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SYNTHESIS OF SOME NEW 5-PHENYLAZOTHIAZOLES AND PYRAZOLO [1,5-*a*] PYRIMIDINES

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ABSTRACT

Condensation of indole-3-carboxaldehyde (1) with thiosemicarbazide **2** afforded 1H-indole-3-carbaldehyde thiosemicarbazone (**4**) which reacted with hydrazonoyl halides **7** to afford 5-arylazothiazoles **9**. Pyrazolo[1,5-*a*]pyrimidines **15** and 7-(2-naphthyl)pyrazolo[1,5-*a*]pyrimidine **23** were obtained by reaction of sodium salt of (2-oxocycloalkylidine)methanolate **11** and 1-naphthyl-3-hydroxy-2-propene-1-one **17** with aminopyrazoles **10**. Structures of the newly synthesized compounds were elucidated by elemental analysis, spectral data, alternative synthesis route whenever possible and X-ray single crystal.

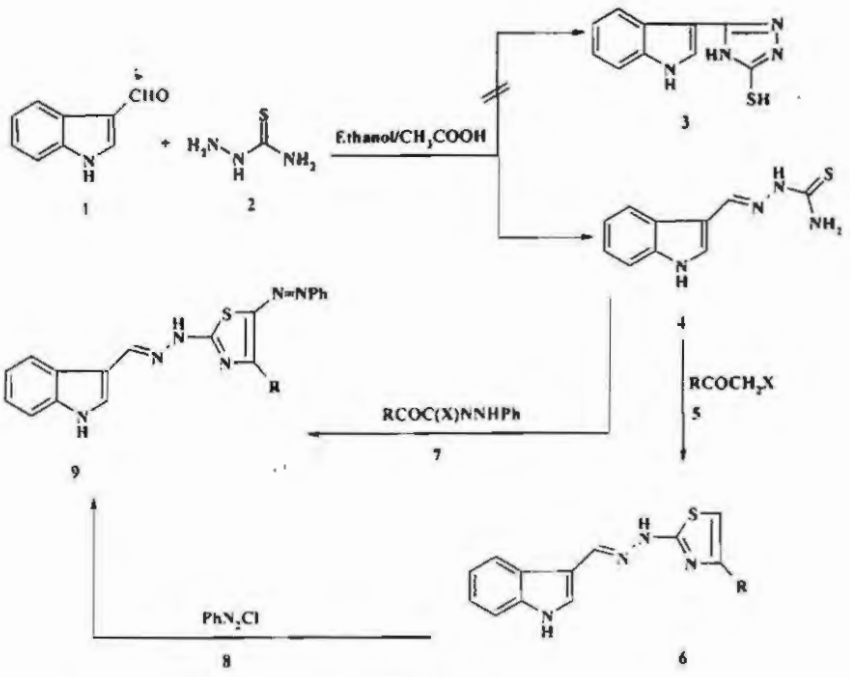
INTRODUCTION

Thiazoles are common substructures of monocyclic natural products, **[Shaojiang & Jack (2005)]**, that exhibit a range of biological activities **[Sasse et al. (2002); Cheng et al. (2002); Roy et al. (1999); Konz et al. (1997); Molnar et al. (2000) and Tang et al. (2000)]** including potent immunosuppression, inhibition of bacterial protein synthesis **[Cameron et al. (2002)]**. Also, pyrazolo[1,5-*a*]pyrimidines are potent and selective antagonist of carticotropin releasing factor receptor-1 with an efficacious anxiolityic profile in preclinical animal models **[Wong et al. (2005)]**. Preliminary tests of some pyrazolo[1,5-*a*]pyrimidines showed strong antischistosomiasis **[Yuh-Wen (1999) and Elnagdi et al. (1981)]**. As a part of our program directed for development of new simple and efficient procedures for the synthesis of antimetabolites **[Abdelhamid et al. (2005); Abdelhamid et al. (2006) and Zaki et al. (2006)]**. We have recently reported different successful

approaches for synthesis of purine analogues and pyrimidines **[Ahmed et al. (2007)]**. Derivatives of these ring system are interesting because they have useful properties as antimetabolites in biochemical reactions. Elgemeie and Coworkers have been reported the synthesis of purine analogues and other antimetabolites by using the sodium salt of cycloalkanones **[Elgemeie et al. (2002); Elgemeie & Hussain (1994); Elgemeie & Metwally (1999) and Rees & Yelland (1972)].**

