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# On the Chemistry of 5-Aryl-2-hydrazino-benzo[6,7]cyclohepta[1,2-*b*]pyrido[2,3-*e*] pyrimidin-4-one

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ABSTRACT: *Several pyrido[2,3-e]pyrimidine fused with other rings have been prepared by intramolecular cyclization of 5-(4-chlorophenyl)-2-hydrazino-benzo [6,7]cyclohepta-[1,2-b]pyrido[2,3-e]pyrimidine-4-one (***1***) with acids, carbon disulfide to form triazole derivatives (***2,4***), halo-ketones to give triazine derivative (***5***), β-ketoesters, β-cyanoesters, and β-diketones to yield 2-(1-pyrazolyl) derivatives (***7,9,10***), and aldehydes to form arylhydrazone derivatives (***11a,b***) which cyclized to form triazoles (***12a,b***). Also, acyclic N-nucleosides are prepared by heating under reflux 2-hydrazino-benzo[6,7]cyclohepta[1,2-b]pyrido[2,3-e] pyrimidin-4-one (***1***) with xylose and glucose to give the corresponding acyclic N-nucleosides (***13a,b***) which are cyclized to afford the corresponding protected tetra and penta–O-acetate C-nucleosides (***14a,b***). Deacetylating of the latter nucleosides afforded the free acyclic C-nucleosides (***15a,b***).* © 2007 Wiley Periodicals, Inc. Heteroatom Chem 18:34–43, 2007; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20248

## *INTRODUCTION*

Pyrimidines, being an integral part of nucleic acids and many chemotherapeutic agents, display a wide range of pharmacological activities as phosphodiesterase inhibitor [1], fungicide [2], viricide [3], bactericide [4], and leishmanicide [5,6]. This aroused considerable interest to design and synthesize compounds that have profound leishmanicidal activity. Thus, in continuation of our work on the synthesis of pyridopyrimidines [7] and pyridopyrimidines fused with other ring systems [8–10] as a biologically active materials, we report in this paper the synthesis of new compounds derived from the biologically active starting material.

Heating under reflux the solution of 5-(4-chlorophenyl)-2-hydrazino-benzo-[6,7]cyclohepta[1,2-*b*] pyrido[2,3-*e*]pyrimidine-4-one (**1**) with aliphatic acids, namely formic or acetic acid, resulted in the formation of 6-(4-chlorophenyl)-3-(un)substituted-1*H*-benzo[6,7] cyclohepta[1,2-*b*] pyrido[2,3-*e*][1,2,4] triazolo[2',3':5,6]pyrimidin-5(5*H*)-one (**2a,b**) (see Scheme 1). Besides the correct values in elemental analysis, the IR and $^1$H-NMR spectra of **2a,b** are in agreement with the assigned structure. The $^1$H-NMR (DMSO-$d_6$) of **2a** as an example showed signals at $\delta$ 1.72–1.84 (m, 4H, $2CH_2$), 2.56 (m, 2H, $CH_2$), 7.35–7.38 (d, 2H *p*-subs-phenyl), 7.54–7.57 (m, 1H, disub-phenyl), 7.82–7.91 (m, 2H, disub-phenyl), 8.23–8.26 (d, 2H, *p*-subs-phenyl), 8.34–8.37 (m, 1H, disubs-phenyl), 8.62 (s, 1H, triazole proton), and 13.02 (brs, 1H, NH, $D_2O$ exchangeable). The MS of this compound showed molecular ion peak at *m/z*: 413 ($M^+$) 100%, 415 ($M^+ + 1$) 37%, 385 ($M^+ - CO$) 56%. On the other hand, the 2-acetylhydrazino derivative **3** was produced upon heating compound **1** with acetic acid for 2 h under reflux. The IR of compound **3** showed the absorption of two carbonyl bands at 1700 and 1689 cm$^{-1}$. The MS of this

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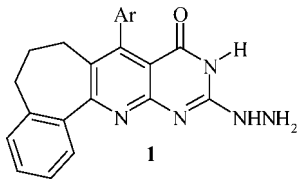
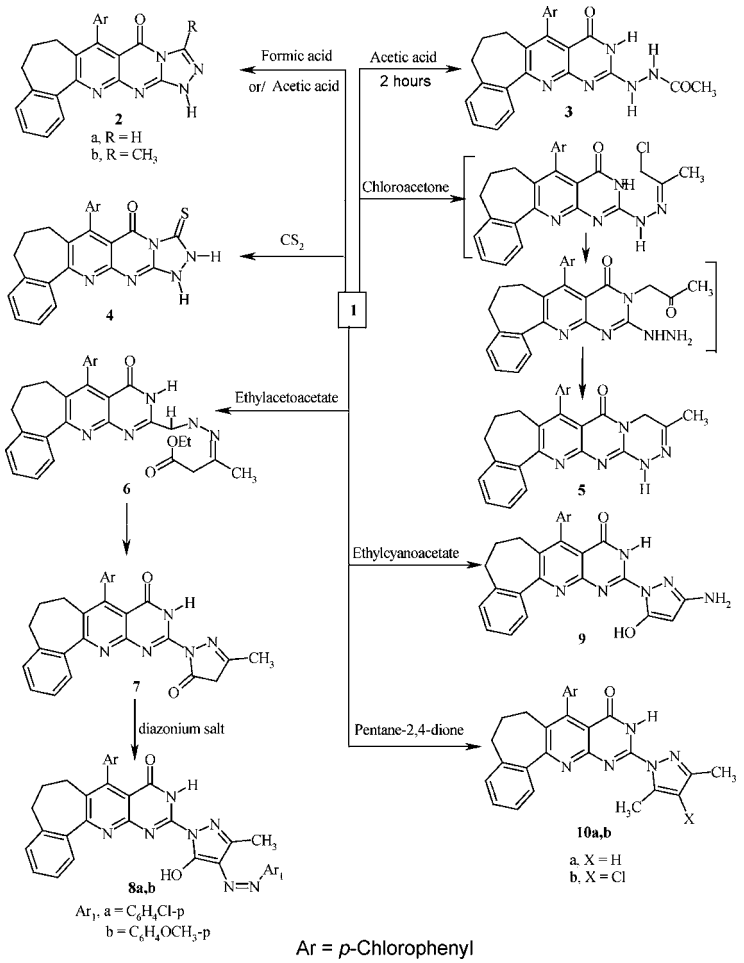
compound showed ion peaks at *m/z*: 445 ($M^+$) 100% and 446 ($M^+ + 1$) 29%.




**1**

Similarly, the 2-hydrazino **1** reacted with carbon disulfide in ethanolic potassium hydroxide solution to afford 3(3*H*)-thioxo-6-(4-chlorophenyl) benzo[6,7]-cyclohepta[1,2-*b*]pyrido[2,3-*e*][1,2,4]triazolo[2',3':5,6]pyrimidin-5(5*H*)-one (**4**). The IR spectrum of **4** displayed absorption bands at 3400 $cm^{-1}$ (NH) and 1686 $cm^{-1}$ (CO). Its $^1$H-NMR spectrum (DMSO-$d_6$) showed signals at δ 1.73–1.81 (m, 4H, $2CH_2$), 2.54 (m, 2H, $CH_2$), 7.33–7.35 (d, 2H *p*-subs-phenyl), 7.51–7.53 (m, 1H, disub-phenyl), 7.77–7.80 (m, 2H, disub-phenyl), 8.19–8.21 (d, 2H, *p*-subs-phenyl), 8.40–8.42 (m, 1H, disubs-phenyl), and 11.09 (brs, 1H, NH, $D_2O$ exchangeable). The MS of this compound showed ion peak at *m/z*: 445 ($M^+$) 100%. The cyclization of 2-hydrazino derivatives with formic acid and/or carbon disulfide at N-3 nitrogen atom producing the 1,2,4-triazolo pyrimidinone was previously noted [11,12]. Also, the 2-hydrazino derivative **1** was used for the preparation of pyrido-pyrimidotriazine derivative **5**. Thus, heating under reflux compound **1** with chloroacetone in dry xylene for 6 h yielded directly 3-methyl-7-(4-chlorophenyl)benzo[6,7]cyclohepta[1,2-*b*]pyrido[2,3-*e*][1,2,4]triazino-[2',3':5,6]-pyrimidin-5(5*H*)-one (**5**).

