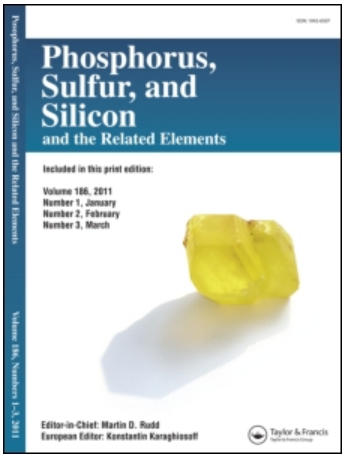

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The Synthesis of Some New Quinazolone Derivatives of Potential Biological Activity

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The Synthesis of Some New Quinazolone Derivatives of Potential Biological Activity

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*The refluxing of 3-amino-6,8-dibromo-2-thioxo-2,3-dihydro-1H-quinazolin-4-one (**5**) with ethyl chloroformate and/or ethyl chloroacetate afforded compounds **6** and **7**. The reaction of **5** with ethyl bromobutyrate, chloroacetyl chloride, phenacyl chloride, and phenyl isocyanate yielded compounds **8**, **9**, **11**, and **12**. The coupling of 5 with (2,3,4,6-tetra-O-acetyl-α-D-gluopyranosyl)bromide(**ABG**) in DMF at r.t. gave 3-amino-6,8-dibromo-2-(2′,3′,4′,6′-tetra-O-acetyl-β-D-glucopyranosyl)thioxo-2,3-dihydro-1H-quinazolin-4-one (**14**). The deblocking of **14** in sodium methoxide gave **5**. 3-Amino-6,8-dibromo-2-methylthio-3H-quinazolin-4-one (**16**) was prepared by stirring **5** with methyl iodide in methanol. The treatment of **16** with hydrazine hydrate afforded **4**. The condensation of **4** with aldehydes furnished 3,5-dibromo-2-arylaminobenzoic acid hydrazide (**18a–c**). The refluxing of **18a** with acetic anhydride gave 3-(benzylideneamino)-6,8-dibromo-2-methyl-3H-quinazolin-4-one (**19**). Hydrazones **20a–f** were prepared by the condensation of **4** with pentoses and/or hexoses. The acetylation of (**20a–f**) with acetic anhydride gave the acetyl derivatives **21a–f**.*

Keywords Aldopentoses and hexoses; aminoquinazolenes; HIV; hydrazides; microbial activity

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INTRODUCTION

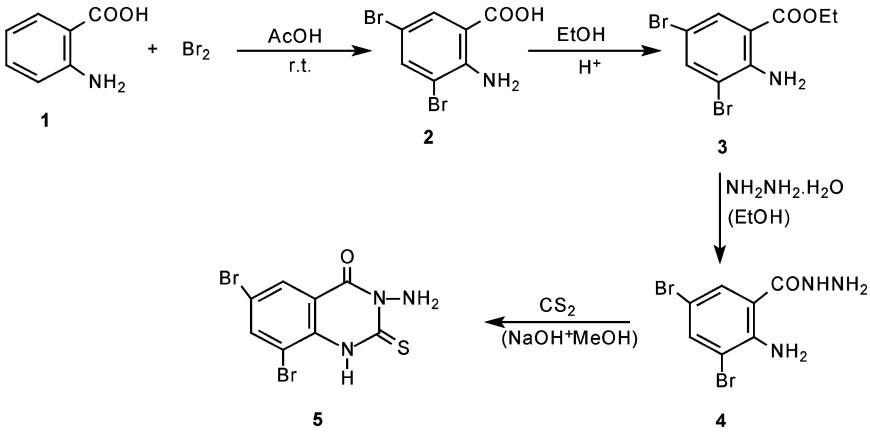
3*H*-quinazolin-4-one and their derivatives have been reported to possess significant activity as antihypertensive,[1] antifibrillatory, choleretic, antiphlogistic,[2] antimitotic anticancer,[3] antifungal,[4,5] and anticonvulsant agents.[6] Quinazolinones were reported to possess diverse pharmacological activities such as a CNS depressant,[7] hypnotic, antiinflamatory,[8] antitumor,[9] muscle relaxants,[10] and antineoplastic activity.[11] These results prompted us to continue our earlier work of synthesizing some other new derivatives for evaluating their biological antimicrobial activity as anti–HIV, anti–HBV, and schistosomiasis.

RESULTS AND DISCUSSION

The bromination of 2-aminobenzoic acid (**1**) with bromine in glacial acetic acid at r.t. gave 2-amino-3,5-dibromobenzoic acid (**2**), which was esterified by refluxing in a mixture of ethanol and sulfuric acid to afford **3**,[12] which, on treatment with hydrazine hydrate in ethanol, furnished 2-amino-3,5-dibromo benzoic acid hydrazide (**4**).[13] The cyclization of **4** with carbon disulfide in boiling ethanol afforded the new compound 3-amino-6,8-dibromo-2-thioxo-2,3-dihydro-1*H*-quinazolin-4-one (**5**) (**Scheme 1**). A similar structure of **5** was prepared through the reaction of isatoic anhydride with thioamide to afford 2-substituted-4(3H) quinazolinones.[14]

The IR spectrum of **5** showed the existence of NH at 2814 cm^{-1}. Its ^1H NMR spectrum showed the presence of a singlet at 6.55 ppm (2H, NH_2) and a broad signal at 14.61 ppm (1H, NH). Its ^{13}C NMR spectrum showed the existence of C=N at 158.84 ppm and C=O at 176.08 ppm. The mass spectrum of **5** containing bromine atoms showed fragments corresponding to the typical bromine isotope ^{79}Br and ^{81}Br patterns. Thus, the mass spectrum showed its M^{+1} and M^{+2} peaks at *m/z* 351 (93%, $C_8H_5Br_2N_3OS$) and 278 (100%, $C_7H_4Br_2NO$), respectively (Scheme 1).

The fusion of **5** with either ethyl chloroformate or ethyl chloroacetate yielded thiocarbonic acid S-(3-amino-6,8-dibromo-4-oxo-3,4-dihydroquinazolin-2-yl)ester-*O*-ethyl ester (**6**) and/or (3-amino-6,8-dibromo-4-oxo-3,4-dihydroquinazolin-2-ylsulfanyl)acetic acid ethyl ester (**7**), respectively. The reaction of **5** with ethyl 2-bromobutyrate in sodium ethoxide at r.t. afforded 2-(3-amino-6,8-dibromo-3,4-dihydroquinazolin-2-ylsulfanyl)butyric acid ethyl ester (**8**). The structures of **6–8** were suggested by different spectroscopic data (IR,^1H, ^{13}C NMR, and MS). Their IR spectra showed the existence of the C=O (ester) in the range 1735–1765 cm^{-1}. Their ^1H NMR spectra showed



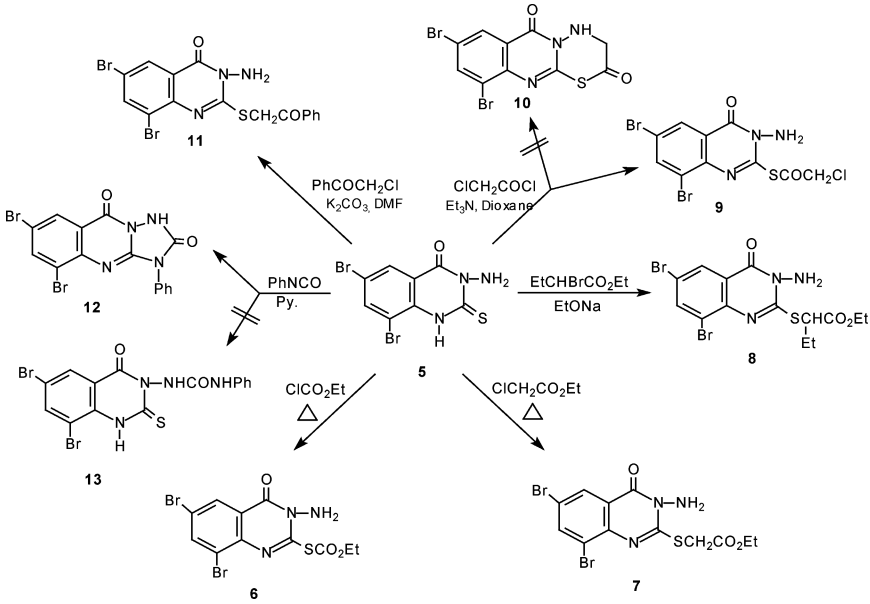
SCHEME 1

the appearance of a triplet (3H, CH_3) in the range of 1.20–1.54, and a quartet (2H, CH_2) in the range 4.14–4.65 ppm. The ^{13}C NMR spectra of compounds **6–8** showed the existence of the C=O (ester) in the range of 145.54–163.66 ppm. The mass spectrum of **7** showed *m/z* 435 (M^+, 71 %).