RESULTS AND DISCUSSION

Recently an ambiguous product namely 3-indol-3-yl-triazolin-5-thione (**3**) was claimed [**Abdel-Latif et al. (2005)**] to be obtained in 80% yield from reaction of 3-formylindole with thiosemicarbazide (Scheme 1), the identity of the product from this reaction has to be reinvestigated. Accordingly, I have studied the reaction between 3-formylindole and thiosemicarbazide and the obtained product **4** was compared with **3**. Structure **4** was confirmed by elemental analysis, spectral data, X-ray and chemical transformation. Thus compound **4** is supported by its mass spectrum which showed a molecular formula $C_{10}H_{10}N_4S$ (M^+ 218). ^1H NMR spectrum revealed signals at δ = 7.0-7.6 (m, 4H, aromatic protons), 7.8 (s, 2H, NH_2), 8.1(s, 1H, aromatic CH), 8.5 (s, 1H, vinyl CH), 11.2 (s, 1H, NH) and 11.8 (s, 1H, NH). Conclusion evidence was obtained by X-ray crystallographic analysis of compound **4** (Fig 1). Thus, compound **4** reacted with the appropriate hydrazonyl halides **7a-d** to give 5-phenylazothiazoles **9a-d**. Compounds **9** were elucidated by elemental analysis, spectral data and alternative synthesis route. Thus, compound **9a** is supported by its mass spectrum, which showed a molecular formula $C_{19}H_{16}N_6S$ (M^+ 360). ^1H NMR spectrum showed signals at δ = 3.1 (s, 3H, CH_3), 7.3-8.6 (m, 10H, aromatic protons), 8.9 (s, 1H, yiledinic CH), 10 (s, 1H, NH) and 11.8 (s, 1H, NH). Also, compound **4** reacted with the appropriate halo ketone **5a-d** to give the thiazole **6a-d**, (Scheme 1). The latter, was treated with benzendiazonum chloride **8** in pyridine to give product **9** in all aspects (mp., mixed mp. and spectra).



RCOC(X)NNHPh

7a, X = Cl, R = CH_3
b, X = Br, R = C_6H_5
c, X = Br, R = 2-C_4H_3S
d, X = Br, R = 2-$C_{10}H_7$

