kept overnight at room temperature. The mixture was then diluted with ice-cold water and acidified with acetic acid (1

ml). The precipitate was then collected washed with water and recrystallized $CHCl_3$/ethanol or CH_2Cl_2 as yellow crystals.

4-Amino-2-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-6-styryl-3-thioxo-2,3-dihydro-1,2,4-triazin-5(4*H*)-one (**3a**)

From **1a** (52%), mp. 180°C; IR, 3311, 3215, 1755, 1693 (NH_2, C=O acetate, C=O amide) cm^{-1}; ^1H NMR ($CDCl_3$) δ = 7.96, 7.13 (2d, 2H, J=16.4 Hz, trans CH=CH), 7.65-7.37 (m, 5H, ArH's), 6.7 (d, 1H, J = 9.4 Hz, $H^{1'}$), 6.41 (s, 2H, NH_2), 5.95 (t, 1H, $H^{2'}$), 5.42 (t, 1H, $H^{3'}$), 5.25 (t, 1H, $H^{4'}$), 4.23 (2dd, 2H, $H^{6'}$), 3.98 (ddd, 1H, $H^{5'}$), 2.07-1.93 (4s, 12H, CH_3CO).

Anal. for $C_{25}H_{28}N_4O_{10}S$ Calcd.: C, 52.08; H, 4.89. Found: C, 52.30; H, 4.80.

4-Amino-2-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-6-β-(4-methoxyphenyl)vinyl-3-thioxo-2,3-dihydro-1,2,4-triazin-5(4*H*)-one (**3b**)

From **1b** (71%), mp. 228°C; IR, 3306, 3220 (NH_2), 1751 (C=O acetate), 1682 (C=O amide) cm^{-1}; ^1H NMR ($CDCl_3$) δ = 7.92, 7.01 (2d, 2H, J=16.4 Hz, trans CH=CH), 7.59, 6.93 (2d, 4H, ArH's), 6.7 (d, 1H, J = 9.4 Hz, $H^{1'}$), 6.41 (s, 2H, NH_2), 5.96 (t, 1H, $H^{2'}$), 5.42 (t, 1H, $H^{3'}$), 5.25 (t, 1H, $H^{4'}$), 4.23 (2dd, 2H, $H^{6'}$), 3.99 (ddd, 1H, $H^{5'}$), 3.85 (s, 3H, OCH_3), 2.08-1.94 (4s, 12H, CH_3CO).

Anal. for $C_{26}H_{30}N_4O_{11}S$ Calcd.: C, 51.48; H, 4.98. Found: C, 51.60; H, 5.20.

4-Amino-2-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-6-β-(4-chlorophenyl)vinyl-3-thioxo-2,3-dihydro-1,2,4-triazin-5(4*H*)-one (**3c**)

From **1c** (60%), mp. 240-242°C; IR, 3319, 3222 (NH_2), 1747 (C=O acetate), 1693 (C=O amide) cm^{-1}; ^1H NMR ($CDCl_3$) δ = 7.92, 7.11 (2d, 2H, J=16.4 Hz, trans CH=CH), 7.57-7.37 (2d, 4H, ArH's), 6.7 (d, 1H, J = 9.4 Hz, $H^{1'}$), 6.7 (s, 2H, NH_2), 5.95 (t, 1H, $H^{2'}$), 5.42 (t, 1H, $H^{3'}$), 5.25 (t, 1H, $H^{4'}$), 4.22 (2dd, 2H, $H^{6'}$), 3.97 (ddd, 1H, $H^{5'}$), 2.05-1.91 (4s, 12H, CH_3CO).

Anal. for $C_{25}H_{27}ClN_4O_{10}S$ Calcd.: C, 49.14; H, 4.45. Found: C, 49.30; H, 4.40.

4-Arylideneamino-6-β-arylvinyl-2-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-3-thioxo-2,3-dihydro-1,2,4-triazin-5(4*H*)-ones (**7a-d**)

General Procedure: A mixture of each of **3a-c** (1.5 mmol) and benzaldehyde and/or *p*-methoxybenzaldehyde (1 ml) was heated at 140-150°C (oil bath) for 15 minutes. After cooling and washing with cold ethanol the remaining solid was collected and recrystallized from $CHCl_3$/ethanol as yellow crystals.

4-Benzylideneamino-6-styryl-2-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-3-thioxo-2,3-dihydro-1,2,4-triazin-5(4*H*)-one **7a**

From **3a** and benzaldehyde (76%), mp. 268°C; IR, 1747 (C=O acetate), 1698 (C=O amide)

cm^{-1}; ^1H NMR ($CDCl_3$) δ = 8.4 (s, 1H, CH=N), 7.98, 7.19 (2d, 2H, J=16.4 Hz, trans CH=CH), 7.93-7.27 (m, 10H, ArH's), 6.86 (d, 1H, J = 9.2 Hz, $H^{1'}$), 5.99 (t, 1H, $H^{2'}$), 5.43 (t, 1H, $H^{3'}$), 5.28 (t, 1H, $H^{4'}$), 4.24 (2dd, 2H, $H^{6'}$), 3.95 (ddd, 1H, $H^{5'}$), 2.09-1.98 (4s, 12H, CH_3CO).

Anal. for $C_{32}H_{32}N_4O_{10}S$ Calcd.: C, 57.82; H, 4.85. Found: C, 57.80; H, 4.90.

4-*p*-Methoxybenzylideneamino-6-styryl-2-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-3-thioxo-2,3-dihydro-1,2,4-triazin-5(4*H*)-one (**7d**)

From **3a** and *p*-methoxybenzaldehyde (70%), mp. 262°C; ^1H NMR ($CDCl_3$) δ = 8.29 (s, 1H, CH=N), 8.0, 7.18 (2d, 2H, J=16.4 Hz, trans CH=CH), 8.02-6.98 (m, 9H, ArH's), 6.87 (d, 1H, J = 9.4 Hz, $H^{1'}$), 5.98 (t, 1H, $H^{2'}$), 5.43 (t, 1H, $H^{3'}$), 5.27 (t, 1H, $H^{4'}$), 4.24 (2dd, 2H, $H^{6'}$), 3.99 (ddd, 1H, $H^{5'}$), 3.9 (s, 3H, OCH_3), 2.09-1.98 (4s, 12H, CH_3CO).