The stirring of **5** with chloroacetyl chloride in dioxane at 25°C or at boiling temperature in the presence of triethylamine yielded 3-amino-6,8-dibromo-4-oxo-3,4-dihydroquinazolin-2-ylsulfanyl)acetyl chloride (**9**) and not the desired cyclic compound 6,8-dibromo-3,4-dihydro-1-thia-4,4a,9-triazaanthracene-2,10-dione (**10**). The IR pectrum of **9** showed the ($COCH_2Cl$) at 1718 cm^{-1}. Its ^1H NMR spectrum showed a singlet at 4.27 ppm (2H, CH_2) and a singlet at 6.89 ppm (2H, NH_2). Its ^{13}C NMR spectrum showed the existence of a (CH_2) signal at 34.14 ppm; ($C_{arom.}$) signals at 105.78, 106.65, 109.91, 128.99, 136.96, and 143.18 ppm; a (C=N) signal at 162.55 ppm; a (cyclic, C=O) at 163.36 ppm; and a ($COCH_2Cl$) at 168.89 ppm. The stirring of **5** with phenacyl chloride at 25°C in anhydrous DMF and anhydrous potassium carbonate afforded 3-amino-6,8-dibromo-2-(2-oxo-2-phenylethylsulfanyl)-3*H*-quinazol-in-4-one (**11**). The IR spectrum of **11** showed (COPh) at 1728 cm^{-1}. Its ^1H NMR spectrum showed a singlet at 5.35 ppm (2H, CH_2CO), a broad singlet at 6.62 (2H, NH_2), and a multiplet at 7.65-7.82 ppm (5H, C_6H_5). The ^{13}C NMR spectrum of **11** showed the CH_2 signal at 40.39 ppm, (C=N) at 162.57 ppm, (C=O, cyclic) at 163.36 ppm, and (COPh) at 192.65 ppm.

The treatment of **5** with phenyl isocyanate in anhydrous pyridine either at r.t. or by reflux yielded 5,7-dibromo-3-phenyl-3*H*-[1,2,4]triazolo[5,1-b]quinazoline-2,9-dione (**12**) as the sole product (TLC) and not the open structure (**13**). The IR spectrum of **12** showed

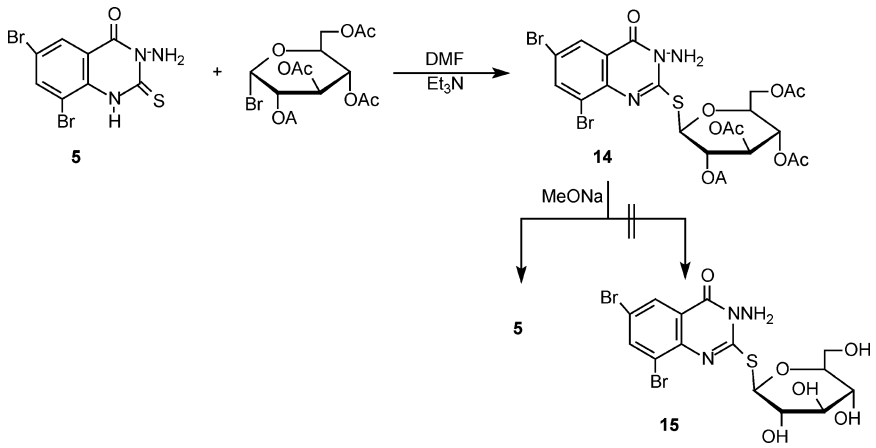
the C=O at 1598 cm^{-1} and (C=O, cyclic) at 1645 cm^{-1}. Its ^1H NMR spectrum showed a multiplet at 6.43–7.04 ppm (5H, H_{arom}), and a singlet (1H, NH) at 11.02 ppm. Its ^{13}C NMR spectrum showed a C=N at 163.72 ppm and a C=ONH at 171.23 ppm (Scheme 2).



SCHEME 2

The coupling of **5** with (2,3,4,6-tetra-*O*-acetyl-α-*D*-glucopyranosyl)bromide (**ABG**) in DMF at r.t. yielded 3-amino-6,8-dibromo-2(2',3',4',6'-tetra-*O*-acetyl-β-*D*-glucopyranosyl)thioxo-2,3-dihydro-1*H*-quinazolin-4-one (**14**). Its IR spectrum showed a sharp band at 1748 cm^{-1} (C—O, acetyl). The ^1H NMR spectrum showed the presence of 4 characteristic signals due to four acetyl groups CH_3CO (s) of the sugar moiety in the range 1.95–2.12 ppm and the anomeric proton in the range 4.95–5.96 ppm. Its ^{13}C NMR spectrum showed 4 signals (4 CH_3) in the range 20.14–20.23 and 4 signals (4 C=O, acetyl) in the range 169.21–169.73 ppm. The mass spectrum of compound **14** showed *m/z* 681 (M^+, $C_{22}H_{23}Br_2N_3O_{10}S$, 75%).

The deblocking of **14** using sodium methoxide at r.t. yielded the starting aglycone[15] and not the desired deblocked compound 6,8-dibromo-2-(3,4,5-trihydroxy-6-hydroxymethyl-tetrahydropyran-2-ylsulfanyl)-3*H*-quinazolin-4-one (**15**) (Scheme 3). 3-amino-6,8-dibromo-2-methylthio-3*H*-quinazolin-4-one (**16**) can be synthesized by stirring **5** with methyl iodide in methanol at 25°C. The IR spectrum of **16** showed

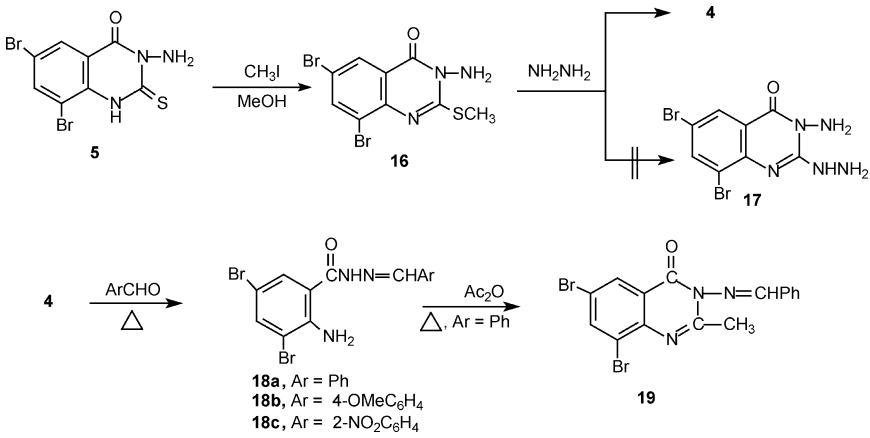


SCHEME 3

the $NH_{2\,sym}$ at 3338 cm^{-1} and 3453 cm^{-1} due to ($NH_{2\,antisym}$). Its ^1H NMR spectrum showed the appearance of s, 3H, and CH_3 at 2.80 ppm and s, 2H, and NH_2 at 6.89 ppm. Its ^{13}C NMR spectrum showed CH_3 at 14.19 ppm. The mass spectrum of **16** showed *m/z* at 365 (M^+, 98 %). The refluxing of **16** with hydrazine hydrate in ethanol furnished 2-amino-3,5-dibromobenzoic acid hydrazide (**4**) instead of the expected 3-amino-6,8-dibromo-2-hydrazino-3H-quinazolin-4-one (**17**).