Moreover, the 2-hydrazino derivative **1** reacted with some β-ketoesters, β-cyanoesters, and β-diketones to form 2-(1-pyrazolyl) derivatives. Thus, when compound **1** was heated with ethyl acetoacetate in absolute ethanol, it gave the hydrazone derivative **6**, while the pyrazolyl derivative **7** was produced by heating **1** with ethyl acetoacetate under reflux in ethanolic sodium ethoxide. Compound **6**




**SCHEME 1**

**TABLE 1** Physical Data for the Products **2–15**

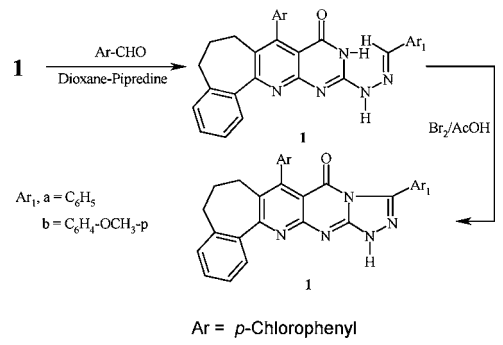
| *Compound* | *MP. (°C)* | *Yield (%)* | *M.F. (M.Wt.)* | *Elemental Analyses Calcd./Found* | | |
|---|---|---|---|---|---|---|
| | | | | *C* | *H* | *N* |
| **2a** | 304–307 | 67 | $C_{23}H_{16}N_5ClO$ | 66.75 | 3.90 | 16.92 |
| | decom. | | (413.85) | 66.72 | 3.86 | 16.85 |
| **2b** | 269–271 | 63 | $C_{24}H_{18}N_5ClO$ | 67.36 | 4.24 | 16.37 |
| | decom. | | (427.87) | 67.29 | 4.25 | 16.35 |
| **3** | 310–312 | 72 | $C_{24}H_{20}N_5ClO_2$ | 64.64 | 4.52 | 15.71 |
| | melted | | (445.89) | 64.59 | 4.54 | 15.67 |
| **4** | 342–345 | 65 | $C_{23}H_{16}N_5ClOS$ | 61.94 | 3.62 | 15.71 |
| | decom. | | (445.91) | 61.87 | 3.71 | 15.65 |
| **5** | 323–325 | 54 | $C_{25}H_{20}N_5ClO$ | 67.94 | 4.56 | 15.85 |
| | decom. | | (441.90) | 67.89 | 4.52 | 15.74 |
| **6** | 271–273 | 79 | $C_{28}H_{26}N_5ClO_3$ | 65.17 | 5.08 | 13.57 |
| | melted | | (515.98) | 65.20 | 5.11 | 13.54 |
| **7** | 329–331 | 48 | $C_{26}H_{20}N_5ClO_2$ | 66.45 | 4.29 | 14.90 |
| | decom. | | (469.91) | 66.43 | 4.31 | 14.78 |
| **8a** | 296–298 | 63 | $C_{32}H_{23}N_7Cl_2O_2$ | 63.16 | 3.81 | 16.11 |
| | decom. | | (608.46) | 63.09 | 3.77 | 16.02 |
| **8b** | 282–285 | 59 | $C_{33}H_{26}N_7ClO_3$ | 65.61 | 4.34 | 16.23 |
| | decom. | | (604.04) | 65.58 | 4.29 | 16.19 |
| **9** | 339–341 | 61 | $C_{25}H_{19}N_6ClO_2$ | 63.76 | 4.07 | 17.85 |
| | decom. | | (470.90) | 63.73 | 4.09 | 17.78 |
| **10a** | 301–303 | 78 | $C_{27}H_{22}N_5ClO$ | 69.30 | 4.74 | 14.97 |
| | melted | | (467.94) | 69.25 | 4.71 | 14.81 |
| **10b** | 293–295 | 75 | $C_{27}H_{21}N_5Cl_2O$ | 64.55 | 4.21 | 13.94 |
| | melted | | (502.39) | 64.50 | 4.17 | 13.89 |
| **11a** | 285–287 | 69 | $C_{29}H_{22}N_5ClO$ | 70.79 | 4.51 | 14.24 |
| | melted | | (491.96) | 70.81 | 4.48 | 14.17 |
| **11b** | 263–265 | 76 | $C_{30}H_{24}N_5ClO_2$ | 69.02 | 4.63 | 13.42 |
| | melted | | (521.98) | 69.04 | 4.59 | 13.39 |
| **12a** | 329–331 | 55 | $C_{29}H_{20}N_5ClO$ | 71.09 | 4.11 | 14.29 |
| | decom. | | (489.94) | 71.11 | 4.09 | 14.23 |
| **12b** | 341–343 | 57 | $C_{30}H_{22}N_5ClO_2$ | 71.49 | 4.40 | 13.90 |
| | decom. | | (503.97) | 71.39 | 4.51 | 13.67 |
| **13a** | 182–184 | 69 | $C_{27}H_{26}N_5O_5Cl$ | 60.50 | 4.89 | 13.07 |
| | decom. | | (536.02) | 60.61 | 4.90 | 12.98 |
| **13b** | 171–173 | 76 | $C_{28}H_{28}N_5ClO_6$ | 59.41 | 4.98 | 12.37 |
| | decom. | | (565.99) | 59.33 | 4.99 | 12.34 |
| **14a** | 62–64 | 52 | $C_{35}H_{32}N_5ClO_9$ | 59.87 | 4.59 | 9.97 |
| | melted | | (702.10) | 59.89 | 4.62 | 10.01 |
| **14b** | 58–60 | 63 | $C_{38}H_{36}N_5ClO_{11}$ | 57.86 | 4.81 | 9.29 |
| | melted | | (754.16) | 57.78 | 4.84 | 9.32 |
| **15a** | 161–163 | 48 | $C_{27}H_{24}N_5ClO_5$ | 60.73 | 4.53 | 13.12 |
| | decom. | | (533.95) | 60.68 | 4.50 | 13.09 |
| **15b** | 143–145 | 56 | $C_{28}H_{26}N_5ClO_6$ | 59.63 | 4.65 | 12.42 |
| | decom. | | (563.98) | 59.43 | 4.67 | 12.39 |

could be converted to **7** upon heating with ethanolic sodium ethoxide solution. The $^1$H-NMR spectrum ($CDCl_3$) of **6** showed signals at $\delta$ 1.30 ppm (t, 3H, $CH_3$), 1.71 (m, 4H, $2CH_2$), 2.00 (s, 3H, $CH_3$), 2.60 (m, 2H, $CH_2$), 3.31 (s, 2H, $CH_2$), 4.19 (q, 2H, $CH_2$), 7.33–7.35 (d, 2H *p*-subs-phenyl), 7.51–7.53 (m, 1H, disub-phenyl), 7.77–7.80 (m, 2H, disub-phenyl), 8.19–8.21 (d, 2H, *p*-subs-phenyl), 8.40–8.42 (m, 1H, disubs-phenyl), 9.51 (brs, 1H, NH, $D_2O$ exchangeable), and 10.06 (brs, 1H, NH, $D_2O$ exchangeable). And its IR spectrum displayed absorption bands at 3279, 3206 cm$^{-1}$ 2(NH), 1741 and 1686 cm$^{-1}$ 2(CO). Also, the $^1$H-NMR spectrum of **7** showed no signals corresponding to ethyl group protons (cf. Experimental). Compound **7** was coupled with aromatic diazonium salts to afford the corresponding azo derivatives **8a,b**. The IR spectra of **8a** displayed absorption bands around 3450 cm$^{-1}$ (OH), 3180 cm$^{-1}$ (NH), and 1671 cm$^{-1}$ (CO). The $^1$H-NMR spectrum (DMSO-$d_6$) of **8**a, as an example, showed signals at $\delta$ 1.72 ppm (m, 4H, $2CH_2$), 2.34 (s, 3H, $CH_3$), 2.58 (m, 2H, $CH_2$), 7.33–7.35 (two d, 4H *p*-subs-phenyl), 7.51–7.53 (m, 1H, disub-phenyl), 7.77–7.80 (m, 2H, disub-phenyl), 8.19–8.21 (d, 2H, *p*-subs-phenyl), 8.23–8.26 (d, 2H,