6,9, a = CH_3
b = C_6H_5
c = 2-C_4H_3S
d = 2-$C_{10}H_7$

Scheme I

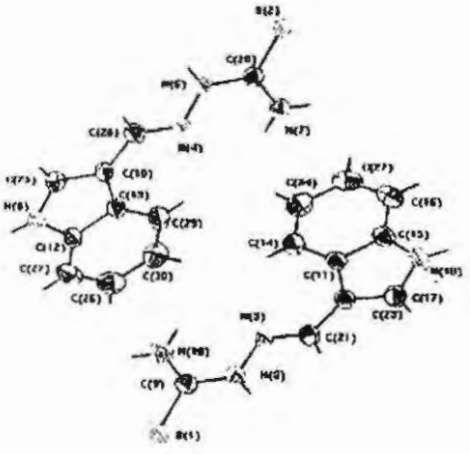
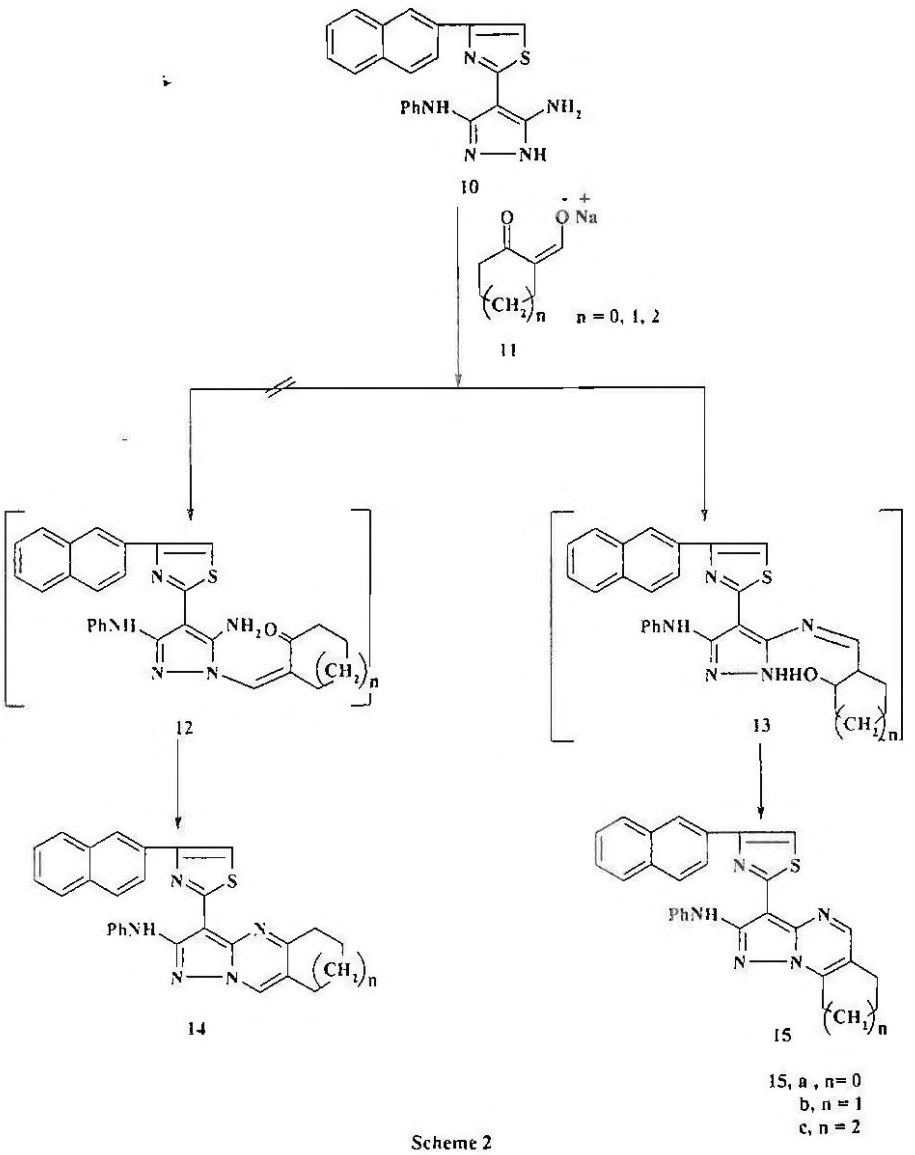