Anal. for $C_{33}H_{34}N_4O_{11}S$ Calcd.: C, 57.05; H, 4.93. Found: C, 57.10; H, 5.01.

4-Benzylideneamino-6-β-(4-methoxyphenyl)vinyl-2-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-3-thioxo-2,3-dihydro-1,2,4-triazin-5(4*H*)-one (**7b**)

From **3b** and benzaldehyde (88%), mp. 242°C; IR, 1751 (C=O acetate), 1698 (C=O amide) cm^{-1}; ^1H NMR ($CDCl_3$) δ = 8.39 (s, 1H, CH=N), 7.9, 7.03 (2d, 2H, J=16.4 Hz, trans CH=CH), 7.93-6.88 (m, 9H, ArH's), 6.85 (d, 1H, J = 9.2 Hz, $H^{1'}$), 5.98 (t, 1H, $H^{2'}$), 5.43 (t, 1H, $H^{3'}$), 5.27 (t, 1H, $H^{4'}$), 4.23 (2dd, 2H, $H^{6'}$), 3.95 (ddd, 1H, $H^{5'}$), 2.09-1.98 (4s, 12H, CH_3CO).

Anal. for $C_{33}H_{34}N_4O_{11}S$ Calcd.: C, 57.05; H, 4.93. Found: C, 57.00; H, 4.80.

4-Benzylideneamino-6-β-(4-chlorophenyl)vinyl-2-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-3-thioxo-2,3-dihydro-1,2,4-triazin-5(4*H*)-one (**7c**)

From **3c** and benzaldehyde (57%), mp. 242°C; IR, 1750 (C=O acetate), 1700 (C=O amide) cm^{-1}; ^1H NMR ($CDCl_3$) δ = 8.39 (s, 1H, CH=N), 7.92, 7.12 (2d, 2H, J=16.4 Hz, trans CH=CH), 7.93-7.26 (m, 9H, ArH's), 6.85 (d, 1H, J = 9.2 Hz, $H^{1'}$), 5.97 (t, 1H, $H^{2'}$), 5.43 (t, 1H, $H^{3'}$), 5.26 (t, 1H, $H^{4'}$), 4.23 (2dd, 2H, $H^{6'}$), 3.95 (ddd, 1H, $H^{5'}$), 2.08-1.98 (4s, 12H, CH_3CO).

Anal. for $C_{32}H_{31}ClN_4O_{10}S$ Calcd.: C, 54.98; H, 4.47. Found: C, 55.00; H, 4.50.

6-β-Arylvinyl-2-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-3-thioxo-2,3-dihydro-1,2,4-triazin-5(4*H*)-ones (**6a-c**)

General Procedure:

(A) A mixture of each of **3a-c** (1.5 mmol) and benzaldehyde and/or p-methoxybenzaldehyde (1 ml) was heated 200-210°C for 10 min. After cooling and washing with cold ethanol the remaining solid was collected and recrystallized from ethanol as yellow crystals of **6a-c**.

(B) To a solution of each of **3a-c** (5 mmol) in glacial acetic acid (50 ml) was added a solution of sodium nitrite (0.5 g in 3 ml of H_2O) dropwise with stirring and cooling at 5°C over a period of

10 min. After dilution with ice-water mixture (200 g) the precipitate was collected and recrystallized from ethanol (in case of **6a,b**) or CH_2Cl_2/EtOH (in case of **6c**) as yellow crystals.

2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-6-styryl-3-thioxo-2,3-dihydro-1,2,4-triazin-5(4*H*)-one (**6a**)

Using the general procedure (A, B) **3a** gave **6a** (50%, 51%) , mp. 215°C; IR, 3568 (NH), 1755 (C=O acetate), 1716 (C=O amide) cm^{-1}; ^1H NMR ($CDCl_3$) δ = 10.04(s, 1H, NH), 7.97, 7.08 (2d, 2H, J=16.4 Hz, trans CH=CH), 7.64-7.27 (m, 5H, ArH's), 6.66 (d, 1H, J = 9.4 Hz, $H^{1'}$), 5.86 (t, 1H, $H^{2'}$), 5.42 (t, 1H, $H^{3'}$), 5.25 (t, 1H, $H^{4'}$), 4.25 (2dd, 2H, $H^{6'}$), 3.95 (ddd, 1H, $H^{5'}$), 2.09-1.97 (4s, 12H, CH_3CO).

Anal. for $C_{25}H_{27}N_3O_{10}S$ Calcd.: C, 53.47; H, 4.85. Found: C, 53.30; H, 4.80.

2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-6-β-(4-methoxyphenyl)vinyl-3-thioxo-2,3-dihydro-1,2,4-triazin-5(4*H*)-one (**6b**)

Using the general procedure (A, B) **3b** gave **6b** (51%, 59%) , mp. 242°C; IR, 3475 (NH), 1748 (C=O acetate), 1720 (C=O amide) cm^{-1}; ^1H NMR ($CDCl_3$) δ = 9.76 (s, 1H, NH), 7.91, 6.94 (2d, 2H, J=16.4 Hz, trans CH=CH), 7.57-6.9 (m, 4H, ArH's), 6.65 (d, 1H, J = 9.4 Hz, $H^{1'}$), 5.87 (t, 1H, $H^{2'}$), 5.42 (t, 1H, $H^{3'}$), 5.25 (t, 1H, $H^{4'}$), 4.25 (2dd, 2H, $H^{6'}$), 3.98 (ddd, 1H, $H^{5'}$), 3.85 (s, 3H, OCH_3), 2.09-1.97 (4s, 12H, CH_3CO).

Anal. for $C_{26}H_{29}N_3O_{11}S$ Calcd.: C, 52.79; H, 4.94. Found: C, 53.20; H, 4.70.