*p*-subs-phenyl), 8.40–8.42 (m, 1H, disubs-phenyl), 9.21 (brs, 1H, NH, $D_2O$ exchangeable), and 13.02 (brs, 1H, OH, $D_2O$ exchangeable). Its mass spectrum showed the molecular ion peak at *m/z* 608 ($M^+$), 100%. Similarly, the 2-hydrazino derivative **1** reacted with ethyl cyanoacetate in ethanolic sodium ethoxide solution afforded the 2-(3-amino-5-hydroxy-4*H*-pyrazol-l-yl) derivative **9**. The IR spectrum of **9** displayed absorption bands at 3340 $cm^{-1}$ ($NH_2$), 3260 $cm^{-1}$ (NH), and 1687 $cm^{-1}$ (CO). Its $^1$H-NMR spectrum (DMSO-$d_6$) showed signals at $\delta$ 1.73–181 (m, 4H, $2CH_2$), 2.54 (m, 2H, $CH_2$), 5.02 (brs, 2H, $NH_2$, $D_2O$ exchangeable), 7.23–7.35 (d, 2H *p*-subs-phenyl), 7.50–7.53 (m, 1H, disub-phenyl), 7.71–7.74 (m, 2H, disub-phenyl), 8.0 (s, 1H, pyrazole proton), 8.20–8.24 (d, 2H, *p*-subs-phenyl), 8.39–8.42 (m, 1H, disubs-phenyl), and 9.68 (brs, 1H, NH, $D_2O$ exchangeable).

When equimolar amounts of **1** and pentane-2,4-dione or 3-chloro-pentane-2,4-dione were heated under ruflux in absolute ethanol, the 2-pyrazolyl-pyrido[2,3-*e*]pyrimidinone **10a,b** was obtained in good yield. The $^1$H-NMR spectrum (DMSO-$d_6$) of **10a**, as an example, showed signals at $\delta$ 1.68 ppm (m, 4H, $2CH_2$), 2.55 (m̃, 2H, $CH_2$), 2.61 (s, 3H, $CH_3$), 6.20 (s, 1H, CH), 7.21–7.30 (d, 2H *p*-subs-phenyl), 7.47–7.51 (m, 1H, disub-phenyl), 7.69–7.72 (m, 2H, disub-phenyl), 8.21–8.25 (d, 2H, *p*-subs-phenyl), 8.36–8.40 (m, 1H, disubs-phenyl), and 11.70 (brs, 1H, NH, $D_2O$ exchangeable). Its IR spectrum displayed absorption bands at 3139 $cm^{-1}$ (NH) and 1688 $cm^{-1}$ (CO). Its mass spectrum showed the molecular ion peak at *m/z* 467.

The interaction of **1** with a proper aldehyde in boiling dioxane in the presence of catalytic amounts of piperidine afforded the arylhydrazone derivatives **11a,b**(see Scheme 2) which could be cyclized into the 3-aryl-benzo[6,7]cyclohepta[1,2-*b*]pyrido[2,3-*e*][1,2,4]-triazolo[2′,3′:5,6]pyrimidin-5(5*H*)-ones (**12a, b**). Compounds **11a,b** gave compatible spectral and analytical data (experimental). The IR spectra of

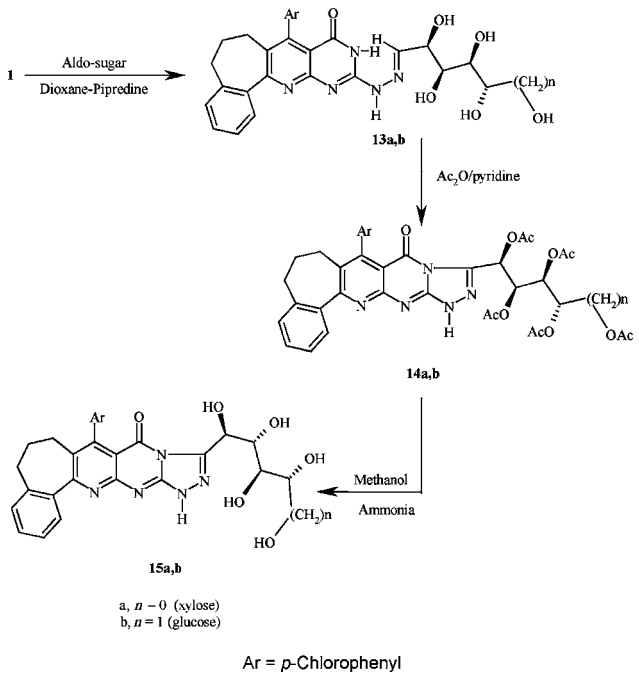



**SCHEME 2**

**12a,b** displayed absorption bands around 3370 $cm^{-1}$ (NH) and 1685 (C=O). The $^1$H-NMR spectrum (DMSO-$d_6$) of **12a**, as an example, showed signals at $\delta$ 1.70 ppm (m, 4H, $2CH_2$), 2.53 (m̃, 2H, $CH_2$), 7.20–7.28 (d, 2H *p*-subs-phenyl), 7.43–7.47 (m, 4H, 1H for disub-phenyl + 3H for phenyl), 7.61–7.70 (m, 4H, 2H for disub-phenyl + 2H for phenyl), 8.21–8.25 (d, 2H, *p*-subs-phenyl), 8.36–8.40 (m, 1H, disubs-phenyl), and 10.65 (brs, 1H, NH, $D_2O$ exchangeable).

According to the Shishoo synthesis of hydrazinopyrimidine [13] derivatives and Elgazzar for *C*-nucleoside synthesis [8], the reaction of compound **1** with some penta monosaccharides, namely, D-xylose or D-glucose in dry dioxane in the presence of catalytic amounts of pipridine, yielded the corresponding 2-(glucosylhydrazon)-5-(4-chlorophenyl)benzo[6,7]cyclohepta[1,2-*b*]pyrido[2,3-*e*]pyrimidin-4-one (**13a,b**). The spectral data besides the correct values in elemental analyses support the open chain nature of the sugar residue in **13a,b**. Moreover, the IR (KBr) spectrum for **13a** displayed absorption bands at 3430 $cm^{-1}$ (broad, OH), 3221 (NH), and 1687 (C=O). Its NMR spectrum of compound **13a**, as an example, showed signals at $\delta$ 1.67 (m, 4H, $2CH_2$), 2.55 (m, 2H, $CH_2$), 3.31 (m, 2H, $CH_2$), 3.53 (m, 4OH, $D_2O$ exchangeable, OH-2′, OH-5′), 4.21 (q, 1H, $J = 6$ Hz, H-4′), 4.45 (m, 2H, H-5″), 4.61 (d, 1H, $J = 5$ Hz, H-3′), 5.76 (dd, 1H, $J = 7$ Hz, H-2′), 7.29 (d, 1H, $J = 4$ Hz, H-1′), 7.35–7.37 (d, 2H, *p*-subs-phenyl), 7.50–7.53 (m, 1H, disub-phenyl), 7.76–7.80 (m, 2H, disub-phenyl), 8.18–8.21 (d, 2H, *p*-subs-phenyl), 8.39–8.42 (m, 1H, disub-phenyl), and 11.25 (brs, 1H, NH, $D_2O$ exchangeable). The MS of the latter compound showed ion peak at *m/z*: 536 ($M^+$) 100%. The hydrazone derivatives **13a,b** were stirred at room temperature in acetic anhydride-pyridine (1:1) mixture to afford the corresponding 3-(2′,3′,4′,5′-*O*-tetraacetyl-glycosyl)- or 3-(1′,2′,3′,4′,5′-*O*-pentaacetyl-glucosyl)-6-(4-chlorophenyl)benzo[6,7]-cyclohepta[1,2-*b*]pyrido [2,3-*e*][1,2,4]triazolo[2′,3′:5,6]pyrimidin-5(5*H*)-one(**14a,b**) (Scheme 3). The spectral data besides the correct values in elemental analyses support the structure. The $^1$H-NMR spectrum of compound **14a**, as an example, showed signals at $\delta$ 1.69 (m, 4H, $2CH_2$), 1.94 (s, 3H, $CH_3$), 2.11 (s, 3H, $CH_3$), 2.14 (s, 3H, $CH_3$), 2.20 (s, 3H, $CH_3$), 2.60 (m, 2H, $CH_2$), 3.22 (m, 2H, $CH_2$), 4.65 (m, 1H, H-3′), 5.23 (m, 2H, H-4′), 5.44 (m, 1H, H-2′), 5.75 (m, 1H, H-1′), 7.29–7.31 (d, 2H *p*-subs-phenyl), 7.46-7.52 (m, 1H, disub-phenyl), 7.74–7.79 (m, 2H, disub-phenyl), 8.20–8.23 (d, 2H, *p*-subs-phenyl), 8.38–8.41 (m, 1H, disub-phenyl), and 10.11 (brs, NH, $D_2O$ exchangeable).