Fig. (1): X-ray crystallography for compound 4

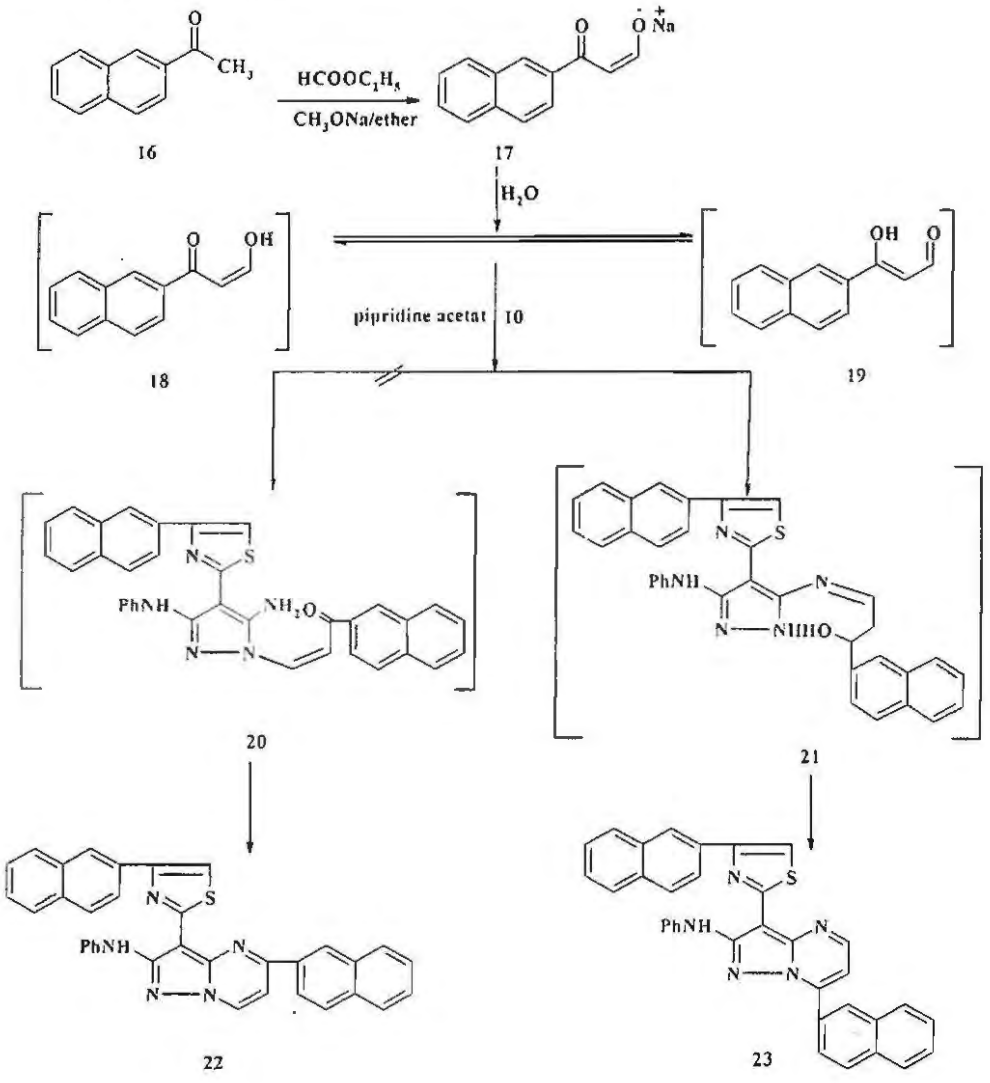
Treatment of amino pyrazole **10** with sodium salt of (2-oxocycloalkylidine)-methanolates **11** in acetic acid containing piperidine acetate afforded 3-[4-(2-naphthyl)-1.3-thiazol-2-yl]-*N*-phenylpyrazolo [1,5-*a*] pyrimidin-2-amine derivatives **15** or isomeric structure **14** through the intermediacy **13** or **12**. The scope and limitation of our procedure for the synthesis of compound **15** was discussed. Thus it has been found that two modes of cyclization are feasible, as outlined in scheme (2). The first mode discussed that the initial nucleophilic attack by the exocyclic amino group takes place at the formyl group of compound **11** and subsequent Michael cyclization followed by elimination two moles of water leads to structures **15.** The second one discussed that the initial nucleophilic attack by endoimino group takes place at the formyl group of salt **11** followed by cyclization of exocyclic amino group of compound **10** with ketonic group of compound **11** leads to isomeric structures **14.** Really, only one isomer was obtained. The structure of **15** was expected due to the initial attack of the exocyclic amino group of compound **10** at the unhindered formyl group of compound **11** leading to the structures of **15** being much more probable than the attack at the hindered ketonic group and this phenomena were elucidated by X-ray single crystals[15]. Moreover, structure of **15** was established by elemental analysis and spectral data. The compound **15b** is supported by its mass spectrum which showed a molecular formula $C_{30}H_{25}N_5S$ (M^+ 487). ^1H NMR spectrum showed signals at δ = 2.1 (quintet, 6H. $3CH_2$), 3.2 (t, 4H, $2CH_2$), 7.0-8.5 (m, 14H, aromatic protons) and 10.3 (s, br., 1H, NH).