The boiling **4** with some aromatic aldehydes, namely benzaldehyde, 4-methoxybenzaldehyde, and 2-nitrobenzaldehyde in ethanol, afforded the corresponding Schiff bases 3,5-dibromo-2-arylamino benzoic acid hydrazide (**18a–c**) (Scheme 4). IR spectra of compounds **18a–c** showed C=N bands in the range 2849–2928 cm^{-1}, NH in the range 3185–3250 cm^{-1}, and NH_2 in the range 3339–3362 cm^{-1}. ^1H NMR spectra showed a signal (1H, CH) in the range 8.12–8.40 ppm. ^{13}C NMR spectra showed C=N signals at 152.13–156.61 ppm. The refluxing of **18a** with acetic anhydride gave 3-(benzylideneamino)-6,8-dibromo-2-methyl-3*H*-quinazolin-4-one (**19**). For the formation of **19**, it is supposed that the acetylation of the NH_2 group of **18a** took place followed by an internal nucleophilic attack and the elimination of H_2O. Its ^1H NMR spectrum showed a CH_3 as a singlet (3H) at 2.45 ppm. Its ^{13}C NMR spectrum showed a CH_3 signal at 20.77 ppm.

The sugar hydrazones **20a–f** were prepared by the refluxing of **4** with an equimolar amounts of L-arabinose, D-ribose, D-xylose, D-glucose, D-galactose, and D-mannose in an aqueous ethanolic solution in the presence of a catalytic amount of acetic acid. IR spectra of **20a–f** showed NH band in the range 3188–3210 cm^{-1} and a broad band of OH in the



SCHEME 4

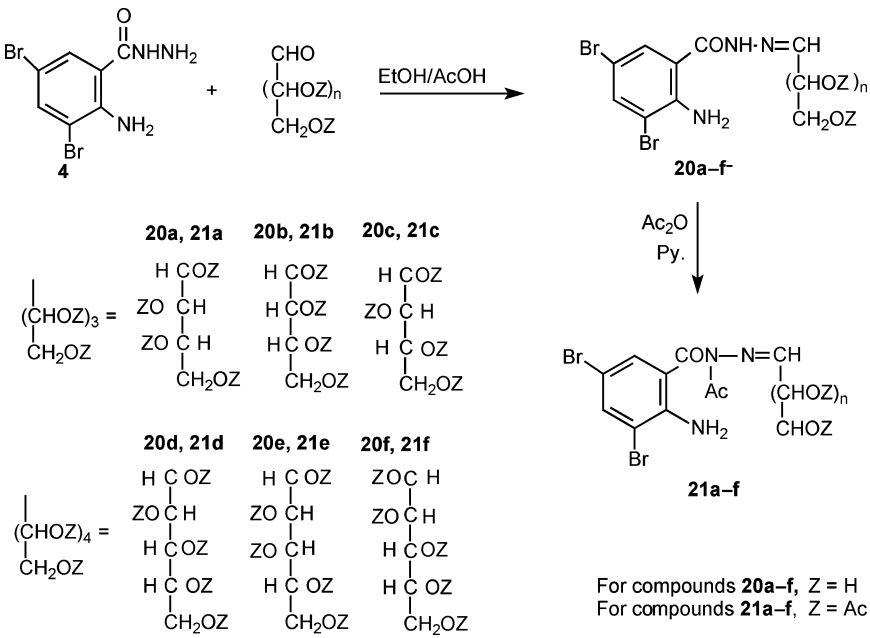
range 3421–3476 cm^{-1}. ^1H NMR spectra of these hydrazones showed signals (1H, CH=N) in the range 7.10–7.79 ppm. The structures of compounds **20a–f** were also confirmed by the ^{13}C NMR data. For example, the ^{13}C NMR spectrum of **20e** was characterized by the presence of signals at 63.02, 66.02, 68.17, 68.90, and 69.68 ppm (C-6′, C-5′, C-4′, C-3′, and C-2′) of the galactose moiety and CH=N at 154.86 ppm.

The acetylation of the aldehydo sugar hydrazones (**20a–f**) with acetic anhydride in pyridine at r.t. gave the corresponding per-*O*-acetylaldehydosugar[1-acetyl-1-(N-acetylamino-2-amino-3,5-dibromobenzoyl]hydrazones (**21a–f**) (Scheme 5). IR spectra of **21a–f** showed C=N at 1615–1618 cm^{-1}, a N–C=O (acetyl) at 1695–1699 cm^{-1}, and an O-acetyl at 1751–1756 cm^{-1}. The structures of compounds **21a–f** were further confirmed by ^1H NMR and ^{13}C NMR data (see the experimental section).

BIOLOGICAL ACTIVITY

All compounds were tested against HIV-1. The test was performed in MT4 cell cultures infected with wild type HIV-1 (strain IIIB) using the assay as previously described.[16] The compounds were inactive at 100 uM or inactive at subtoxic concentrations. None of the tested compounds showed any significant antiviral activity at 100 μM against HIV-1.

In addition, the new products were tested as Accaros: Spider mite (*Tetranychus-urticae*), (Koch), fungicides (*Rhizoctonia solani*, *Fusarium oxysporium*, *Fusarium solani*, *Verticillium dahliae*, and *Verticillium*



SCHEME 5

sulphurellium), and bactericides (*Psedomonas solani- serum*, *Erwinia carotovora*, and *Ralstonia salanceanum*) at a concentration of 10–100 ppm. None of them showed any activity.

EXPERIMENTAL

All melting points were uncorrected and performed in an open capillary melting point apparatus. Microanalyses were performed by Microanalysis Unit, Faculty of Science, Cairo University, Egypt and Microanalysis Unit, Central Laboratory, Tanta University, Egypt. IR spectra were recorded with a Perkin-Elmer 1720 spectrometer. NMR spectra were recorded on a Bruker AC 250 FT NMR spectrometer at 250 MHz for ^{1}H and 62.9 MHz for ^{13}C, on a Varian UNITY 500 NMR spectrometer at 500 MHz for ^{1}H or 125.7 MHz for ^{13}C, and on a Bruker 200 MHz and Bruker 90 MHz spectrometer using TMS as an internal standard DMSO as a solvent. Chemical shifts (δ) are reported in parts per million (ppm), and signals are expressed as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) or br (broad). Mass spectra were recorded using electron ionization on a Varian Mat 311A spectrometer and using fast atom bombardment on a kratos MS 50 spectrometer. Silica gel

(0.040–0.063 mm) was used for the column chromatography and was purchased from Merck.

The Synthesis of 3-Amino-6,8-dibromo-2-thioxo-2,3-dihydro-1*H*-quinazolin-4-one (5)

A mixture of compound **4** (10 g, 0.03 mol),[13] sodium hydroxide (1.2 g, 0.03 mol), and carbon disulphide (0.7 mL, 0.03 mol) in ethanol (120 mL) was refluxed for 15 h (TLC). The solvent was distilled off under reduced pressure, and water was added to the residue (50 mL). The precipitate was filtered off, washed with cold water (100 mL), and neutralized with dil. HCl (1:1). The formed precipitate was filtered off, washed with water (100 mL), and recrystallized from ethanol to afford compound **5**. Yield 5 g (51%); m.p. 260–262°C; **IR** (KBr) $\upsilon = 1610$ (C—O), 3263 (NH_2, sym.), 3317 (NH_2, antisym.) cm^{-1}; ^1H NMR (DMSO-d_6) $\delta = 6.55$ (s, 2H, NH_2), 7.68 (s, 1H, H-7), 7.70 (s, 1H, H-5), 14.52 (s, 1H, NH); ^{13}C NMR (DMSO-d_6) $\delta = 105.87$, 106.38, 110.01, 128.73, 137.08, 142.82 (C_{arom}.), 158.54 (C=O), 176.08 (CS) ppm; **MS** (EI) $m/z = 349$ (M^+, $C_8H_5Br_2N_3OS$, 45%), (^{79}Br, ^{79}Br)], 350 [12%, (^{79}Br, ^{80}Br; ^{80}Br, ^{79}Br)], 351 [92%, $M^+C_{12}H_{11}Br_2N_3O_3S$ (^{80}Br, ^{80}Br; ^{79}Br, ^{81}Br; ^{81}Br, ^{79}Br)], 352 [13%,(^{80}Br, ^{81}Br; ^{81}Br, ^{80}Br)], 353 [46%, (^{81}Br, ^{81}Br)]. 278 (M^+ beak 100%). Anal. calcd. for $C_8H_5Br_2N_3OS$: C, 27.37; H, 1.44; N, 11.97. Found: C, 27.09; H, 1.23; N, 12.00.