Deprotection of the protected acyclic-*C*-nucleosides **14a,b** could be achieved by treatment with




**SCHEME 3**

ethanolic sodium hydroxide solution (25%) at room temperature for 24 h. The deprotected acyclic-*C*-nucleosides, mainly 3-xylosyl and 3-glucosyl-6-(4-chlorophenyl)benzo[6,7]cyclohepta[1,2-*b*]pyrido[2,3-*e*][1,2,4]triazolo[2′,3′:5,6]pyrimidin-5(5*H*)-ones (**15a,b**) were obtained (Scheme 3). The IR (KBr) for compound **15b**, as an example, displayed absorption bands around 3439, 3465 (hydroxyl groups) and 3262 (NH) $cm^{-1}$ and revealed the absence of any absorption in the carbonyl region except that of the carbonyl pyrimidone. Also, its $^1$H-NMR spectrum showed signals at $\delta$ 1.67 (m, 4H, $2CH_2$), 2.59 (m, 2H, $CH_2$), 3.12 (m, 5H, 5OH, $D_2O$ exchangeable), 3.31 (m, 2H, $CH_2$), 3.37 (m, 1H, H-3′), 3.77 (m, 2H, H-5′, H-5″), 4.25 (m, 1H, H-2′), 4.60 (m, 1H, H-1′), 7.32–7.36 (d, 2H *p*-subs-phenyl), 7.51–7.55 (m, 1H, disub-phenyl), 7.75–7.78 (m, 2H, disub-phenyl), 8.21–8.32 (d, 2H, *p*-subs-phenyl), 8.40–8.45 (m, 1H, disub-phenyl), and 10.35 (brs, NH, $D_2O$ exchangeable).

## *EXPERIMENTAL*

All melting points are uncorrected. Microanalysis was carried out at the Microanalytical units, National Research Center and Faculty of Science, Cairo University. IR spectra were registered on a FT/IR-300 E Jasco using KBr disks. $^1$H-NMR spectra were measured in DMSO or $CDCl_3$, using JEOL-JNM-Ex270 NMR spectrometer. The mass spectra were recorded on Finnigan SSQ 7000 spectrometer. All reactions were followed up by TLC. The starting 2-hydrazino derivative was prepared according to El-Gazzar et al. [7].

### *6-(4-Chlorophenyl)benzo[6,7]cyclohepta[1,2-b]pyrido[2,3-e][1,2,4]triazolo[2′,3′:5,6]-pyrimidin-5(5H)-one* **2a**

A mixture of compound **1** (4.03 g, 0.01 mol) and formic acid (10 mL) was heated under reflux for 5 h. The reaction mixture was allowed to cool to room temperature and poured onto water. The solid product so precipitated was filtered off and recrystallized from dioxane to produce **2a** as colorless crystals. IR spectrum (KBr) ($cm^{-1}$): 3224 (NH), 2921 (CH aliphatic), and 1689 (CO). $^1$H-NMR (DMSO-$d_6$) $\delta$ (ppm): 1.72–1.84 (m, 4H, $2CH_2$), 2.56 (m, 2H, $CH_2$), 7.35–7.38 (d, 2H *p*-subs-phenyl), 7.54–7.57 (m, 1H, disub-phenyl), 7.82–7.91 (m, 2H, disub-phenyl), 8.23–8.26 (d, 2H, *p*-subs-phenyl), 8.34–8.37 (m, 1H, disubs-phenyl), 8.62 (s, 1H, triazole proton), and 13.02 (brs, $^1$H, NH, $D_2O$ exchangeable). MS (*m*/*z*): 413 ($M^+$) 100%, 415 ($M^+ + 1$) 37%.

### *3-Methyl-6-(4-chlorophenyl)benzo [6,7]cyclohepta-[1,2-b]pyrido[2,3-e][1,2,4] triazolo-[2′,3′:5,6]pyrimidin-5(5H)-one* **2b**

A mixture of compound **1** (4.03 g, 0.01 mol) and glacial acetic acid (30 mL) was refluxed for 5 h. The reaction mixture was allowed to cool to room temperature and poured into water. The precipitate was collected by filtration, dried, and recrystallized from acetic acid to produce **2b** as colorless crystals. IR spectrum (KBr) ($cm^{-1}$): 3277 (NH), 2985 (CH aliphatic), 1681 (CO). $^1$H-NMR (DMSO-$d_6$) $\delta$ (ppm): 1.73–181 (m, 4H, $2CH_2$), 2.41 (s, 3H, $CH_3$), 2.56 (m, 2H, $CH_2$), 7.31–7.35 (d, 2H, *p*-subs-phenyl), 7.45–7.47 (m, 1H, disub-phenyl), 7.86–7.90 (m, 2H, disub-phenyl), 8.25–8.27 (d, 2H, *p*-subs-phenyl), 8.32–8.35 (m, 1H, disub-phenyl), and 12.34 (brs, 1H, NH, $D_2O$ exchangeable).

### *2-(Acetylhydrazone)-5-(4-chlorophenyl)benzo [6,7]cyclohepta[1,2-b]pyrido[2,3-e]-pyrimidin-4-one* **3**

A mixture of compound **1** (4.03 g, 0.01 mol) and glacial acetic acid (30 mL) was refluxed for 2 h. The reaction mixture was allowed to cool to room temperature and poured into water. The precipitate was

collected by filtration, dried, and recrystallized from acetic acid to produce **3** as colorless crystals. IR spectrum (KBr) ($cm^{-1}$): 3287 (NH), 3215 (NH), 2985 (CH aliphatic), 1700 (CO), and 1689 (CO). $^1$H-NMR (DMSO-$d_6$) $\delta$ (ppm): 1.70–1.83 (m, 4H, $2CH_2$), 2.66 (s, 3H, $CH_3$), 2.54 (m, 2H, $CH_2$),7.31–7.33 (d, 2H *p*-subs-phenyl), 7.58–7.60 (m, 1H, disub-phenyl), 7.81–7.84 (m, 2H, disub-phenyl), 8.34–8.36 (d, 2H, *p*-subs-phenyl), 8.41–8.44 (m, 1H, disubs-phenyl), and two bands at 12.18 (brs, 1H, NH) and 13.17 (brs, 1H, NH, $D_2O$ exchangeable).