Scheme 2

Similar treatment of sodium salt of 1-naphthyl-3-hydroxy-2-propene-1-one **17** with aminopyrazole **10** yielded 7-naphthyl-3-[4-(2-naphthyl)-1,3-thiazol-2-yl]-*N*-phenyl-pyrazolo[1,5-*a*]pyrimidin-2-amine **23** or isomeric structure **22**. The scope and limitation of our procedure for the synthesis of compound **23** also was discussed by the same two modes of action. . Thus according to the above confirmation the compound **23** is much more probable than compound **22** and structure of **23** was

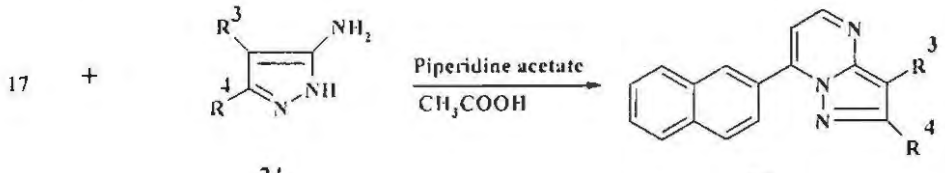
established on the basis of its elemental analysis and spectral data. Thus, compound **23** is supported by its mass spectrum, which showed a molecular formula $C_{35}H_{23}N_5S$ (M^+ 545). ^1H NMR spectrum revealed multiple band at δ = 7.0-8.7 (m, 22H, aromatic protons) and 10.9 (s, br., 1H, NH)(Scheme 3).



16 17 18 19 20 21 22 23

Scheme 3

Analogously, treatment of sodium salt of 1-naphthyl-3-hydroxy-2-propene-1-one **17** with aminopyrazole **24** yielded 3-methyl-2-(methylthio)-7-(2-naphthyl)pyrazolo-[1,5-*a*]pyrimidine **25** (Scheme 4).



24

25

25	R^3	R^4	25	R^3	R^4
a	CONH-C_6H_5	SCH_3	h	CONH-C_6H_4-4-Cl	SC_2H_5
b	CONH-C_6H_5	SC_2H_5	i	CONH-C_6H_4-4-Cl	NHC_6H_5
c	CONH-C_6H_5	NHC_6H_5	j	H	C_6H_5-4-CH_3
d	CONH-C_6H_4-4-CH_3	SCH_3	k	H	C_6H_5-4-Cl
e	CONH-C_6H_4-4-CH_3	SC_2H_5	l	C_6H_5	H
f	CONH-C_6H_4-4-CH_3	NHC_6H_5	m	C_6H_5	CH_3
g	CONH-C_6H_4-4-Cl	SCH_3			

Scheme 4

Compounds **25** were established by elemental analysis and spectral data. Thus compound **25f** is supported by its mass spectrum, which showed a molecular formula $C_{30}H_{23}N_5O$ (M^+ 469). ^1H NMR spectrum showed signals at δ = 2.6 (s, 3H, CH_3), 7.2-8.9 (m, 18H, aromatic protons), 10.1 (s, br., 1H, NH) and 10.9 (s, br., 1H, NH). All compounds obtained are now under biological evaluation studies.