The Reaction of Compound 5 with Ethyl Chloroformate and/or Ethyl Chloroacetate

Compound **5** (1 g, 0.02 mol) was fused in ethyl chloroformate and/or ethyl chloroacetate for 4 h (TLC). The excess of the reagent was evaporated to dryness under vaccum. The solid residue was crystallized from petroleum ether (80–100°C) to give compounds **6** and **7**, respectively.

Thiocarbonic Acid S-(3-amino-6,8-dibromo-4-oxo-3,4-dihydroquinazolin-2-yl) Ester O-ethyl Ester (6)

Yield 1 g (87%); m.p. 190–192°C; **IR** (KBr) $\upsilon = 1626$ (cyclic, C=O), 1765 (COO), 2987 (CH), 3356 (NH_2, sym), 3459 (NH_2, antisym) cm^{-1}; ^1H NMR (DMSO-d_6) $\delta = 1.54$ (t, 3H, CH_3), 4.65 (q, 2H, CH_2), 6.11 (s, 2H, NH_2), 7.75 (s, 1H, H-7), 7.87 (s, 1H, H-5); ^{13}C NMR ($CDCl_3$) $\delta = 14.11$ (CH_3), 65.68 (CH_2), 129.88 (C=N), 138.83 (cyclic, C=O), 143.07 (COO), 162.21 (NCN) ppm. Anal. calcd. for $C_{11}H_9Br_2N_3O_3S$: C, 31.23; H, 2.14; N, 9.93. Found: C, 31.30; H, 2.04; N, 9.89.

(3-Amino-6,8-dibromo-4-oxo-3,4-dihydroquinazolin-2-ylsulfanyl)acetic Acid Ethyl Ester (7)

Yield 1.2 g (89%); m.p. 120–122°C; **IR** (KBr) $\upsilon = 1615$ (C=O), 1730 (COO), 2924 (CH), 3329 (NH_2, sym), 3452 (NH_2, antisym) cm^{-1}; ^1H NMR (DMSO-d_6) $\delta = 1.20$ (t, 3H, CH_3), 4.21 (q, 2H, CH_2), 4.36 (s, 2H, SCH_2), 6.86 (s, 2H, NH_2), 7.80 (s, 1H, H-7), 7.84 (s, 1H, H-5); ^{13}C NMR (DMSO-d_6) $\delta = 13.91$ (CH_3), 33.70 (CH_2CH_3), 61.55 (SCH_2), 105.74, 106.56, 109.91, 128.95, 136.96, 143.17 ($C_{arom.}$), 162.21 (C=N), 163.42 (C=O), 167.66 (COO) ppm; **MS** (EI) $m/z = 435$ [$M^+C_{12}H_{11}Br_2N_3O_3S$, 71%, ($^{79}Br$, ^{79}Br)], 436 [14%, (^{79}Br, ^{80}Br; ^{80}Br, ^{79}Br)], 437 [100%, (^{80}Br, ^{80}Br; ^{79}Br, ^{81}Br; ^{81}Br, ^{79}Br)], 438 [23%, (^{80}Br, ^{81}Br; ^{81}Br, ^{80}Br)], 439 [70%, (^{81}Br, ^{81}Br)]. Anal. calcd. for $C_{12}H_{11}Br_2N_3O_3S$: C, 32.97; H, 2.54; N, 9.61. Found: C, 32.92; H, 2.34; N, 9.70.

2-(3-Amino-6,8-dibromo-3,4-dihydroquinazolin-2-ylsulfanyl)-butyric Acid Ethyl Ester (8)

Compound **5** (1.5 g, 0.004 mol) was dissolved in sodium ethoxide (0.2 g of Na in 20 mL of absolute ethanol), and ethyl 2-bromobutyrate (2 mL) was added. The reaction mixture was stirred at r.t. for 10 h (TLC). The solid product was filtered off, washed with dis. water (50 mL), recrystallized from methanol, filtered, and dried to afford 8. Yield 1.1 g (93%); m.p. 120–122°C; **IR** (KBr) $\upsilon = 1617$ (C=O), 1742 (COO), 2937 (CH), 3359 (NH_2, sym), 3430 (NH_2, antisym) cm^{-1}; ^1H NMR (DMSO-d_6) $\delta = 1.26$ (t, 3H, CH_3CH_2CH), 1.332 (t, 3H, CH_3CH_2O), 4.16 (m, 2H, CH_2CH), 4.27 (q, 2H, OCH_2CH_3), 6.319 (s, 2H, NH_2), 7.69 (s, 1H, H-7), 7.72 (s, 1H, H-5); ^{13}C NMR (DMSO-d_6) $\delta = 13.90$ (CH_3CH_2CH), 14.76 (CH_3CH_2O), 64.16 (CH_2CH), 84.92 (CH_3CH_2O), 105 (CH), 109.77, 118.55, 129.93, 135.75 and 144.82 (C_{arom}) ppm; **MS** (EI) $m/z = 466$ (M^{+1} $C_{14}H_{15}Br_2N_3O_3S$, 5%), 278 ($C_7H_4Br_2NO$, 100%); Anal. calcd. for $C_{14}H_{15}Br_2N_3O_3S$: C, 36.15; H, 11.25; N, 9.03. Found: C, 36.01; H, 11.37; N, 8.89.

3-Amino-6,8-dibromo-4-oxo-3,4-dihydroquinazolin-2-ylsulfanyl)acetyl Chloride (9)

To a solution of compound **5** (1.5 g, 0.004 mol) in dioxane (15 mL) was added chloroacetyl chloride (0.3 mL, 0.004 mol), followed by the addition of few drops of triethylamine. The reaction mixture was stirred at 5°C for 5 h (TLC). The solid product that formed was filtered off, recrystallized from petroleum ether (80–100°C), and dried to give **9**. Yield 1.6 g (94%); m.p. 170–172°C; **IR** (KBr) $\upsilon = 1614$ (cyclic, C=O), 1718 (COCl), 2924 (CH), 3464 (NH_2) cm^{-1}; ^1H NMR (DMSO-d_6) $\delta = 4.27$ (s,

2H, CH_2), 6.89 (s, 2H, NH_2), 7.84 (s, 1H, H-7), 7.87 (s, 1H, H-5); ^{13}C NMR (DMSO-d_6) $\delta = 34.14$ (CH_2), 105.78, 106.65, 109.91, 128.99, 136.96, 143.18 (C_{arom}), 162.55 (C=N), 163.36 (cyclic, C=O), 168.89 (COCl) ppm. Anal. calcd. for $C_{10}H_6Br_2ClN_3O_2S$: C, 28.10; H, 1.41; N, 9.83. Found: C, 28.50; H, 1.60; N, 9.68.