### *3(3H)-Thioxo-6-(4-chlorophenyl)benzo [6,7]cyclohepta[1,2-b]pyrido[2,3-e][1,2,4]-triazolo[2′,3′:5,6]pyrimidin-5(5H)-one* **4**

To a warmed ethanolic sodium hydroxide solution (prepared by dissolving sodium hydroxide (0.40 g, 0.01 mol) in ethanol (50 mL)), compound **1** (4.03 g, 0.01 mol) and carbon disulfide (10 mL) was added. The mixture was heated on a water bath at 80°C under reflux for 10 h, then it was poured into water, neutralized by diluted acetic acid, and the formed precipitate was filtered off. The product was recrystallized from dioxane to produce **4** as yellow crystals. IR spectrum (KBr) ($cm^{-1}$): 3404 (NH), 3122 (NH), 2929 (CH aliphatic), and 1664 (CO). $^1$H-NMR (DMSO-$d_6$ $\delta$ 1.73–1.81 (m, 4H, $2CH_2$), 2.54 (m, 2H, $CH_2$), 7.33–7.35 (d, 2H, *p*-subs-phenyl), 7.51–7.53 (m, 1H, disub-phenyl), 7.77–7.80 (m, 2H, disub-phenyl), 8.19–8.21 (d, 2H, *p*-subs-phenyl), 8.40–8.42 (m, 1H, disub-phenyl), and 11.09 (brs, 1H, NH, $D_2O$ exchangeable). MS (*m/z*): 445 ($M^+$) 100%.

### *3-Methyl-7-(4-chlorophenyl)benzo [6,7]cyclohepta[1,2-b]pyrido[2,3-e][1,2,4]-triazin[2′,3′:5,6]pyrimidin-5(5H)-one* **5**

A mixture of compound **1** (4.03 g, 0.01 mol) and chloroacetone (0.93 g, 0.01 mole) was heated under reflux for 6 h in dry xylene (30 mL). The solid product precipitated was filtered off and recrystallized from dioxane to produce **5** as yellow crystals. IR spectrum (KBr) ($cm^{-1}$): 3373 (NH), 2918 (CH aliphatic), and 1688 (CO).$^1$H-NMR (DMSO-$d_6$) $\delta$ (ppm): 1.71–1.83 (m, 4H, $2CH_2$), 2.05 (s, 3H, $CH_3$), 2.56 (m, 2H, $CH_2$), 4.80 (s, 2H, $CH_2$), 7.20–7.30 (d, 2H, *p*-sub-phenyl), 7.35–7.40 (m, 1H, disub-phenyl), 7.45–7.55 (m, 4H, 2H, disub-phenyl + 2H *p*-sub-phenyl), 8.25–8.40 (m, 1H, disub-phenyl), and 11.05 (brs, NH, $D_2O$ exchangeable). MS (*m/z*): 441 ($M^+$).

### *2-Ethylacetoacetatehydrazon-3H-5-(4-chlorophenyl)benzo[6,7]cyclohepta[1,2-b]-pyrido[2,3-e]pyrimidin-4-one* **6**

A mixture of compound **1** (4.03 g, 0.01 mol) and ethyl acetoacetate (1.30 g, 0.01 mol) was heated under reflux in absolute ethanol for 5 h. The reaction mixture was allowed to cool to room temperature and poured into water. The precipitate so formed was collected by filtration, dried, and recrystallized from ethanol to produce **6** as colorless crystals. IR spectrum (KBr) ($cm^{-1}$): 3279 (NH), 3206 (NH), 2975 (CH aliphatic), 1741 (CO), and 1643 (CO). $^1$H-NMR ($CDCl_3$) $\delta$(ppm): $\delta$ 1.25 (t, 3H, $CH_3$), 1.72–1.84 (m, 4H, $2CH_2$), 2.00 (s, 3H, $CH_3$), 2.58 (m, 2H, $CH_2$), 3.35 (s, 2H, $CH_2$), 4.15 (q, 2H, $CH_2$), 7.15–7.25 (d, 2H, *p*-sub-phenyl), 7.25–7.30 (m, 1H, disub-phenyl), 7.30–7.35 (m, 2H, disub-phenyl), 7.40–7.50 (d, 2H, *p*-sub-phenyl), 8.20–8.30 (m, 1H, disub-phenyl), 9.80–10.40 (brs, 1H, NH, $D_2O$ exchangeable), and 11.15 (brs, NH, $D_2O$ exchangeable).

### *2-(3-Methyl-5-oxo-4H-pyrazol-1-yl)-3H-5-(4-chlorophenyl)benzo[6,7]cyclohepta[1,2-b]pyrido[2,3-e]pyrimidin-4-one* **7**

*Method A.* A solution of compound **1** (4.03 g, 0.01 mol) and ethyl acetoacetate (1.30 g, 0.01mol) in sodium ethoxide solution (prepared by dissolving sodium metal (0.23 g , 0.01 mol) in absolute ethanol (30 mL)) was heated under reflux for 5 h. The reaction mixture was allowed to cool to room temperature, poured into water, and neutralized by diluted acetic acid solution. The solid product so precipitated was filtered off, dried, and recrystallized from dimethylformamide to produce **7** as colorless crystals.

*Method B.* A solution of compound **6** (5.15 g, 0.01 mol) was heated under reflux with sodium ethoxide solution (prepared by dissolving sodium metal (0.23 g, 0.01 mol) in absolute ethanol (30 mL)) for 5 h. The reaction mixture was allowed to cool to room temperature then poured into water and neutralized by diluted acetic acid solution. The precipitate formed was collected by filtration, dried, and recrystallized from dimethylformamide to produce **7** as colorless crystals. IR spectrum (KBr) ($cm^{-1}$): 3446 (OH), 2922 (CH aliphatic), and 1654 (CO) .$^1$H-NMR ($CDCl_3$-TFA) (ppm): $\delta$ 1.73–1.86 (m, 4H, $2CH_2$), 2.50 (s, 3H, $CH_3$), 2.55–2.70 (m, 2H, $CH_2$), 3.45 (s, 2H, $CH_2$), 7.15–7.25 (d, 2H, *p*-sub-phenyl), 7.25–7.30 (m, 1H, disub-phenyl), 7.35–7.40 (m, 2H, disub-phenyl), 7.45–7.50 (d, 2H,

*p*-sub-phenyl), 8.35–8.45 (m, 1H, disub-phenyl), and 14.3 (brs, NH, $D_2O$ exchangeable). MS (*m/z*): 469 ($M^+$).

### *Synthesis of the adducts* **8a,b**

*General Procedure.* To an ice-cold solution of the appropriate aromatic amine (0.01 mol) in concentrated hydrochloric acid (3 mL) was added dropwise a solution of sodium nitrite (1.03 g, 0.01 mol) dissolved in the least amount of water, in an ice bath at −5°C. This previously prepared diazonium salt was added dropwise to a mixture of **7** (4.69 g, 0.01 mol) and anhydrous sodium acetate in ethanol. The reaction mixture was allowed to stand overnight at room temperature, then it was poured into water. The formed solid was filtered off, washed with water, dried and recrystallized from dioxane to produce **8a,b**, respectively.

*Preparation of* **8a**. From 4-chloroaniline (1.27 g, 0.01 mol), **8a** was obtained as dark yellow crystals. IR (KBr) ($cm^{-1}$): 3450 (OH), 3180 (NH), and 1671 (CO). The $^1$H-NMR spectrum (DMSO-$d_6$) (ppm): $\delta$ 1.72 (m, 4H, $2CH_2$), 2.34 (s, 3H, $CH_3$), 2.58 (m, 2H, $CH_2$), 7.33–7.35 (two d, 4H, *p*-subs-phenyl), 7.51–7.53 (m, 1H, disub-phenyl), 7.77–7.80 (m, 2H, disub-phenyl), 8.19–8.21 (d, 2H, *p*-subs-phenyl), 8.23–8.26 (d, 2H, *p*-subs-phenyl), 8.40–8.42 (m, 1H, disub-phenyl), 9.21 (brs, 1H, NH, $D_2O$ exchangeable), and 13.02 (brs, 1H, OH, $D_2O$ exchangeable). Its mass spectrum showed the molecular ion at peak *m/z* 608 ($M^+$), 100%.