2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-6-β-(4-chlorophenyl)vinyl-3-thioxo-2,3-dihydro-1,2,4-triazin-5(4*H*)-one (**6c**)

Using the general procedure (A, B) **3c** gave **6c** (40%, 32%) , mp. 228°C; IR, 3562 (NH), 1751 (C=O acetate), 1724 (C=O amide) cm^{-1}; ^1H NMR ($CDCl_3$) δ = 9.8 (s, 1H, NH), 7.91, 7.04 (2d, 2H, J=16.4 Hz, trans CH=CH), 7.56-7.34 (2d, 4H, ArH's), 6.65 (d, 1H, J = 9.4 Hz, $H^{1'}$), 5.85 (t, 1H, $H^{2'}$), 5.41 (t, 1H, $H^{3'}$), 5.24 (t, 1H, $H^{4'}$), 4.24 (2dd, 2H, $H^{6'}$), 3.95 (ddd, 1H, $H^{5'}$), 2.09-1.97 (4s, 12H, CH_3CO).

Anal. for $C_{25}H_{26}ClN_3O_{10}S$ Calcd.: C, 50.38; H, 4.40. Found: C, 50.30; H, 4.20.

Action of methyl iodide on compounds **6a-c**

General Procedure: To a solution of each of **6a-c** (1 mmol) in DMF (5 ml) was added anhydrous sodium carbonate (0.6 g, 5.6 mmol) and methyl iodide (0.1 ml, 1.5 mmol). The reaction mixture was then stirred at 40-50°C for 5 minutes. After cooling and dilution with water the precipitate was collected and crystallized from ethanol. Compound **6a** gave colorless crystals composed of a mixture of **8a, 9a, 10a** in a ratio of 77.5:13.5:9, respectively, mp 196-200°C. Anal. for $C_{26}H_{29}N_3O_{10}S$ Calcd.: C, 54.25; H, 5.08. Found: C, 54.20; H, 4.60.

Compound **6b** gave a yellow mixture of **8b** and **9b** in a ratio of 90:10, respectively, mp 247-

252°C. Anal. for $C_{27}H_{31}N_3O_{11}S$ Calcd.: C, 53.55; H, 5.16. Found: C, 53.60; H, 5.40.

Compound **6c** gave a yellow mixture of **8c, 9c** and **10c** in a ratio of 65.5:21.7:12.8, respectively, mp 194-200°C. Anal. for $C_{26}H_{28}ClN_3O_{10}S$ Calcd.: C, 51.19; H, 4.63. Found: C, 51.20; H, 4.50.

3-Methylmercapto-2-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-6-styryl-1,2,4-triazin-5(4*H*)-one (**8a**)

Compound **6a** gave a mixture of **8a, 9a, 10a** which upon fractional recrystallization from ethanol gave colorless needles of **8a** (50%) , mp. 196-8°C; IR, 1748 (C=O acetate), 1672 (C=O amide) cm^{-1}; ^1H NMR ($CDCl_3$) δ = 7.97, 7.14 (2d, 2H, J=16.6 Hz, trans CH=CH), 7.62-7.26 (m, 5H, ArH's), 5.96 (t, 1H, $H^{2'}$), 5.60 (d, 1H, J = 9 Hz, $H^{1'}$), 5.37 (t, 1H, $H^{3'}$), 5.23 (t, 1H, $H^{4'}$), 4.21 (2dd, 2H, $H^{6'}$), 3.93 (ddd, 1H, $H^{5'}$), 2.63 (s, 3H, SCH_3), 2.06-1.91 (4s, 12H, CH_3CO); ^{13}C NMR δ = 14.21 (SCH_3), 20.25, 20.29, 20.45 ($\underline{C}H_3CO$), 61.33, 67.45, 68.01, 73.67, 74.59, 86.61 ($C^{1'}$, $C^{2'}$, $C^{3'}$, $C^{4'}$, $C^{5'}$, $C^{6'}$), 118.17, 127.89, 128.81, 128.9, 139.36 (CH of aromatic carbons and CH=CH), 136.11, 145.92, 165.84, 168.74, 169.43, 170.39, 170.66 (C of aromatic group, C=N, C=O).

Anal. for $C_{26}H_{29}N_3O_{10}S$ Calcd.: C, 54.25; H, 5.08. Found: C, 54.30; H, 4.80.

3-Methylmercapto-2-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-6-β-(4-methoxyphenyl)vinyl-1,2,4-triazin-5(4*H*)-one (**8b**)

Using the general procedure, **6b** gave mixture which upon fractional recrystallization from ethanol gave colorless needles of **8b** (87%) , mp. 247°C; IR, 1756 (C=O acetate), 1666 (C=O amide) cm^{-1}; ^1H NMR ($CDCl_3$) δ = 7.94, 7.04 (2d, 2H, J=16.4 Hz, trans CH=CH), 7.6, 6.9 (2d, 4H, ArH's), 5.98 (t, 1H, $H^{2'}$), 5.59 (d, 1H, J = 9.4 Hz, $H^{1'}$), 5.38 (t, 1H, $H^{3'}$), 5.25 (t, 1H, $H^{4'}$), 4.2 (2dd, 2H, $H^{6'}$), 3.95 (ddd, 1H, $H^{5'}$), 3.84 (s, 3H, OCH_3), 2.65 (s, 3H, SCH_3), 2.09-1.93 (4s, 12H, CH_3CO); ^{13}C NMR δ = 14.19 (SCH_3), 20.29, 20.43 ($\underline{C}H_3CO$), 55.19 (OCH_3), 61.36, 67.49, 68.04, 73.52, 74.59, 86.61 ($C^{1'}$, $C^{2'}$, $C^{3'}$, $C^{4'}$, $C^{5'}$, $C^{6'}$), 114.24, 115.74, 128.98, 129.46 (CH of aromatic carbons and CH=CH), 138.93, 146.22, 159.09, 160.93, 165.60, 168.74, 169.43, 170.39, 170.65 (C of aromatic group, C=N, C=O).

Anal. for $C_{27}H_{31}N_3O_{11}S$ Calcd.: C, 53.55; H, 5.16. Found: C, 53.50; H, 5.30.