3-Amino-6,8-dibromo-2-(2-oxo-2-phenylethylsulfanyl)-3*H*-quinazolin-4-one (11)

To a solution of compound **5** (2.3 g, 0.006 mol) in anhydrous dimethylformamide (15 mL) was added anhydrous potassium carbonate (0.8 g, 0.006 mol) followed by the addition of phenacyl chloride (0.9 g, 0.006 mol). The reaction mixture was stirred at r.t. for 8 h (TLC). The solid product that formed was filtered off and recrystallized from methanol to afford **11**. Yield 1.8 g (64%); m.p. 200–202°C; **IR** (KBr) $\upsilon = 1613$ (cyclic, C=O), 1728 (C=O C_6H_5), 3338 (NH_2, sym), 3460 (NH_2, antisym) cm^{-1}; ^{1}H NMR (DMSO-d_6) $\delta =$ 5.35 (s, 2H, CH_2CO), 6.62 (s, 2H, NH_2), 7.65–7.82 (m, 5H, C_6H_5), 8.12 (s, 1H, H-7), 8.14 (s, 1H, H-5); ^{13}C NMR (DMSO-d_6) $\delta = 40.39$ (CH_2), 105.75, 106.61, 109.89, 128.38, 128.83, 128.96,133.96, 134.92, 136.94 and 143.16 ($C_{arom.}$), 162.57 (C=N), 163.36 (cyclic, C=O), 192.65 (COC_6H_5) ppm. Anal. calcd. for $C_6H_{11}Br_2N_3O_2S$: C, 40.96; H, 2.36; N, 8.96. Found: C, 40.90; H, 2.46; N, 8.77.

5,7-Dibromo-3-phenyl-3*H*-[1,2,4]triazolo[5,1-*b*]quinazoline-2,9-dione (12)

To a solution of compound **5** (1g, 0.003 mol) in anhydrous pyridine (25 mL) was added phenyl isocyanate (0.3 mL, 0.003 mol). The reaction mixture was refluxed for 6 h (TLC). The solvent was evaporated to dryness under vacuum, and the residual solid was crystallized from methanol and dried to give **12**. Yield 1.8 g (64%); m.p. 200–202°C; **IR** (KBr) $\upsilon = 1598$ (CONH), 1645 (cyclic, C=O), 2920 (CH), 3718 (NH_2, sym), 3838 (NH_2, antisym) cm^{-1}; ^{1}H NMR (DMSO-d_6)$\delta = 6.43$–7.04 (m, 5H, $H_{arom.}$), 7.80 (s, 1H, H-5), 8.01 (s, 1H, H-7), 10.42 (s, 1H, NH); ^{13}C NMR (DMSO-d_6) $\delta = 112.3$, 129.4, 116.4 and 143.01 (Ph, C_{arom}), 163.33(C=N), 168.45 (cyclic, C=O), 171.23 (CONH) ppm. Anal. calcd. for $C_{15}H_8Br_2N_4O_2$: C, 41.32; H, 1.85; N, 12.85. Found: C, 41.47; H, 1.79; N, 12.77.

3-Amino-6,8-dibromo-2(2′,3′,4′,6′-tetra-*O*-acetyl-β-*D*-glucopyranosyl)thioxo-2,3-dihydro-1*H*-quinazolin-4-one (14)

To a solution of compound **5** (1.5 g, 0.004 mol) in dimethylformamide (10 mL) was added a few drops of triethylamine and **ABG** (1.6 g,

0.004 mol). The reaction mixture was stirred at r.t. for 3 h (TLC). The solvent was evaporated to dryness under vacuum. The solid residue was poured onto cold water, and the solid formed was filtered off, washed with cold water, dried, and recrystallized from ethanol to afford **14**. Yield 0.7 g (26%); m.p. 170–172 °C; **IR** (KBr) $\upsilon = 1617$ (cyclic, C=O), 1748 (C=O, acetyl), 3385 (NH_2, sym), 347 (NH_2, antisym) cm^{-1}; ^1H NMR (DMSO-d_6) $\delta = 1.95$–2.12 (s, 12H, $4CH_3$), 3.35 (s, 2H, C′6H_2), 4.55-5.96 (H, sugar moiety), 6.92 (s, 2H, NH_2), 7.85 (s, 1H, H-7), 7.92 (s, 1H, H-5); ^{13}C NMR (DMSO-d_6) $\delta = 20.14$ (CH_3, C′6), 20.19(CH_3, C′4), 20.23(CH_3, C′2), 20.28 (CH_3, C′3), 61.65, 67.65, 70.20, 72.47, 74.66, 81.01 (C′6,C′4,C′2, C′3, C′5, C′$1_{\text{anomeric,respectively}}$), 105.81, 106.43, 109.61, 128.99, 137.30, 142.69 (C_{arom}), 158.58 (C=N), 163.98 (C=O, cyclic), 169.21, 169.46, 169.72, 169.73 (C=O, acetyl) ppm; **MS** (EI) $m/z = 681$ (M^+, $C_{22}H_{23}Br_2N_3O_{10}S$, 75%), 603 (100%); Anal. calcd. for $C_{23}H_{23}Br_2N_3O_{10}S$: C, 38.78; H, 3.40; N, 6.17. Found: C, 39.02; H, 3.52; N, 6.49.

The Deblocking of 14

Compound **14** was dissolved in methanol (1.5 g, 0.01 mL), and two drops of sodium methoxide solution (0.001 N) were added. The reaction mixture was left at r.t. for 4 h (TLC). The solvent was evaporated under vacuum, and the residual solid was dissolved in water neutralized with dill. HCl. The solid formed was filtered off, washed with water, dried, and recrystallized from ethanol to give the starting material **5**. Yield 1.2 g (92%); m.p. 260–262°C. M.p. and mixed m.p. of the product and an authentic sample of **5** gave no depression.

3-Amino-6,8-dibromo-2-methylthio-3*H*-quinazolin-4-one (16)

Compound **5** (2 g, 0.0056 mol) was dissolved in methanol (20 mL) and sodium hydroxide (0.3 g). Methyl iodide (0.03 mL, 0.0056 mol) was added, and the reaction mixture was stirred at r.t. for 4 h (TLC). The formed solid product was filtered off, recrystallized from methanol, filtered, and dried to afford **16**. Yield 3.5 g (58%); m.p. 178–180°C; **IR** (KBr) $\upsilon = 1619$ (cyclic, C=O), 2925 (CH), 3338 (NH_2, sym), 3454 (NH_2, antisym) cm^{-1}; ^1H NMR (DMSO-d_6) $\delta = 2.80$ (s, 3H, CH_3), 6.89 (s, 2H, NH_2), 7.82 (s, 1H, H-7), 7.85 (s, 1H, H-5); ^{13}C NMR (DMSO-d_6) $\delta = 14.19$ (CH_3), 105.73, 106.82, 109.85, 128.91, 136.81, 143.12 ($C_{\text{arom.}}$), 163.26 (C=N), 163.97 (cyclic, C=O) ppm; **MS** (EI) $m/z = 363$ [$C_9H_7Br_2N_3OS$, 50%, (^{79}Br, ^{79}Br)], 364 [6.3%, (^{79}Br, ^{80}Br; ^{80}Br, ^{79}Br)], 365 [100%, (^{80}Br, ^{80}Br; ^{79}Br, ^{81}Br; ^{81}Br, ^{79}Br)], 366 [10%, (^{80}Br, ^{81}Br; ^{81}Br, ^{80}Br)], 367 [50%,

(^{81}Br, ^{81}Br). Anal. calcd. for $C_9H_7Br_2N_3OS$: C, 29.61; H, 1.93; N, 11.51. Found: C, 29.52; H, 2.00; N, 11.70.

2-Amino-3,5-dibromobenzoicaid Hydrazide (4)

A mixture of compound **16** (2 g, 0.01 mol) and hydrazine hydrate (0.5 mL, 0.01 mol) in ethanol (20 mL) was refluxed for 4 h (TLC) and then allowed to cool. The solid product was collected and recrystallized from ethanol to afford **4**. Yield 1.3 g (68%), m.p. 176–178°C.[13]

The Synthesis of 3,5-Dibromo-2-aryl Aminobenzoic Acid Hydrazide (18a–c)

A mixture of compound **4** (1.9 g, 0.01 mol) with the aromatic aldehydes, namely benzaldehyde, 4-methoxybenzaldehyde, and 2-nitrobenzaldehyde (0.01), in ethanol (20 mL) and few drops of glacial acetic acid, was added. The reaction mixture was refluxed in ethanol (20 mL) for 1–2.5 h (TLC). The solid product separated was filtered off and recrystallized from ethanol to afford (**18a–c**), respectively.