*Preparation of* **8b**. From 4-methoxyaniline (1.13 g, 0.01 mol), **8b** was obtained as orange crystals. IR (KBr) ($cm^{-1}$): 3398 (OH), 3230 (NH), and 1681 (CO). The $^1$H-NMR spectrum (DMSO-$d_6$) (ppm): $\delta$ 1.70 ppm (m, 4H, $2CH_2$), 2.31 (s, 3H, $CH_3$), 2.56 (m, 2H, $CH_2$), 4.20 (s, 3H, $OCH_3$) 7.34–7.36 (two d, 4H, *p*-subs-phenyl), 7.51–7.54 (m, 1H, disub-phenyl), 7.79–7.81 (m, 2H, disub-phenyl), 8.21–8.24 (d, 2H, *p*-subs-phenyl), 8.33–8.36 (d, 2H, *p*-subs-phenyl), 8.42–8.45 (m, 1H, disub-phenyl), and 9.56 (brs, 1H, NH, $D_2O$ exchangeable). 13.22 (brs, 1H, OH, $D_2O$ exchangeable).

### *2-(3-Amino-5-oxo-4H-pyrazol-1-yl)-3H-5-(4-chlorophenyl)benzo[6,7]cyclohepta[1,2-b]pyrido[2,3-e]pyrimidin-4-one* **9**

To a warmed ethanolic sodium ethoxide solution (prepared by dissolving sodium metal (0.23 g, 0.01 mol) in absolute ethanol (30 mL)) was added compound **1** (4.03 g, 0.01 mol) and ethyl cyanoacetate (1.13 g, 0.01 mol). The heating was continued for 5 h. The reaction mixture was allowed to cool to room temperature, poured into water, and neutralized by diluted acetic acid solution. The solid product so precipitated was filtered off, dried, and recrystallized from dimethylformamide to produce **9** as yellow crystals. IR spectrum (KBr) ($cm^{-1}$): 3340 ($NH_2$), 3260 (NH), and 1687 (CO). Its $^1$H-NMR spectrum (DMSO-$d_6$) (ppm): $\delta$ 1.73–181 (m, 4H, $2CH_2$), 2.54 (m, 2H, $CH_2$), 5.02 (brs, 2H, $NH_2$, $D_2O$ exchangeable), 7.23–7.35 (d, 2H *p*-subs-phenyl), 7.50–7.53 (m, 1H, disub-phenyl), 7.71–7.74 (m, 2H, disub-phenyl), 8.0 (s, 1H, pyrazole proton), 8.20–8.24 (d, 2H, *p*-subs-phenyl), 8.39–8.42 (m, 1H, disub-phenyl), 9.68 (brs, 1H, NH, $D_2O$ exchangeable).

### *2-(3,5-Dimethyl-pyrazol-1-yl)-3H-5-(4-chlorophenyl)benzo[6,7]cyclohepta[1,2-b]pyrido[2,3-e]pyrimidin-4-one* **10a,b**

*General Procedure.* A mixture of compound **1** (4.03 g, 0.01 mol) and the appropriate β-diketone (0.01 mol) was heated under reflux in absolute ethanol (30 mL) for 5 h. The reaction mixture was allowed to cool to room temperature. The precipitate solid was collected by filtration, dried, and crystallized from dioxane to produce **10a,b**, respectively.

*2-(3,5-Dimethyl-pyrazol-1-yl)-3H-5-(4-chlorophenyl)benzo[6,7]cyclohepta[1,2-b]-pyrido[2,3-e]pyrimidin-4-one* **10a**. Obtained from compound **1** (4.03 g, 0.01 mol) and pentane-2,4-dione (1.00 g, 0.01 mol), the product was recrystallized from dioxane to produce **10a** as pale yellow crystals. IR spectrum (KBr) ($cm^{-1}$): 3239 (NH), 2917 (CH aliphatic), and 1686 (CO). The $^1$H-NMR spectrum (DMSO-$d_6$) (ppm): $\delta$ 1.68 (m, 4H, $2CH_2$), 2.5 5 (m̃, 2H, $CH_2$), 2.61 (s, 3H, $CH_3$), 2.98 (s, 3H, $CH_3$), 6.20 (s, 1H, CH), 7.21–7.30 (d, 2H *p*-subs-phenyl), 7.47–7.51 (m, 1H, disub-phenyl), 7.69–7.72 (m, 2H, disub-phenyl), 8.21–8.25 (d, 2H, *p*-subs-phenyl), 8.36–8.40 (m, 1H, disubs-phenyl), and 11.70 (brs, 1H, NH, $D_2O$ exchangeable). Its mass spectrum showed the molecular ion peak at *m/z* 467.

*2-(4-Chloro-3,5-dimethyl-pyrazol-1-yl)-3H-5-(4-chlorophenyl) benzo[6,7]cyclohepta-[1,2-b]pyrido[2,3-e]pyrimidin-4-one* **10b**. Obtained from compound **1** (4.03 g, 0.01 mol) and 3-chloropentane-2,4-dione (1.34 g, 0.01 mol). The product was recrystallized from dioxane to produce **10b** as orange crystals. IR spectrum (KBr) ($cm^{-1}$): 3254 (NH), 2914 (CH aliphatic), and 1694 (CO). The $^1$H-NMR spectrum (DMSO-$d_6$) (ppm): $\delta$ 1.73 (m, 4H, $2CH_2$), 2.52 (m, 2H, $CH_2$), 2.64 (s, 3H, $CH_3$), 2.92 (s, 3H, $CH_3$),

7.19–7.27 (d, 2H, *p*-subs-phenyl), 7.44–7.50 (m, 1H, disub-phenyl), 7.67–7.67 (m, 2H, disub-phenyl), 8.15–8.22 (d, 2H, *p*-subs-phenyl), 8.38–8.41 (m, 1H, disub-phenyl), and 11.40 (brs, 1H, NH, $D_2O$ exchangeable). Its mass spectrum showed the molecular ion peak at *m/z* 502.

### *2-(Arylmethylenehydrazone)-5-(4-chlorophenyl)-benzo[6,7]cyclohepta[1,2-b]pyrido[2,3-e]pyrimidin-4-one* **11a,b**

*General Procedure*. A mixture of compound **1** (4.03 g, 0.01 mol) and the appropriate aromatic aldehyde (0.01 mol), dioxane (30 mL), and a catalytic amount of piperidine was heated under reflux for 6 h. The reaction mixture was allowed to cool to room temperature, then it was poured into water. The formed precipitate was filtered off, washed with water, dried and recrystallized from dimethylformamide to produce **11a,b**.

*2-(Phenylmethylenehydrazone)-5-(4-chlorophenyl)-benzo[6,7]cyclohepta[1,2-b]-pyrido[2,3-e]pyrimidin-4-one* **11a**. Obtained from benzaldehyde (1.06 g, 0.01 mol). The product was recrystallized from dimethylformamide to produce **11a** as pale yellow crystals. IR spectrum (KBr) ($cm^{-1}$): 3326 2 (NH), 2914 (CH aliphatic), and 1686 (CO). The $^1$H-NMR spectrum (DMSO-$d_6$) (ppm): $\delta$ 1.68 (m, 4H, $2CH_2$), 2.59 (m, 2H, $CH_2$), 7.19–7.25 (d, 2H, *p*-subs-phenyl), 7.40–7.47 (m, 4H, 1H for disub-phenyl + 3H for phenyl), 7.64–7.70 (m, 4H, 2H for disub-phenyl + 2H for phenyl), 8.19–8.23 (d, 2H, *p*-subs-phenyl), 8.29 (s, 1H, methylenic proton), 8.37–8.42 (m, 1H, disub-phenyl), and 11.25 (brs, 1H, NH, $D_2O$ exchangeable), 13.05 (brs, 1H, NH, $D_2O$ exchangeable). Mass spectrum showed the molecular ion peak at *m/z* 491.