3-Methylmercapto-2-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-6-β-(4-chlorophenyl)vinyl-1,2,4-triazin-5(4*H*)-one (**8c**)

Using the the general procedure, **6c** gave mixture which upon fractional recrystallization from ethanol gave colorless needles of **8c** (50%) , mp. 294°C; ^1H NMR ($CDCl_3$) δ = 7.94, 7.13 (2d, 2H, J=16.4 Hz, trans CH=CH), 7.58-7.29 (m, 4H, ArH's), 5.97 (t, 1H, $H^{2'}$), 5.6 (d, 1H, J = 9.4 Hz, $H^{1'}$), 5.39 (t, 1H, $H^{3'}$), 5.25 (t, 1H, $H^{4'}$), 4.24 (2dd, 2H, $H^{6'}$), 3.95 (ddd, 1H, $H^{5'}$), 2.66 (s, 3H, SCH_3), 2.08-1.93 (4s, 12H, CH_3CO).

Anal. for $C_{26}H_{28}ClN_3O_{10}S$ Calcd.: C, 51.19; H, 4.63. Found: C, 51.30; H, 4.60.

4-Methyl-2-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-6-styryl-3-thioxo-2,3-dihydro-1,2,4-triazin-5(4*H*)-one (**9a**)

To a solution of **11** (0.25 g, 1 mmol) in DMF (1.5 ml), triethylamine (0.4 ml, 2.9 mmol) was added followed by ABG (**2**) (0.42 g, 0.12 mmol). The reaction mixture was stirred for 20 min. and then kept overnight at room temperature. The mixture was then diluted with ice-cold water and acidified with acetic acid (0.5 ml). The precipitate was then collected, washed with water and recrystallized ethanol to give yellow crystals of **9a** (33%), mp. 230°C; ^{1}H NMR ($CDCl_3$) δ = 7.91, 7.14 (2d, 2H, J=16.4 Hz, trans CH=CH), 7.65-7.38 (m, 5H, ArH's), 6.80 (d, 1H, J = 9.6 Hz, $H^{1'}$), 5.95 (t, 1H, $H^{2'}$), 5.41 (t, 1H, $H^{3'}$), 5.25 (t, 1H, $H^{4'}$), 4.22 (2dd, 2H, $H^{6'}$), 3.95 (ddd, 1H, $H^{5'}$), 3.75 (s, 3H, NCH_3), 2.08-1.95 (4s, 12H, CH_3CO).

Anal. for $C_{26}H_{29}N_3O_{10}S$ Calcd.: C, 54.25; H, 5.08. Found: C, 54.30; H, 5.10.

2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-6-β-arylvinyl-1,2,4-triazine-3,5(2*H*,4*H*)-dithiones (**13a-c**)

General Procedure:

(A) To a solution of each of **17a-c** (1 mmol) in DMF (1 ml), triethylamine (0.2 ml) was added followed by **2** (0.45 g, 1.1 mmol). The reaction mixture was stirred for 20 min. and then kept overnight at room temperature. The mixture was then diluted with ice-cold water and acidified with acetic acid (1 ml). The precipitate was then collected, washed with water, dried at room temperature and recrystallized three times from absolute ethanol to give yellow crystals of **13a-c**.

(B) To a solution of each of **3a-c, 6a-c** (1 mmol) in dry pyridine (5 ml) was added phosphorus pentasulfide (0.45 g, 2 mmol). The reaction mixture was then heated under reflux for 6 hr. After cooling, the mixture was then acidified with acetic acid (0.5 ml) and the product was extracted from the oily materials with ethanol. The supernatant solution was decanted, concentrated and diluted with water. The precipitate was collected and recrystallized from aqueous ethanol (50%) (in case of **13a,c**) and from aqueous pyridine (50%) (in case of **13b**) as yellow crystals.

2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-6-styryl-1,2,4-triazine-3,5(2*H*,4*H*)-dithione (**13a**)

Using the general procedure (A), **17a** gave **13a** (15%), and using the general procedure (B) **3a** and/or **6a** gave **13a** (50%); mp. 214°C; Ms: m/z 577 (M^+, 13,6%); ^{1}H NMR ($CDCl_3$) δ = 11.34 (s, 1H, NH); 7.65-7.32 (2d, 2H, J=16.2 Hz, trans CH=CH), 7.65-7.32 (m, 5H, ArH's), 6.58 (d, 1H, J = 9.6 Hz, $H^{1'}$), 5.95 (t, 1H, $H^{2'}$), 5.42 (t, 1H, $H^{3'}$), 5.28 (t, 1H, $H^{4'}$), 4.26 (2dd, 2H, $H^{6'}$), 3.95 (ddd, 1H, $H^{5'}$), 2.08-1.98 (4s, 12H, CH_3CO); ^{13}C NMR δ = 20.40, 20.48, 20.56 ($\underline{C}H_3CO$), 61.48, 67.72, 68.18, 73.87, 74.68, 86.46 ($C^{1'}$, $C^{2'}$, $C^{3'}$, $C^{4'}$, $C^{5'}$, $C^{6'}$), 117.62, 128.24, 128.92, 129.86, 138.07 (CH of aromatic carbons and CH=CH), 135.69, 147.82, 169.21, 169.71, 169.84, 170.41, 170.86, 176.75 (C of aromatic group, C=N, C=O).

Anal. for $C_{25}H_{27}N_3O_9S_2$ Calcd.: C, 51.98; H, 4.71. Found: C, 51.80; H, 4.90.

2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-6-β-(4-methoxyphenyl)vinyl-1,2,4-triazine-3,5(2*H*,4*H*)-dithione (**13b**)

(a) Using the general procedure (A), **17b** gave **13b** (25%), and using the general procedure (B) **3b** and/or **6b** gave **13b** (65 and 68% respectively); mp. 206°C; IR, 3223 (NH), 1751 (C=O acetate) cm^{-1}; ^1H NMR ($CDCl_3$) δ = 7.58-6.86 (m, 7H, NH, CH=CH, ArH's), 6.58 (d, 1H, J = 9.4 Hz, $H^{1'}$), 5.94 (t, 1H, $H^{2'}$), 5.41 (t, 1H, $H^{3'}$), 5.28 (t, 1H, $H^{4'}$), 4.26 (2dd, 2H, $H^{6'}$), 3.98 (ddd, 1H, $H^{5'}$), 3.8 (s, 3H, OCH_3), 2.08-1.96 (4s, 12H, CH_3CO); ^{13}C NMR δ = 20.38, 20.46, 20.53 ($\underline{C}H_3CO$), 55.20 (OCH_3), 61.46, 67.72, 68.17, 73.89, 74.64, 86.42 ($C^{1'}$, $C^{2'}$, $C^{3'}$, $C^{4'}$, $C^{5'}$, $C^{6'}$), 114.31, 115,20, 129.86, 137.62 (CH of aromatic carbons and CH=CH), 128.56, 147.81, 161.18, 169.19, 169.70, 170.37, 170.82, 176.99, 180.96 (C of aromatic group, C=N, C=O).