2-Amino(benzylideneamino)-3,5-dibromobenzoic Acid Hydrazide (18a)

Yield 1.1 g (83%); m.p. 218-220°C; **IR** (KBr) $\upsilon = 1632$ (C=O), 2923 (CH), 3220 (NH), 3397 (NH_2, sym), 3439 (NH_2, antisym) cm^{-1}; ^{1}H NMR (DMSO-d_6) $\delta = 6.55$ (s, 2H, NH_2), 7.46-7.80 (m, 5H, $H_{arom.}$), 8.40 (s, 1H, CH.), 11.86 (s, 1H, NH); ^{13}C NMR (DMSO-d_6) $\delta = 105.14$ (CH), 127.04, 128.78, 130.12, 134.07, 136.81, 145.57 (C_{arom}.), 152.14(C=N), 168.17 (C=O) ppm. Anal. calcd. for $C_{14}H_{11}Br_2N_4O_3$: C, 42.35; H, 2.79; N, 10.58. Found: C, 42.58; H, 2.76; N, 10.83.

3,5-Dibromo-2-amino[(4-methoxybenzylidene)amino]benzoic Acid Hydrazide (18b)

Yield 1 g (71%); m.p. 210–212°C; **IR** (KBr) $\upsilon = 1618$ (C=O, cyclic), 2928 (CH), 3225 (NH), 3362 (NH_2, sym), 3498 (NH_2, antisym) cm^{-1}; ^{1}H NMR (DMSO-d_6) $\delta = 3.73$ (s, 3H, CH_3), 6.46 (s, 2H, NH_2), 6.81–7.84 (m, 5H, $H_{arom.}$), 8.13 (s, 1H, N=CH.), 11.15 (s, 1H, NH); ^{13}C NMR (DMSO-d_6) $\delta = 57.29$ (OCH_3), 126.98, 127.12, 128.33, 129.45, 130.61, 131.72, 132.01, 132.98 (C_{arom}), 154.71 (C=N), 164.32 (C=O), 170.01 (C-OCH $_3$) ppm. Anal. calcd. for $C_{15}H_{13}Br_2N_3O_2$: C, 42.18; H, 3.07; N, 9.84. Found: C, 42.34; H, 2.89; N, 9.70.

3,5-Dibromo-2-amino[(2-nitrobenzylidene)amino]benzoic Acid Hydrazide (18c)

Yield 1.7g (71%); m.p. 286–288°C; **IR** (KBr) $\upsilon = 1654$ (C=O, cyclic), 2849 (CH), 3185 (NH), 3339 (NH_2, sym), 3417 (NH_2, antisym) cm^{-1}; ^1H NMR (DMSO-d_6)$\delta = 6.82$ (s, 2H, NH_2), 6.61–8.24 (m, 5H, $H_{arom.}$), 8.12 (s, 1H, N=CH.), 11.32 (s, 1H, NH); ^{13}C NMR (DMSO-d_6) $\delta = 112.12$, 115.42, 123.73, 124.51, 130.43, 139.72, 147.94, 148.01, ($C_{arom.}$), 156.62 (C=N), 166.53 (C=O) ppm. Anal. calcd. for $C_{14}H_{10}Br_2N_4O_3$: C, 38.04; H, 2.28; N, 12.67. Found: C, 37.89; H, 2.40; N, 12.79.

3-(Benzylideneamino)-6,8-dibromo-2-methyl-3*H*-quinazolin-4-one (19)

Compound **18a** (1 g, 0.002 mol) was refluxed with acetic anhydride (15 mL) for 4 h (TLC). The excess of solvent was evaporated under vacuum to dryness. The solid product that formed was crystallized from ethanol and dried to give **19**. Yield 0.8 g (80%); m.p. 218–220°C; **IR** (KBr) $\upsilon = 1711$ (C=O, cyclic), 2922 (CH) cm^{-1}; ^1H NMR (DMSO-d_6) $\delta = 2.45$ (s, 3H, CH_3), 7.45–7.60 (m, 6H, $H_{arom} + N{=}CH$), 8.33–8.45 (s, 2H, H_{arom}); ^{13}C NMR (DMSO-d_6) $\delta = 20.77$ (CH_3), 67.36 (CH), 118.86–143.93 (C_{arom}), 157.74 (C=N), 166.01 (C=O) ppm. Anal. calcd. for $C_{16}H_{11}Br_2N_3O$: C, 45.64; H, 2.63; N, 9.98. Found: C, 45.46; H, 2.88; N, 8.36.

The Synthesis of Aldehydosugars (2-Amino-3, 5-dibromobenzoyl) Hydrazones (20a–f)

A solution of the respective sugar pentoses and/or hexoses (0.01 mol) in water (5 mL) was refluxed with a solution of (2-amino-3,5-dibromobenzoyl)hydarzone (**4**) (2 g, 0.01 mol) in ethanol (20 mL) containing 1 mL of glacial acetic acid for 5 h (TLC). The solid product that separated on cooling was collected and recrystallized from ethanol/water (1:1) to give (**20a–f**).

Aldehydo-*L*-arabinose(2-amino-3,5-dibromobenzoyl)hydrazone (20a)

Yield 2.5 g (87%); m.p. 204–206°C; **IR** (KBr) υ = 1615 (C=N), 1675 (C=O), 3180 (NH), 3435 (OH) cm^{-1}; ^1H NMR (DMSO-d_6) $\delta = 3.62$–4.35 (m, 5H, arabinosyl protons), 6.01 (s, 2H, NH_2), 7.5 (s, 1H, CH=N-), 7.12–7.731 (m, 2H, H_{arom}), 11.02 (s, 1H, NH); ^{13}C NMR (DMSO-d_6) $\delta = 62.11$, 65.83, 70.12, 74.03 (arabinosyl moiety), 109.82, 115.22,

122.13, 133.76, 136.92, 145.19 (C_{arom}), 159.20 (C=N), 168.02 (C=O) ppm; **MS** (Maldi) $m/z = 462$ [48%, M^+ + Na, (^{79}Br, ^{79}Br)], 464 [100%, M^+ + Na, (^{80}Br, ^{80}Br or ^{79}Br, ^{81}Br)], 466 [48%, M^+ + Na, (^{81}Br, ^{81}Br)]. Anal. calcd. for $C_{12}H_{15}Br_2N_3O_5$: C, 32.68; H, 3.43; N, 9.53. Found: C, 32.59; H, 3.38; N, 9.60.

Aldehydo-*D*-ribose(2-amino-3,5-dibromobenzoyl)hydrazone (20b)

Yield 2.1g (75%); m.p. 210–212°C; **IR** (KBr) $\upsilon = 1611$ (C=N), 1671 (C=O), 3142 (NH), 3450 (OH) cm^{-1}; ^{1}H NMR (DMSO-d_6) $\delta = 3.51$–5.92 (m, 5H, ribosyl protons), 6.55 (s, 2H, NH_2), 7.31–7.96 (m, 2H, H_{arom}), 10.25 (s, 1H, NH); ^{13}C NMR (DMSO-d_6) $\delta = 62.12$, 72.50, 73.41, 74.53 (carbon of ribosyl moiety), 115.42, 120.51, 126.12, 132.97, 138.53, 140.72 (C_{arom}), 154.91 (C=N), 166.02(C=O) ppm. Anal. calcd. for $C_{12}H_{15}Br_2N_3O_5$: C, 32.68; H, 3.43; N, 9.53. Found: C, 32.60; H, 3.62; N, 9.27.