EXPERIMENTAL

All melting points are uncorrected. IR spectra were obtained (KBr disk) on a Perkin Elmer 11650 FT-IR instrument. The ^1H NMR spectra were measured on a Varian 400 MHz spectrometer for solutions in $(CD_3)_2$ SO using TMS as an internal standard. Mass spectra were recorded on a Varian MAT 112 spectrometer. Analytical data were obtained from the Microanalytical Data Center at Cairo University. X-ray crystal data for compound **4** was performed at the national research center.

1*H*-indole-3-carbaldehyde thiosemicarbazone (4):

A mixture of (0.01mol) Indole-3-carboxaldehyde **1** and (0.01 mol) thiosemicarbazide **2** in 20ml Ethanol in presence of few drops of glacial acetic acid was refluxed for 4h. After cooling the solid product was filtered of and recrystallized from ethanol.

4 : Colorless (85 %), m. p. over 226-228 °C, ν_{max} / cm^{-1} (KBr) 3556, 3511, 3480, 3450 (NH_2), and 3434, 3054 (NH); ^1H NMR (DMSO) δ = 7.0-7.6 ppm (m, 4H, aromatic); 7.8 (s, 2H, NH_2); 8.1 (s, 1H, CH); 8.5 (s, 1H, yieledinicCH); 11.2 (s, 1H, NH); 11.8 (s, 1H, NH), m/z 218 (Calcd for $C_{10}H_{10}N_4S$: C, 55.02; H, 4.62; N, 25.67; S,14.69 Found: C, 55.2; H, 4.8; N, 25.4; S,14.7%).

1*H*-indole-3-carbaldehyde [(2*E*)-4-substituted-1,3-thiazol-2(5*H*)-ylidene]hydrazone derivatives 6a-d:

Reaction of (0.01mol) compound **4** with (0.01 mol) haloderivatives **5** in 25 ml ethanol. The mixture was refluxed for 20 min and the solid product was collected at the pump and recrystallized from ethanol.

6a: yellow (70 %), m. p. 210 °C, ν_{max} / cm^{-1} (KBr) 3434 and 3054 (NH), m/z 256 (Calcd for $C_{13}H_{12}N_4S$: C, 60.91; H, 4.72; N, 21.86; S,12.51 % Found: C, 60.66; H, 4.8; N, 21.92; S, 12.62%).

6b: yellow (75 %), m. p. 250 °C, ν_{max} / cm^{-1} (KBr) 3534 and 3454 (NH), m/z 318 (Calcd for $C_{18}H_{14}N_4S$: C, 67.90; H, 4.43; N, 17.60; S,10.07 % Found: C, 67.66; H, 4.55; N, 17.44, S, 10.33%).

6c: yellow (80 %), m. p. 275 °C, ν_{max} / cm^{-1} (KBr) 3555 and 3456 (NH), m/z 368 (Calcd for $C_{22}H_{16}N_4S$: C, 71.71; H, 4.38; N, 15.21; S,8.70 % Found: C, 71.92; H, 4.15; N, 15.32, S, 8.66%).

6d: red (65 %), m. p. 260 °C, ν_{max} / cm^{-1} (KBr) 3574 and 3480 (NH), m/z 324 (Calcd for $C_{16}H_{12}N_4S_2$: C, 59.23; H, 3.73; N, 17.27; S,19.77 % Found: C, 59.63; H, 4.00; N, 17.52, S, 19.56%).

1*H*-indole-3-carbaldehyde [(2*E*)-4-methyl-5-phenylazo-1,3-thiazol-2(5*H*)-ylidene]hydrazone 9a-d:

Method A: A mixture of (0.01mol) Indole-3-carboxaldehyde thiosemicarbazone **4** and (0.01 mol) hydrazonoylhalides **7** in 20ml Ethanol in presence of few drops of triethylamine was stirred for 1h . The solid product was filtered of and recrystallized from ethanol.