Anal. for $C_{26}H_{29}N_3O_{10}S_2$ Calcd.: C, 51.39; H, 4.81. Found: C, 51.70; H, 4.80.

(b) To a solution of **17b** (10 mmol) in water (10 ml) containing KOH (0.6 g, 10 mmol) was added ABG (**2**) (4.1 g, 10 mmol). The reaction mixture was stirred for 20 min. and then kept overnight at room temperature. The precipitate formed after acidification with acetic acid (1 ml) and dilution with cold water was collected, washed with water and dried at room temperature and crystallized from absolute ethanol to yellow crystals of **13b** (5%).

2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-6-β-(4-chlorophenyl)vinyl-1,2,4-triazine-3,5(2*H*,4*H*)-dithione (**13c**)

Using the general procedure (A), **17c** gave **13c** (20%), and using the general procedure (B) **3c** and/or **6c** gave **13c** (48 and 50% respectively); mp. 204°C; ^1H NMR ($CDCl_3$) δ = 8.0-7.0 (m, 7H, NH, CH=CH, ArH's), 6.57 (d, 1H, J = 9.4 Hz, $H^{1'}$), 5.92 (t, 1H, $H^{2'}$), 5.41 (t, 1H, $H^{3'}$), 5.27 (t, 1H, $H^{4'}$), 4.26 (2dd, 2H, $H^{6'}$), 3.98 (ddd, 1H, $H^{5'}$), 2.08-1.97 (4s, 12H, CH_3CO); ^{13}C NMR δ = 20.39, 20.49 ($\underline{C}H_3CO$), 61.46, 67.67, 68.15, 73.81, 74.68, 86.42 ($C^{1'}$, $C^{2'}$, $C^{3'}$, $C^{4'}$, $C^{5'}$, $C^{6'}$), 118.11, 129.16, 129.37, 136.53 (CH of aromatic carbons and CH=CH), 134.16, 135.67, 147.19, 169.29, 169.73, 169.84, 170.39, 170.84, 176.66 (C of aromatic group, C=N, C=O).

Anal. for $C_{25}H_{26}ClN_3O_9S_2$ Calcd.: C, 49.06; H, 4.28. Found: C, 49.10; H, 4.20.

Action of methyl iodide on **13a**

To a solution of **13a** (0.25 g, 1 mmol) in DMF (0.5 ml) was added triethylamine (0.2 ml) and methyl iodide (0.1 ml, 1.5 mmol). The reaction mixture was then stirred at 40-50°C for 5 min. After cooling and dilution with water, the precipitate was collected and crystallized from ethanol to give a mixture of yellow products of **14** and **15** in a ratio of 57: 43 as indicated by ^1H NMR.

4-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-6-β-arylvinyl-3-thioxo-2,3-dihydro-1,2,4-triazin-5(4*H*)-ones (**19a-c**)

General Procedure: To a solution of each of **16a-c** (20 mmol) in water (15 ml) containing KOH (1.15 g, 20 mmol) was added **2** (0.9 g, 0.22 mmol). The reaction mixture was stirred for 20 min.

and then kept overnight at room temperature. The precipitate was then collected, washed with water and recrystallized from ethanol (in case of **19a,c**) or acetone (in case of **19b**) as yellow crystals of **19a-c**. The mother liquor from the crystallization was concentrated to precipitate crystals consisting of a mixture of **19a-c** and **20a-c** (as indicated by ^{1}H NMR).

4-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-6-styryl-3-thioxo-2,3-dihydro-1,2,4-triazin-5(4*H*)-one (**19a**)

From **16a** (20%), mp. 256°C; IR, 3227 (NH), 1752 (C=O acetate), 1712 (C=O amide) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 10.57 (s, 1H, NH), 7.84-7.07 (m, 7H, CH=CH, ArH's), 6.89 (d, 1H, J = 9.2 Hz, $H^{1'}$), 6.09 (t, 1H, $H^{2'}$), 5.41 (t, 1H, $H^{3'}$), 5.28 (t, 1H, $H^{4'}$), 4.25 (2dd, 2H, $H^{6'}$), 3.91 (ddd, 1H, $H^{5'}$), 2.1-1.99 (4s, 12H, CH_3CO); ^{13}C NMR δ = 20.41, 20.59 (CH_3CO), 61.51, 67.69, 68.37, 73.06, 74.68, 85.25 ($C^{1'}$, $C^{2'}$, $C^{3'}$, $C^{4'}$, $C^{5'}$, $C^{6'}$), 117.61, 127.2, 128.95, 129.7, 138.42 (CH of aromatic carbons and CH=CH), 135.89, 145.37, 151.50, 169.74, 170.35, 170.52, 171.08, 174.99 (C of aromatic group, C=N, C=O, C=S).

Anal. for $C_{25}H_{27}N_3O_{10}S$ Calcd.: C, 53.47; H, 4.85, N, 7.48. Found: C, 53.20; H, 4.70; N, 7.50.

4-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-6-β-(4-methoxyphenyl)vinyl-3-thioxo-2,3-dihydro-1,2,4-triazin-5(4*H*)-one (**19b**)

From **16b** (15%), mp. 232°C; IR, 3197 (NH), 1751 (C=O acetate), 1711 (C=O amide) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 10.35 (s, 1H, NH), 7.95, 7.79 (2d, 2H, J = 16.2 Hz, trans CH=CH), 7.52, 6.88 (2d, 4H, ArH's), 6.88 (d, 1H, J = 9.0 Hz, $H^{1'}$), 6.09 (t, 1H, $H^{2'}$), 5.4 (t, 1H, $H^{3'}$), 5.27 (t, 1H, $H^{4'}$), 4.15 (2dd, 2H, $H^{6'}$), 3.89 (ddd, 1H, $H^{5'}$), 3.84 (s, 3H, OCH_3), 2.1-1.99 (4s, 12H, CH_3CO).