Aldehydo-*D*-xylose(2-amino-3,5-dibromobenzoyl)hydrazone (20c)

Yield 2.6 g (92%); m.p. 198–200°C; **IR** (KBr) $\upsilon = 1613$ (C=N), 1670 (C=O), 3185 (NH), 3432 (OH) cm^{-1}; ^{1}H NMR (DMSO-d_6) $\delta = 3.32$–5.51 (m, 5H, xylosyl protons), 6.59 (s, 2H, NH_2), 7.62–7.83 (m, 2H, H_{arom}), 10.35 (s, 1H, NH); ^{13}C NMR (DMSO-d_6) $\delta = 62.39$, 66.76, 69.70, 71.32, 76.50 (carbon of xylosyl moiety), 105.12, 110.06, 116.08, 130.07, 136.52, 145.25 (C_{arom}), 165.92 (C=O) ppm. Anal. calcd. for $C_{12}H_{15}Br_2N_3O_5$: C, 32.68; H, 3.43; N, 9.53. Found: C, 32.82; H, 3.53; N, 9.05.

Aldehydo-*D*-glucose(2-amino-3,5-dibromobenzoyl)hydrazone (20d)

Yield 2.5 g (85%); m.p. 210–212°C; **IR** (KBr) $\upsilon = 1613$ (C=N), 1673 (C=O), 3182 (NH), 3433 (OH) cm^{-1}; ^{1}H NMR (DMSO-d_6) $\delta = 3.60$–5.67 (m, 6H, glucosyl protons), 6.59 (s, 2H, NH_2), 7.56–7.85 (m, 2H, H_{arom} and CH=N), 10.60 (s, 1H, =N–H); ^{13}C NMR (DMSO-d_6) $\delta = 60.73$, 71.46, 76.67, 77.87, 87.72, 90.89 (carbon of glucosyl moiety), 105.24, 110.03, 116.52, 129.69, 136.40, 145.06 (C_{arom}), 157.42 (C=N), 165.64 (C=O) ppm. Anal. calcd. for $C_{13}H_{17}Br_2N_3O_6$: C, 33.14; H, 3.64; N, 8.92. Found: C, 33.30; H, 3.72; N, 9.00.

Aldehydo-*D*-galactose(2-amino-3,5-dibromobenzoyl)hydrazone (20e)

Yield 2.8 g (89%) cm^{-1}; m.p. 214–216°C; **IR** (KBr) $\upsilon = 1618$ (C=N), 1679 (C=O), 3188 (NH), 3421 (OH); ^{1}H NMR (DMSO-d_6) $\delta = 3.65$–6.10 (m, 6H, galactosyl protons), 6.53 (s, 2H, NH_2), 7.75–7.99 (m, 2H, H_{arom} and CH=N), 11.66 (s, 1H, NHC=O); ^{13}C NMR (DMSO-d_6) $\delta = 60.40$, 66.02, 68.17, 68.90, 76.44 (C-6′, C-5′, C-4′, C-3′ and C-2 carbon of galactosyl moiety), 105.18, 110.01, 116.20, 130.17, 136.47, 145.35 (C_{arom}), 154.86 (C=N), 166.01 (C=O) ppm; **MS** (Maldi) $m/z = 492$ [48%, M^++ Na, (^{79}Br, ^{79}Br)], 494 [100%, M^+ + Na, (^{80}Br, ^{80}Br or ^{79}Br, ^{81}Br)], 496 [48%, M^++ Na, (^{81}Br, ^{81}Br)]. Anal. calcd. for $C_{13}H_{17}Br_2N_3O_6$: C, 33.14; H, 3.64; N, 8.92. Found: C, 33.12; H, 3.56; N, 8.75.

Aldehydo-*D*-mannose(2-amino-3,5-dibromobenzoyl)hydrazone (20f)

Yield 1.3 g (46%) cm^{-1}; m.p. 197–199°C; **IR** (KBr) $\upsilon = 1642$ (C=N), 1674 (C=O), 3110 (NH), 3476 (OH) cm^{-1}; ^{1}H NMR (DMSO-d_6) $\delta = 3.54$–5.62 (m, 6H, mannose protons), 6.54 (s, 2H, NH_2), 7.15–7.97 (m, 2H, H_{arom} and CH=N), 10.55 (s, 1H, NHC=O); ^{13}C NMR (DMSO-d_6) δ =62.87, 64.10, 68.17, 68.97, 70.40 (C-6′, C-5′, C-4′, C-3′ and C-2′ (carbon of mannose moiety), 106.78, 107.38, 111.73, 130.51, 135.23, 143.41 (C_{arom}), 157.61 (C=N), 167.21(C=O) ppm. Anal. calcd. for $C_{13}H_{17}Br_2N_3O_6$: C, 33.14; H, 3.64; N, 8.92. Found: C, 32.99; H, 3.72; N, 9.03.

2′,3′,4′,5-Tetra-O-acetylaldehydo-*L*-arabinose[1-acetyl-1-(*N*-acetylamino)-3,5-dibromobenzoyl]hydrazone (21a)

Yield 1.1 g (78%); m.p. 80–82°C; **IR** (KBr) $\upsilon = 1645$(C=N), 1667 (C=O, cyclic), 1763 (C=O), 2855 (CH), 3348 (NH_2, sym), 3435 (NH_2, antisym) cm^{-1}; ^{1}H NMR (DMSO-d_6) $\delta = 1.89$, 1.91, 1.94, 2.02, 2.05 (5s, 15H, $5CH_3CO$), 2.28 (s, 2H, CH_2OAc), 5.28 (m, 1H, C′-5), 5.41 (d, 1H, $J = 9.57$ Hz, C′-4), 5.44 (d, 1H, $J = 8.22$ Hz, C′-3), 5.61 (m, 1H, C′-2), 6.34 (m, 1H, C′-1), 6.57 (s, 2H, NH_2), 7.15-7.97 (m, 2H, H_{arom}); ^{13}C NMR (DMSO-d_6) $\delta = 20.38$, 20.43, 20.50, 21.43 (4 O*C*H_3CO), 22.20 (N*C*H_3CO), 62.48, 67. 55, 68.55, 68.88, 87.55 (C′-5, C′-4, C′-3, C′-2, C′-1), 106.51, 108.07, 109.61, 129.48, 138.07, 148.46 (C_{arom}), 153.85 (C=N), 169.05 (C=O, base), 169.24, 169.40, 169.92 (4C=O, acetyl), 170.01 (NCH_3*C*=O) ppm. Anal. Calcd. for $C_{22}H_{25}Br_2N_3O_{10}$: C, 40.57; H, 3.87; N, 6.45. Found: C, 40.72; H, 3.91; N, 6.60.

2′,3′,4′,5-Tetra-*O*-acetylaldehydo-*D*-ribose[1-acetyl-1-(*N*-acetylamino)-3,5-dibromobenzoyl]hydrazone (21b)

Yield 0.8 g (57%); m.p. 92–94°C; **IR** (KBr) $\upsilon = 1657$(C=N), 1697 (C=O, cyclic), 1775 (C=O), 2840 (CH), 3330 (NH_2 sym), 3425 (NH_2, antisym) cm^{-1}; ^1H NMR (DMSO-d_6) $\delta = 1.75$, 1.83, 1.98, 2.12, 2.20 (5s, 15H, $5CH_3CO$), 2.56 (s, 2H, CH_2OAc), 5.11 (m, 1H, C′-5), 5.44 (d, 1H,$J = 9.55$ Hz, C′-4), 5.48 (d, 1H, $J = 8.51$ Hz, C′-3), 5.54 (m, 1H, C′-2), 6.24 (m, 1H, C′-1), 6.35 (s, 2H, NH_2), 7.41–7.95 (m, 2H, H_{arom}); ^{13}C NMR (DMSO-d_6) $\delta = 20.23$, 20.42, 20.53, 20.61 (4 O*C*H_3CO), 21.75 (N*C*H_3CO), 68.24, 68. 53, 71.46, 72.56, 78.42 (C′-5, C′-4, C′-3, C′-2, C′-1), 110.16, 115.34, 119.49, 121.21, 138.47, 144.58 (C_{arom}), 165.80 (C=O, cyclic), 169.52 (5C=O) ppm. Anal. Calcd. for $C_{22}H_{25}Br_2N_3O_{10}$: C, 40.57; H, 3.87; N, 6.45. Found: C, 40.68; H, 4.16; N, 6.15.