*2-(4-Methoxyphenylmethylenehydrazone)-5-(4-chlorophenyl)benzo[6,7]cyclohepta-[1,2-b]pyrido[2,3-e] pyrimidin-4-one* **11b**. Obtained from 4-methoxybenzaldehyde (1.36 g, 0.01 mol). The product was crystallized from dimethylformamide to produce **11b** as yellow crystals. IR spectrum (KBr) ($cm^{-1}$): 3312 2(NH), 2934 (CH aliphatic), and 1692 (CO). The $^1$H-NMR spectrum (DMSO-$d_6$) (ppm): $\delta$ 1.71 (m, 4H, $2CH_2$), 2.54 (m, 2H, $CH_2$), 3.97 (s, 3H, $OCH_3$), 7.09–7.14 (d, 2H, *p*-subs-phenyl), 7.18–7.23 (d, 2H *p*-subs-phenyl), 7.39–7.44 (m, 1H, disub-phenyl), 7.56–7.67 (m, 4H, 2H for disub-phenyl + 2H for *p*-subs-phenyl), 8.20–8.23 (d, 2H, *p*-subs-phenyl), 8.37 (s, 1H, methylenic proton), 8.45–8.50 (m, 1H, disubs-phenyl), 10.60 (brs, 1H, NH, $D_2O$ exchangeable), and 12.90 (brs, 1H, NH, $D_2O$ exchangeable). Mass spectrum showed the molecular ion peak at *m/z* 521.

### *3-Aryl-6-(4-chlorophenyl)benzo[6,7]cyclohepta-[1,2-b]pyrido[2,3-e][1,2,4]triazolo-[2′,3′:5,6] pyrimidin-5(5H)-ones* **12a,b**

*General Procedure*. A mixture of compound (**11a** or **11b**) (10 mmol), anhydrous sodium acetate (1.64 g, 20 mmol), and bromine (1.60 g, 10 mmol) was heated gently in glacial acetic acid (30 mL) in water bath at 80°C for long time (under TLC control). The reaction mixture was allowed to cool to room temperature, poured into water (100 mL), and the solid so-formed was collected by filtration and crystallized from appropriate solvents, to produce **12a,b**, respectively.

*3-Phenyl-6-(4-chlorophenyl)benzo[6,7]cyclohepta [1,2-b ]pyrido[2,3-e][1,2,4]triazolo-[2′,3′:5,6]pyrimidin-5(5H)-ones* **12a**. Obtained from compound **11a** (4.91 g, 10 mmol). The product was recrystallized from dimethylformamide to produce **12a** as orange powder. IR spectrum (KBr) ($cm^{-1}$): 3370 (NH) and 1685 (C=O). The $^1$H-NMR spectrum (DMSO-$d_6$) (ppm): $\delta$ 1.70 (m, 4H, $2CH_2$), 2.54 (m, 2H, $CH_2$), 7.20–7.28 (d, 2H, *p*-subs-phenyl), 7.43–7.47 (m, 4H, 1H for disub-phenyl + 3H for phenyl), 7.61–7.70 (m, 4H, 2H for disub-phenyl + 2H for phenyl), 8.21–8.25 (d, 2H, *p*-subs-phenyl), 8.36–8.40 (m, 1H, disub-phenyl), and 10.65 (brs, 1H, NH, $D_2O$ exchangeable). Mass spectrum showed the molecular ion peak at *m/z* 489.

*3-(4-Methoxyphenyl)-6-(4-chlorophenyl)benzo[6,7] cyclohepta[1,2-b]pyrido[2,3-e]-[1,2,4]triazolo[2′,3′:5,6] pyrimidin-5(5H)-ones* **12b**. Obtained from compound **11b** (5.21g, 10 mmol). The product was recrystallized from dimethylformamide to produce **12b** as yellow powder. IR spectrum (KBr) ($cm^{-1}$): 3354 (NH) and 1687 (C=O). The $^1$H-NMR spectrum (DMSO-$d_6$) (ppm): $\delta$ 1.72 (m, 4H, $2CH_2$), 2.53 (m, 2H, $CH_2$), 3.39 (s, 3H, $OCH_3$), 7.07–7.12 (d, 2H, *p*-subs-phenyl), 7.22–7.27 (d, 2H *p*-subs-phenyl), 7.40–7.45 (m, 1H, disub-phenyl), 7.59–7.68 (m, 4H, 2H for disub-phenyl + 2H for *p*-subs-phenyl), 8.20–8.23 (d, 2H, *p*-subs-phenyl), 8.39–8.42 (m, 1H, disubs-phenyl), and 10.24 (brs, 1H, NH, $D_2O$ exchangeable). Mass spectrum showed the molecular ion peak at *m/z* 503.

*2-(Glycosylhydrazon)-5-(4-chlorophenyl)benzo [6,7]cyclohepta[1,2-b]pyrido[2,3-e]-pyrimidin-4-one* **13a,b**

*General Procedure.* A solution of compound **1** (10 mmol) and xylose or glucose (10 mmol) in dry dioxane in the presence of catalytic amounts of pipridine was refluxed for 6 h, poured into water (100 mL), and neutralized with hydrochloric acid. The solid that was separated filtered, washed with ethanol, dried, and crystallized from the proper solvent to produce **13a,b** in good yields.

*2-(Xylosylhydrazon)-5-(4-chlorophenyl)benzo [6,7]cyclohepta[1,2-b]pyrido[2,3-e]pyr-imidin-4-one* **13a**

Obtained from D-xylose (1.50 g, 10 mmol). The compound was obtained as white powder, crystallized from dioxane. IR (KBr) ($cm^{-1}$): 3430 (broad, OH), 3221 (NH), 1687 (C=O). $^1$H-NMR (DMSO-$d_6$) (ppm): $\delta$ 1.67 (m, 4H, $2CH_2$), 2.55 (m, 2H, $CH_2$), 3.31 (m, 2H, $CH_2$), 3.53 (m, 4OH, $D_2O$ exchangeable, OH-2′, OH-5′), 4.21 (q, 1H, $J = 6$ Hz, H-4′), 4.45 (m, 2H, H-5″), 4.61 (d, 1H, $J = 5$ Hz, H-3′), 5.76 (dd, 1H, $J = 7$ Hz, H-2′), 7.29 (d, 1H, $J = 4$ Hz, H-1′), 7.35–7.37 (d, 2H *p*-subs-phenyl), 7.50–7.53 (m, 1H, disub-phenyl), 7.76–7.80 (m, 2H, disub-phenyl), 8.18–8.21 (d, 2H, *p*-subs-phenyl), 8.39–8.42 (m, 1H, disubs-phenyl), and 11.25 (brs, 1H, NH, $D_2O$ exchangeable). MS (*m/z*): 536 ($M^+$) 100%.

*2-(Glucosylhydrazon)-5-(4-chlorophenyl)benzo[6,7] cyclohepta-[1,2-b]pyrido[2,3-e]pyrimidin-4-one* **13b**. Obtained from D-glucose (1.80 g, 10 mmol). The compound was obtained as white powder, crystallized from dioxane. IR (KBr) ($cm^{-1}$): 3450 (broad, OH), 3217 (NH), 1688 (C=O). $^1$H-NMR (DMSO-$d_6$) (ppm): $\delta$ 1.67 (m, 4H, $2CH_2$), 2.56 (m, 2H, $CH_2$), 3.25 (m, 2H, $CH_2$), 3.61 (m, 5H, 5OH, $D_2O$ exchangeable OH-2′-OH-6′), 4.24 (m, 1H, CH, H-3′), 4.36 (m, 2H, $CH_2$, H2-6′), 4.53 (m, 2H, 2CH, H-3′, and H-4′), 5.22 (dd, 1H, CH, $J = 7.5$ Hz, H-2′), 7.35–7.37 (d, 2H, *p*-subs-phenyl), 7.43–7.47 (m, 1H, disub-phenyl), 7.53 (d, 1H, $J = 7.5$, H-1′), 7.77–7.80 (m, 2H, disub-phenyl), 8.19–8.23 (d, 2H, *p*-subs-phenyl), 8.40–8.42 (m, 1H, disubs-phenyl), 10.12 (brs, 1H, NH, $D_2O$ exchangeable), and 11.85 (brs, 1H, NH, $D_2O$ exchangeable). MS (*m/z*): 565 ($M^+$) 100%.