Anal. for $C_{26}H_{29}N_3O_{11}S$ Calcd.: C, 52.79; H, 4.94; N, 7.10. Found: C, 53.20; H, 5.00; N, 6.50.

4-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-6-β-(4-chlorophenyl)vinyl-3-thioxo-2,3-dihydro-1,2,4-triazin-5(4*H*)-one (**19c**)

From **16c** (5%), mp. 235°C; IR, 3218 (NH), 1752 (C=O acetate), 1713 (C=O amide) cm^{-1}; ^{1}H NMR ($CDCl_3$ + DMSO-d_6) δ = 13.78 (s, 1H, NH), 7.85, 7.1 (2d, 2H, J=16.4 Hz, trans CH=CH), 7.55-7.37 (2d, 4H, ArH's), 7.04 (d, 1H, J = 9.2 Hz, $H^{1'}$), 6.13 (t, 1H, $H^{2'}$), 5.45 (t, 1H, $H^{3'}$), 5.26 (t, 1H, $H^{4'}$), 4.27 (2dd, 2H, $H^{6'}$), 3.96 (ddd, 1H, $H^{5'}$), 2.12-2.01 (4s, 12H, CH_3CO).

Anal. for $C_{25}H_{26}ClN_3O_{10}S$ Calcd.: C, 50.38; H, 4.40; N, 7.05. Found: C, 50.20; H, 4.50; N, 7.12.

2,4-Bis(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-6-β-arylvinyl-3-thioxo-2,3-dihydro-1,2,4-triazin-5(4*H*)-ones (**20a,c**)

General Procedure: To a solution of each of **16a,c** (5 mmol) in DMF (5 ml), triethylamine (3 ml) and **2** (4.2 g, 10 mmol) were added. The reaction mixture was stirred for 20 min. and then kept overnight at room temperature. The precipitate was then collected, washed with water and recrystallized twice from ethanol as yellow crystals of **20a,c**. The mother liquor from the

crystallization was concentrated to precipitate crystals consisting of a mixture of **19a,c** and **20a,c** (as indicated by ^{1}H NMR).

2,4-Bis(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-6-styryl-3-thioxo-2,3-dihydro-1,2,4-triazin-5(4*H*)-one (**20a**)

(A) Using the general procedure, **16a** gave **20a** (25%), mp. 230°C; IR, 1746 (br) (C=O acetate, C=O amide) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 7.84-7.07 (m, 2H, J = 16.6, trans CH=CH) 7.57-7.37 (m, 5H, ArH's), 7.04 (d, 1H, J = 9.2 Hz, $H^{1'}$ of 4-glucosyl), 6.63 (d, 1H, J = 9.2 Hz, $H^{1'}$ of 2-glucosyl), 6.05 (t, 1H, $H^{2'}$ of 4-glucosyl), 5.84 (t, 1H, $H^{2'}$ of 2-glucosyl), 5.41-5.20 (4t, 4H, $H^{3'}$, $H^{4'}$ of 2 and 4-glucosyls), 4.23-4.15 (4dd, 4H, $H^{6'}$ of 2- and 4-glucosyls), 3.88 (2ddd, 2H, $H^{5'}$ of 2- and 4-glucosyl), 2.08-1.85 (24H, CH_3CO); ^{13}C NMR δ = 20.04, 20.32, 20.45 ($\underline{C}H_3CO$), 61.39, 61.54, 67.57, 67.81, 68.17, 68.30, 72.94, 73.99, 74.56, 74.86, 86.29, 88.32 ($C^{1'}$, $C^{2'}$, $C^{3'}$, $C^{4'}$, $C^{5'}$, $C^{6'}$), 116.4, 127.92, 128.89, 129.81, 135.8 (CH of aromatic carbons and CH=CH), 139.48, 143.9, 150.60, 169.05, 16957, 170.22, 170.30, 170.37, 170.65, 170.80, 176.80, 180.95 (C of aromatic group, C=N, C=O, C=S).

Anal. for $C_{39}H_{45}N_3O_{19}S$ Calcd.: C, 52.52 H, 5.09. Found: C, 52.50; H, 5.10.

(B) Compound **20a** was also prepared from **16a** in 10% yield as described for the synthesis of **19a** but using twice the amount of each KOH and ABG (**2**).

2,4-Bis(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-6-β-(4-chlorophenyl)vinyl-3-thioxo-2,3-dihydro-1,2,4-triazin-5(4*H*)-one (**20c**)

Using the the general procedure **16c** gave **20c** (20%), mp. 235°C; ^{1}H NMR ($CDCl_3$) δ = 7.8, 7.05 (2d, 2H, J = 16.4 Hz, trans CH=CH), 7.55-7.37 (2d, 4H, ArH's), 7.05 (d, 1H, J = 9 Hz, $H^{1'}$ of 4-glucosyl), 6.65 (d, 1H, J = 9.6 Hz, $H^{1'}$ of 2-glucosyl), 6.06 (t, 1H, $H^{2'}$ of 4-glucosyl), 5.86 (t, 1H, $H^{2'}$ of 2-glucosyl), 5.44-5.2 (4t, 4H, $H^{3'}$, $H^{4'}$ of 2 and 4-glucosyls), 4.21 (4dd, 4H, $H^{6'}$ of 2- and 4-glucosyls), 3.88 (2ddd, 2H, $H^{5'}$ of 2- and 4-glucosyl), 2.1-1.94 (24H, CH_3CO).

Anal. for $C_{39}H_{44}ClN_3O_{19}S$ Calcd.: C, 50.57; H, 4.79. Found: C, 51.00; H, 5.00.