Method B: Coupling of (0.01mol) compounds **6** with (0.01 mol) benzendiazonium chloride **8** in 20ml Ethanol in presence of sodium

acetate. The product was diluted by water and collected by filtration and recrystallized from ethanol.

9a: Orange (75%), m. p. 250 °C, ν_{max} / cm^{-1} (KBr) 3534 and 3454 (NH), ^1H NMR (DMSO) δ = 3.1(s, 3H, CH_3), δ = 7.3-8.6 (m, 10H, aromatic) δ = 8.9(s, 1H, yieledinic CH), δ = 10 (s, 1H, ring NH) and δ = 11.8 (s, 1H, NH) m/z 360 (Calcd for $C_{19}H_{16}N_6S$: C, 63.31; H, 4.47; N, 23.32; S,8.90 % Found: C. 63.41; H, 4.66: N, 23.54; S, 9.02%).

9b: red (66 %), m. p. 230 °C, ν_{max} / cm^{-1} (KBr) 3500 and 3430 (NH), ^1H NMR (DMSO) δ = 7.1-8.5 (m, 15H, aromatic) δ = 8.2(s, 1H, yieledinic CH), δ = 10.5 (s, 1H, ring NH) and δ = 12.1 (s, 1H, NH) m/z 422 (Calcd for $C_{24}H_{18}N_6S$: C, 68.23; H, 4.29; N, 19.89; S,7.59 % Found: C, 68.55; H, 4.44; N, 20.1; S, 7.88 %;

9c: yellow (80 %), m. p. 295 °C, ν_{max} / cm^{-1} (KBr) 3480 and 3356 (NH), m/z 472 (Calcd for $C_{28}H_{20}N_6S$: C, 71.16; H, 4.27; N, 17.78; S, 6.79 % Found: C, 71.54; H, 4.33; N, 17.98, S, 7.22%).

9d: red (70 %), m. p. over 300 °C, ν_{max} / cm^{-1} (KBr) 3584 and 3433 (NH), (DMSO) δ = 7.3-8.3 (m, 13H, aromatic) δ = 8.0(s, 1H, yieledinic CH), δ = 10.1 (s, 1H, ring NH) and δ = 11.4 (s, 1H, NH)m/z 428 (Calcd for $C_{22}H_{16}N_6S_2$: C, 61.66; H, 3.76; N, 19.61; S,17.97 % Found: C, 61.88; H, 3.55: N, 17.42. S, 14.65%).

3-[4-(2-naphthyl)-1,3-thiazol-2-yl]-*N*-phenylpyrazolo[1,5-*a*]pyrimidin-2-amine derivatives 15:

A solution of (0.01 mol) sodium salt of (2-oxocycloalkylidine)-methanolates **11,** (0.01 mol) amino pyrazoles **10** (0.01 mol) and piperidine acetate (1 ml) in H_2O (3 ml) was refluxed for 15 minuets. Acetic acid (1.5 ml) was added to the hot solution. The solid product was filtered off and recrystallized from the appropriate solvent

15a: Colorless (yield 70 %), m. p. 210 °C, ν_{max} / cm^{-1} (KBr) 3560, 3433 (NH), ^1H NMR (DMSO) δ = 2.73-2.75 (m, 2H, CH_2), 3.01-3.05 (t, 2H, CH_2), 3.17-3.32 (t, 2H, CH_2), 7.3-8.8 (m, 14H, aromatic), 11.8 (s, br, 1H, NH); m/z 459 (Calcd for $C_{28}H_{21}N_5S$: C, 73.18; H, 4.61; N, 15.24; S, 6.98 %. Found: C, 73.33; H, 4.64; N, 15.55; S, 7.22 %.