2′,3′,4′,5-Tetra-*O*-acetylaldehydo-*D*-xylose [1-acetyl-1-(*N*-acetylamino)-3,5-dibromobenzoyl]hydrazone (21c)

Yield 1 g (71%); m.p. 90–92°C; **IR** (KBr): $\upsilon = 1668$ (C=N), 1686 (C=O, cyclic), 1779 (C=O), 2886 (CH), 3335 (NH_2, sym), 3421 (NH_2, antisym) cm^{-1}; ^1H NMR (DMSO-d_6) $\delta = 1.73$, 1.89, 1.97, 2.15, 2.25 (5s, 15H, $5CH_3CO$), 2.59 (s, 2H, CH_2OAc), 5.15 (m, 1H, C′-5), 5.65 (d, 1H,$J = 9.52$ Hz, C′-4), 5.45 (d, 1H, $J = 8.50$ Hz, C′-3), 5.50 (m, 1H, C′-2), 6.30 (m, 1H, C′-1), 6.37 (s, 2H, NH_2), 7.55–7.99 (m, 2H, H_{arom}); ^{13}C NMR (DMSO-d_6) $\delta = 20.28$, 20.40, 20.61, 20.65 (4 O*C*H_3CO), 20.81 (N*C*H_3CO), 63.22, 67.17, 68.02, 73.27, 80.13 (C′-5, C′-4, C′-3, C′-2, C′-1), 104.99, 110.05, 114.98, 128.22, 130.61, 137. 32 (C_{arom}), 145.48 (C=N), 166.59 (C=O, cyclic), 169.03, 169.48 (4C=O), 172.91(N*C*H_3*C*O) ppm. Anal. calcd. for $C_{22}H_{25}Br_2N_3O_{10}$: C, 40.57; H, 3.87; N, 6.45. Found: C, 40.50; H, 3.80; N, 6.58.

2′,3′,4′,5′,6-Penta-*O*-acetylaldehydo-*D*-glucose[1-acetyl-1-(*N*-acetylamino)-3,5-dibromobenzoyl]hydrazone (21d)

Yield 0.8 g (57%); m.p. 198–200°C; **IR** (KBr) $\upsilon = 1671$ (C=N), 1695 (C=O, cyclic), 1770 (C=O), 2860 (CH), 3340 (NH_2, sym), 3432 (NH_2, antisym) cm^{-1}; ^1H NMR (DMSO-d_6) $\delta = 1.75$, 1.90, 1.99, 2.20, 2.28, 2.51 (5s, 15H, $5CH_3CO$ + NAc), 2.90 (s, 2H, CH_2OAc), 5.11 (m, 1H, C′-5), 5.75 (d, 1H,$J = 9.64$ Hz, C′-4), 5.55 (d, 1H, $J = 9.12$ Hz, C′-3), 5.53 (m, 1H, C′-2), 6.35 (m, 1H, C′-1), 6.53 (s, 2H, NH_2), 7.62–7.96 (m, 2H, H_{arom}); ^{13}C NMR (DMSO-d_6) $\delta = 20.20$, 20.33, 20.45, 20.52 (5 O*C*H_3CO), 20.88 (N*C*H_3CO), 62.06, 67. 48, 72.35, 73.54, 79.40, 79.43 (C′-6, C′-5, C′-4, C′-3, C′-2, C′-1), 105.00, 110.08, 115.03, 130.69, 137.38, 145.46 (C_{arom}),

166.77 (C=O, cyclic), 169.427, 169.44 (4C=O), 172.73 (NCH_3CO) ppm; **MS** (Maldi) $m/z = 722$ [100%, $M^+ - 2$, (^{79}Br, ^{79}Br)], 747 [15%, $M^+ + Na$, (^{80}Br, ^{80}Br or ^{79}Br, ^{81}Br). Anal. calcd. for $C_{25}H_{29}Br_2N_3O_{12}$: C, 41.61; H, 4.04; N, 5.81. Found: C, 41.46; H, 3.78; N, 6.03.

2′,3′,4′,5′,6-Penta-O-acetylaldehydo-*D*-galactose[1-acetyl-1-(*N*-acetylamino)-3,5-dibromobenzoyl]hydrazone (21e)

Yield 0.9 g (64%); m.p. 202–204°C; **IR** (KBr) $\upsilon = 1682$ (C=N), 1676 (C=O, cyclic), 1778 (C=O), 2870 (CH), 3323 (NH_2, sym), 3411 (NH_2, antisym) cm^{-1}; ^1H NMR (DMSO-d_6) $\delta = 1.70$, 1.85, 1.96, 2.10, 2.24, 2.95 (5s, 15H, $5CH_3CO + NAc$), 2.54 (s, 2H, CH_2OAc), 5.13 (m, 1H, C′-5), 5.70 (d, 1H, $J = 9.51$ Hz, C′-4), 5.51 (d, 1H, $J = 9.12$ Hz, C′-3), 5.56 (m, 1H, C′-2), 6.44 (m, 1H, C′-1), 6.68 (s, 2H, NH_2), 7.80–8.20 (m, 2H, H_{arom}); ^{13}C NMR (DMSO-d_6) $\delta = 19.99$, 20.37, 20.59, 20.88 (4 OCH_3CO), 21.23 (NCH_3CO), 61.96, 67.10, 65.88, 68.19, 87.05, 89.24 (C′-6, C′-5, C′-4, C′-3, C′-2, C′-1), 105.46, 106.84, 109.81, 128.89, 137.00, 143.34 (C_{arom}), 164.46 (C=O, cyclic), 169.92 (C=O) ppm; **MS** (Maldi) $m/z = 746$ [100 %, M+ Na, (^{79}Br, ^{80}Br)], 747 [59 %, $M^+ + Na$, (^{80}Br, ^{80}Br or ^{79}Br, ^{81}Br)]. Anal. calcd. for $C_{25}H_{29}Br_2N_3O_{12}$: C, 41.61; H, 4.04; N, 5.81. Found: C, 41.70; H, 4.00; N, 6.01.

2′,3′,4′,5′,6-Penta-*O*-acetylaldehydo-*D*-manose[1-acetyl-1-(*N*-acetylamino)-3,5-dibromobenzoyl]hydrazone (21f)

Yield 1.1 g (78%); m.p. 182–184°C; **IR** (KBr) $\upsilon = 1670$ (C=N), 1672 (C=O, cyclic), 1776 (C=O), 2884 (CH), 3320 (NH_2, sym), 3418 (NH_2, antisym) cm^{-1}; ^1H NMR (DMSO-d_6) $\delta = 1.81$, 1.84, 1.82, 2.15, 2.28, 2.92 (5s, 15H, $5CH_3CO + NAc$), 2.44 (s, 2H, CH_2OAc), 5.10 (m, 1H, C′-5), 5.69 (d, 1H, $J = 9.55$ Hz, C′-4), 5.59 (d, 1H, $J = 9.12$ Hz, C′-3), 5.61 (m, 1H, C′-2), 6.74(m, 1H, C′-1), 6.82 (s, 2H, NH_2), 7.51-8.11 (m, 2H, H_{arom}); ^{13}C NMR (DMSO-d_6) $\delta = 22.43$, 22.35, 22.41, 23.01, 23.15 (5 OCH_3CO), 24.18 (NCH_3CO), 68.10, 68.35, 71.23, 75.41, 79.11, 79.93 (C′-6, C′-5, C′-4, C′-3, C′-2, C′-1), 117.10, 119.27, 134.35, 139.01, 141.74, 145.86 (C_{arom}), 152.81 (C=N), 165.12 (C=O, cyclic), 170.50 (6C=O) ppm; **MS** (Maldi) $m/z = 746$ [86%, M+ Na, (^{79}Br, ^{80}Br)], 747 [57 %, $M^+ + Na$, (^{80}Br, ^{80}Br or ^{79}Br, ^{81}Br)]. Anal. Calcd. for $C_{25}H_{29}Br_2N_3O_{12}$: C, 41.61; H, 4.04; N, 5.81. Found: C, 41.80; H, 3.90; N, 6.01.

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