3-Methylmercapto-4-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-6-styryl-1,2,4-triazin-5(4*H*)-one (**21a**)

To a solution **19a** (0.3 g, 0.5 mmol) in DMF (0.5 ml) was added anhydrous sodium carbonate (0.3 g, 35 mmol) and methyl iodide (0.1 ml, 1.5 mmol). The reaction mixture was then stirred at 40-50°C for 5 minutes. After cooling and dilution with water, the precipitate was collected and crystallized from ethanol to give yellow crystals composed of a mixture of **21a, 22a** in a ratio of 80:20%, respectively, as indicated by ^{1}H NMR. Pure **21a** was obtained after two crystallization from ethanol as yellow crystals (32%), mp. 196-8°C; ^{1}H NMR ($CDCl_3$) δ = 8.11, 7.09 (2d, 2H, J = 16.4 Hz, trans CH=CH), 7.63-7.36 (m, 5H, ArH's), 7.16 (d, 1H, J = 9.2 Hz, $H^{1'}$), 6.21 (t, 1H,

$H^{2'}$), 5.39 (t, 1H, $H^{3'}$), 5.27 (t, 1H, $H^{4'}$), 4.25 (2dd, 2H, $H^{6'}$), 3.9 (ddd, 1H, $H^{5'}$), 2.76 (s, 3H, SCH_3), 2.1-2.04 (4s, 12H, CH_3CO).

Anal. for $C_{26}H_{29}N_3O_{10}S$ Calcd.: C, 54.25; H, 5.08. Found: C, 54.10; H, 4.90.

3-Methylmercapto-4-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-6-β-(4-methoxyphenyl)vinyl-1,2,4-triazin-5(4*H*)-one (**21b**)

To a solution of **19b** (0.3 g, 0.5 mmol) in DMF (0.5 ml) was added triethylamine (0.2 ml) and methyl iodide (0.1 ml, 1.5 mmol). The reaction mixture was then stirred at 40-50°C for 5 minutes. After cooling and dilution with water, the precipitate was collected and crystallized from ethanol to give a yellow mixture of products of **21b** and **22b** in a ratio of 80:20% as indicated by ^1H NMR. Pure **21b** was obtained after two crystallization from ethanol as yellow crystals (40%), mp. 220°C. ^1H NMR ($CDCl_3$) δ = 7.9, 7.8 (2d, 2H, J= 16 Hz, trans CH=CH), 7.5, 6.9 (2d, 4H, ArH's), 7.17 (d, 1H, J = 9 Hz, $H^{1'}$), 6.2 (t, 1H, $H^{2'}$), 5.4 (t, 1H, $H^{3'}$), 5.28 (t, 1H, $H^{4'}$), 4.26 (2dd, 2H, $H^{6'}$), 4.0 (ddd, 1H, $H^{5'}$), 3.83 (s, 3H, OCH_3), 2.76 (s, 3H, SCH_3), 2.1-2.02 (4s, 12H, CH_3CO).

Anal. for $C_{27}H_{31}N_3O_{11}S$ Calcd.: C, 53.55; H, 5.16. Found: C, 53.70; H, 5.30.

Action of methanolic ammonia on **3a, 6a-c, 7a, 8a,c, 13b, 19b.**

General Procedure: A saturated methanolic ammonia solution (40 ml) (prepared by bubbling dry ammonia gas in absolute ammonia gas at 0°C) was added to each of **3a, 6a-c, 7a, 8a,c, 13b, 19b** (1 mmol). The reaction mixture was then left overnight at room temperature in a stoppered flask (after which time all materials went into solution). The solvent was then removed on rotavap at room temperature. The product was then crystallized from the proper solvent.

4-Amino-2-β-D-glucopyranosyl-6-styryl-3-thioxo-2,3-dihydro-1,2,4-triazin-5(4*H*)-one (**23**)

From **3a** (from water, 29%), mp. 118°C; ^1H NMR (DMSO-d_6) δ = 7.97, 7.2 (2d, 2H, J = 16.4 Hz, trans CH=CH), 7.75-7.4 (m, 5H, ArH's), 6.79 (s, 2H, NH_2, exchangeable), 6.42 (d, 1H, *J* = 9 Hz, $H^{1'}$), 5.4-4.0 (m, 5H, 5OH, exchangeable), 3.94 (t, 1H, $H^{2'}$), 3.69 (t, 1H, $H^{3'}$), 3.5-3.17 (m, $H^{4'}$, $H^{5'}$, $H^{6'}$).

Anal. for $C_{17}H_{20}N_4O_6S.H_2O$ Calcd.: C, 47.88; H, 5.20. Found: C, 48.20; H, 4.90.

2-β-D-Glucopyranosyl-6-styryl-3-thioxo-2,3-dihydro-1,2,4-triazin-5(4*H*)-one (**24a**)

From **6a** (67%), mp. 257°C; IR: 3500-3200 (OH, NH), 1692 (C=O amide) cm^{-1}; ^1H NMR (DMSO-d_6) δ = 13.5 (s, 1H, NH), 7.92, 7.12 (2d, 2H, J = 16.6 Hz, trans CH=CH), 7.68-7.14 (m, 5H, ArH's), 6.38 (d, 1H, J = 8.8 Hz, $H^{1'}$), 5.2-4.64 (4d, 4H, 4OH, exchangeable), 4-3 (m, 6H, $H^{2'}$, $H^{3'}$, $H^{4'}$, $H^{5'}$, $H^{6'}$).

Anal. for $C_{17}H_{19}N_3O_6S$ Calcd.: C, 51.90; H, 4.80. Found: C, 51.90; H, 5.10.

2-β-D-Glucopyranosyl-6-β-(4-methoxyphenyl)vinyl-3-thioxo-2,3-dihydro-1,2,4-triazin-5(4*H*)-one (**24b**)

From **6b** (54%), mp. 245°C; IR: 3500-3200 (OH, NH), 1691 (C=O amide) cm^{-1}; ^1H NMR (DMSO-d_6) δ = 13.5 (br, 1H, NH), 7.88, 6.97 (2d, 2H, J = 16 Hz, trans CH=CH), 7.6-6.97 (2d, 4H, ArH's), 6.65 (d, 1H, J = 10 Hz, $H^{1'}$), 5.17-4.61 (4brs, 4H, 4OH, exchangeable), 3.81 (s,3H, OCH_3), 4-3 (m, 6H, $H^{2'}$, $H^{3'}$, $H^{4'}$, $H^{5'}$, $H^{6'}$).