*3-(O-Acetylglycosyl)-6-(4-chlorophenyl)benzo [6,7]cyclohepta[1,2-b]pyrido[2,3-e]-[1,2,4]triazolo [2′,3′ : 5,6]pyrimidin-5(5H)-ones* **14a,b**.

*General Procedure.* A solution of compounds **13a,b** (10 mmol) in a mixture of acetic anhydride-pyridine (20 ml: 20 ml) was stirred at room temperature for 24 h, poured into water (100 mL). The reaction mixture was then extracted with chloroform several times, and after the removal of chloroform under reduced pressure the formed crystals were recrystallized from the proper solvent to produce **14a,b**, in good yields.

*3-(2′,3′,4′,5′-O-tetraacetyl-xylosyl)-6-(4-chlorophenyl)benzo[6,7]cyclohepta-[1,2-b]pyrido[2,3-e][1,2,4] triazolo[2′,3′:5,6]pyrimidin-5(5H)-one* **14a**. Obtained from compound **13a** (3.82 g, 10 mmol). The compound was obtained as white crystals, which was crystallized from ethanol. IR (KBr) ($cm^{-1}$): 3220 (NH), 1751–1729 (4 C=O, acetyl) 1681 (C=O, pyrimidone). $^1$H-NMR ($CDCl_3$) (ppm): $\delta$ 1.69 (m, 4H, $2CH_2$), 1.94 (s, 3H, $CH_3$), 2.11 (s, 3H, $CH_3$), 2.14 (s, 3H, $CH_3$), 2.20 (s, 3H, $CH_3$) 2.60 (m, 2H, $CH_2$), 3.22 (m, 2H, $CH_2$), 4.65 (m, 1H, H-3′), 5.23 (m, 2H, H-4′), 5.44 (m, 1H, H-2′), 5.75 (m, 1H, H-1′), 7.29–7.31 (d, 2H *p*-subs-phenyl), 7.46–7.52 (m, 1H, disub-phenyl), 7.74–7.79 (m, 2H, disub-phenyl), 8.20–8.23 (d, 2H, *p*-subs-phenyl), 8.38–8.41 (m, 1H, disubs-phenyl), and 10.11 (brs, NH, $D_2O$ exchangeable). MS (*m/z*): 702 ($M^+$) 100%.

*3-(1′,2′,3′,4′,5′-O-Pentaacetyl-glucosyl)-6-(4-chlorophenyl)benzo[6,7]cyclohepta-[1,2-b]pyrido[2,3-e][1, 2,4]triazolo[2′,3′:5,6]pyrimidin-5(5H)-one* **14b**. Obtained from compound **13b** (4.12 g, 10 mmol). The compound was obtained as white powder, which was crystallized from ethanol. IR (KBr) ($cm^{-1}$): 3310 (NH), 1743–1720 (5 C=O, acetyl) 1689 (C=O, pyrimidone). $^1$H-NMR ($CDCl_3$) (ppm): $\delta$ 1.70 (m, 4H, $2CH_2$), 1.84 (s, 3H, $CH_3$), 1.90 (s, 3H, $CH_3$), 2.10 (s, 3H, $CH_3$), 2.35 (s, 3H, $CH_3$), 2.44 (s, 3H, $CH_3$), 2.57 (m, 2H, $CH_2$), 3.36 (m, 2H, $CH_2$), 4.67 (m, 1H, H-4′), 5.26 (d, 1H, $J = 10.6$ Hz, H-3′), 5.40 (m, 2H, H2′, 5′), 5.62 (s, 1H, H-2′), 5.73 (s, 1H, H-1′), 7.30–7.32 (d, 2H, *p*-subs-phenyl), 7.44–7.49 (m, 1H, disub-phenyl), 7.69–7.73 (m, 2H, disub-phenyl), 8.22–8.25 (d, 2H, *p*-subs-phenyl), 8.39–8.42 (m, 1H, disubs-phenyl), 10.55 (brs, 1H, NH, $D_2O$ exchangeable). MS (*m/z*): 754 ($M^+$) 100%.

*3-(Glycosyl)-6-(4-chlorophenyl)benzo[6,7] cyclohepta-[1,2-b]pyrido[2,3-e][1,2,4]tri-azolo [2′,3′:5,6]pyrimidin-5(5H)-ones* **15a,b**

*General Procedure.* A solution of compounds **14a,b** (10 mmol) in methanolic ammonia solution (25%, 50 mL) was stirred at room temperature for 24 h, then neutralized with hydrochloric acid solution (under pH control). The excess of methanol was removed under reduced pressure, whereby a solid was precipitated. The precipitate so formed was filtered

off, wash with cold water, dried and was recrystallized from the proper solvent to produce the compounds **15a,b**, in good yield.

*3-Xylosy-6-(4-chlorophenyl)benzo[6,7]cyclohepta-[1,2-b]pyrido[2,3-e][1,2,4]tri-azolo[2′,3′:5,6]pyrimidin-5(5H)-one* **15a**. Obtained from compound **14a** (2.74 g, 5 mmol). The compound was obtained as white powder, which was crystallized from ethanol. IR (KBr) ($cm^{-1}$): 3431–3460 (broads band OH), 3210 (NH), 1681 (C=O, pyrimidone). $^1$H-NMR ($CDCl_3$) (ppm): $\delta$ 1.71 (m, 4H, $2CH_2$), 2.57 (m, 2H, $CH_2$), 4.40 (m, 4H, 4OH, $D_2O$ exchangeable, OH-1′, OH-4′), 4.65 (m, 1H, H-3′), 4.88 (m, 2H, H2–4′), 5.10 (m, 1H, H-2′), 7.29–7.32 (d, 2H *p*-subs-phenyl), 7.43–7.48 (m, 1H, disub-phenyl), 7.70–7.74 (m, 2H, disub-phenyl), 8.23–8.26 (d, 2H, *p*-subs-phenyl), 8.40–8.41 (m, 1H, disubs-phenyl), and 9.20 (brs, NH, $D_2O$ exchangeable).

*3-Glucosyl-6-(4-chlorophenyl)benzo[6,7]cyclohepta[1,2-b]pyrido[2,3-e][1,2,4]tri-azolo[2′,3′:5,6]pyrimidin-5(5H)-one* **15b**. Obtained from compound **14b** (3.10 g, 5 mmol). The compound was obtained as white crystals, which was crystallized from ethanol. IR (KBr) ($cm^{-1}$): 3439, 3465 (broads band OH), 3262 (NH), 1689 (C=O, pyrimidone). $^1$H-NMR ($CDCl_3$) (ppm): $\delta$ 1.67 (m, 4H, $2CH_2$), 2.59 (m, 2H, $CH_2$), 3.12 (m, 5H, 5OH, $D_2O$ exchangeable), 3.31 (m, 2H, $CH_2$), 3.37 (m, 1H, H-3′), 3.77 (m, 2H, H-5′, H-5″), 4.25 (m, 1H, H-2′), 4.60 (m, 1H, H-1′), 7.32–7.36 (d, 2H *p*-subs-phenyl) 7.51–7.55 (m, 1H, disub-phenyl), 7.75–7.78 (m, 2H, disub-phenyl), 8.21–8.32 (d, 2H, *p*-subs-phenyl), 8.40–8.45 (m, 1H, disubs-phenyl), 10.35 (brs, NH, $D_2O$ exchangeable).

## *CONCLUSION*

The present investigation offers rapid and effective new procedures for the synthesis of the *C*-nucleosides systems. Furthermore, the prepared new ring systems and *C*-nucleoside are interesting for biological activity studies. The latter will be published elsewhere.

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