Anal. for $C_{18}H_{21}N_3O_7S.H_2O$ Calcd.: C, 48.98; H, 5.25. Found: C, 48.60; H, 4.80.

2-β-D-Glucopyranosyl-6-β-(4-chlorophenyl)vinyl-3-thioxo-2,3-dihydro-1,2,4-triazin-5(4*H*)-one (**24c**)

From **6c** (67%), mp. 262°C; IR: 3500-3200 (OH, NH), 1696 (C=O amide) cm^{-1}; ^1H NMR (DMSO-d_6) δ = 13.53 (br, 1H, NH), 7.91, 7.14 (2d, 2H, J = 16.4 Hz, trans CH=CH), 7.45-7.78 (2d, 4H, ArH's), 6.37 (d, 1H, J = 9 Hz, $H^{1'}$), 5.2-4.62 (4d, 4H, 4OH, exchangeable), 4-3 (m, 6H, $H^{2'}$, $H^{3'}$, $H^{4'}$, $H^{5'}$, $H^{6'}$).

Anal. for $C_{17}H_{18}ClN_3O_6S$ Calcd.: C, 47.72; H, 4.24; N, 9.82. Found: C, 47.62; H, 4.34; N, 9.80.

3-Benzylidenehydrazono-2-β-D-glucopyranosyl-6-styryl-1,2,4-triazin-5(2*H*)-one (**26**)

From **7a** (from water, 54%) , mp. 270°C; IR: 3500-3200 (OH, NH), 1715 (C=O amide) cm^{-1}; ^1H NMR (DMSO-d_6) δ = 11.79 (s, 1H, NH, exchangeable), 8.4 (s, 1H, CH=N), 7.77, 7.1 (2d, 2H, J = 16.6 Hz, trans CH=CH), 8.08-7.4 (m, 10H, ArH's), 5.81 (d, 1H, J = 8.4 Hz, $H^{1'}$), 5.28-4.67 (3d, t, 4H, 4OH, exchangeable), 3.91-3.18 (m, 6H, $H^{2'}$, $H^{3'}$, $H^{4'}$, $H^{5'}$, $H^{6'}$); Ms: m/z 479 (M^+, 20%).

Anal. for $C_{24}H_{25}N_5O_6$ Calcd.: C, 60.12; H, 5.26; N, 14.61. Found: C, 59.70; H, 5.40; N, 14.50.

3-Amino-2-β-D-glucopyranosyl-6-styryl-1,2,4-triazin-5(2*H*)-one (**27a**)

From **8a** (from water, 50%) , mp. 262°C; IR: 3500-3200 (OH, NH_2), 1661 (C=O amide) cm^{-1}; ^1H NMR (DMSO-d_6) δ = 7.95, 7.07 (2d, 2H, J = 16.4 Hz, trans CH=CH), 7.46 (s, 2H, NH_2, exchangeable), 7.64-7.34 (m, 5H, ArH's), 5.37 (d, 1H, J = 8.8 Hz, $H^{1'}$), 5.21-4.65 (3d, t, 4H, 4OH, exchangeable), 3.97-3.19 (m, 6H, $H^{2'}$, $H^{3'}$, $H^{4'}$, $H^{5'}$, $H^{6'}$); Ms: m/z 376 (M^+, 2%).

Anal. for $C_{17}H_{20}N_4O_6.H_2O$ Calcd.: C, 51.77; H, 5.62. Found: C, 51.70; H, 5.50.

3-Amino-2-β-D-glucopyranosyl-6-β-(4-chlorophenyl)vinyl-1,2,4-triazin-5(2*H*)-one (**27c**)

From **8c** (from water, 50%), mp. 250°C; IR: 3500-3200 (OH, NH_2), 1715 (C=O amide) cm^{-1}; ^1H NMR (DMSO-d_6) δ = 7.95, 7.07 (2d, 2H, J = 16.6 Hz, trans CH=CH), 7.7, 7.4 (2d, 4H, ArH's), 6.8_(s, 2H, NH_2), 5.2 (d, 1H, J = 8.6 Hz, $H^{1'}$), 5.4-4.65 (m, 4H, 4OH), 4.01-3.2 (m, 6H, $H^{2'}$, $H^{3'}$, $H^{4'}$, $H^{5'}$, $H^{6'}$).

Anal. for $C_{17}H_{19}ClN_4O_6.H_2O$ Calcd.: C, 47.62; H, 4.94. Found: C, 47.50; H, 4.80.

2-β-D-Glucopyranosyl-5(4*H*)-imino-6-β-(4-methoxyphenyl)vinyl-1,2,4-triazin-3(2*H*)-thione (**28**)

From **13b** (from water, 60%), mp. 194°C; IR: 3500-3200 (OH, NH) cm^{-1}; ^1H NMR (DMSO-d_6) δ = 8.7, 8.25 (2s, 2H, 2NH, exchangeable), 7.48, 7.18 (2d, 2H, J = 15.6 Hz, trans CH=CH), 7.68, 7.02 (2d, 4H, ArH's), 6.63 (d, 1H, J = 9.2 Hz, $H^{1'}$), 5.16-4.58 (3d, t, 4H, 4OH, exchangeable), 3.91-3.2 (m, 6H, $H^{2'}$, $H^{3'}$, $H^{4'}$, $H^{5'}$, $H^{6'}$).

Anal. for $C_{18}H_{22}N_4O_6S.2H_2O$ Calcd.: C, 47.16; H, 5.72; N, 12.22. Found: C, 46.91; H, 5.64; N, 11.90.

Action of methanolic ammonia on **19b**:

This gave **16b** (97%) mp. 276°C (identical with authentic sample),[23-26] ^1H NMR (DMSO-d_6) δ = 13.58, 13.20 (2s, 2H, 2NH), 7.76, 6.95 (2d, 2H, J = 16.4 Hz, trans CH=CH), 7.61, 6.98 (2d, 4H, ArH's), 3.82 (s, 3H, OCH_3).

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