15b: Yellow (85 %), m. p. 238 °C, ν_{max} / cm^{-1} (KBr) 3447 and 3175 (NH),); ^1H NMR (DMSO): δ = 1.80-2.1 (m, 4H, $2CH_2$), 2.5-2.8 (t, 2H, CH_2), 2.9 (t, 2H, CH_2), 7.3-8.6 (m, 14H, aromatic), and 11.40 (s, br, 1H, NH); m/z 473 (Calcd for $C_{29}H_{23}N_5S$: C, 73.55; H, 4.90; N, 14.79; S,6.77 % Found: C,73.7; H, 4.65; N, 14.87; S, 6.52 %).

15c: yellow (80 %), m. p. 195 °C, ν_{max} / cm^{-1} (KBr) 3440 and 3104 (NH), ^1H NMR (DMSO): δ = 1.56 (m, 4H, $2CH_2$), 1.78 (m, 2H, CH_2), 2.62-2.66(t, 2H, CH_2), 3.16- 3.28 (t, 2H, CH_2), 7.3-8.5 (m, 14H, aromatic), and 11.8 (s, br, 1H, NH). m/z 545 (Calcd for $C_{30}H_{25}N_5S$: C, 73.89; H, 5.17; N, 14.36; S, 6.58 %. Found: C, 73.68; H, 5.44; N, 14.22; S, 6.76 %).

Sodium salt of 3-hydroxy-1-(2-naphthyl)prop-2-ene-1-one 17:

In three nicked flask take (0.01 mol) of sodium methoxide and 20 ml ether and pour over it through separating funnel (0.01 mol) 2-acetyl naphthalene **16** with 0.01 (mol) of ethyl format with efficient stirring. The solid product was collected at the pump and used directly in the reactions.

7-naphthyl-3-[4-(2-naphthyl)-1,3-thiazol-2-yl]-*N*-phenyl-pyrazolo[1,5-*a*]-pyrimidin-2-amine 23:

A solution of (0.01 mol) sodium salt of 1-naphthyl-3-hydroxy-2-propene-1-one **17**, (0.01 mol), amino pyrazoles **10** (0.01 mol) and piperidine acetate (1 ml) in H_2O (3 ml) was refluxed for 10 minuets. Acetic acid (1.5 ml) was added to the hot solution. The solid product was filtered off and recrystallized from ethanol.

23: yellow (yield 75 %), m. p. 260 °C, ν_{max} / cm^{-1} (KBr) 3540, 3453 (NH), ^1H NMR (DMSO) δ = 7.1-8.8 (m, 22H, aromatic), 10.25 (s, br, 1H, NH); m/z 545 (Calcd for $C_{35}H_{23}N_5S$: C, 77.04; H, 4.25; N, 12.83; S, 5.88 %. Found: C, 77.32; H, 4.64; N, 12.66; S, 6.02 %.

7-(2-naphthyl)pyrazolo[1,5-a]pyrimidine derivatives 25a-m

A solution of Sodium salt of 3-hydroxy-1-(2-naphthyl)prop-2-ene-1-one **17** (0.01 mol), amino pyrazoles **24** (0.01 mol) and piperidine acetate (1 ml) in H_2O (3 ml) was refluxed for 10 minuets. Acetic acid (1.5 ml) was added to the hot solution. The solid product was filtered off and recrystallized from the appropriate solvent.

25a: Colorless (yield 60 %), m. p. 188 °C, ν_{max} / cm^{-1} (KBr) 3560, 3433 (NH), 1670 (CO); ^1H NMR (DMSO) δ = 2.5 (s, 3H, SCH_3), δ = 7.1-8.5 (m, 14H, aromatic)and δ = 11.5 (s, 1H, NH); m/z 410 (Calcd for $C_{24}H_{18}N_4OS$: C, 70.22; H, 4.42; N, 13.65; S, 7.81 %. Found: C, 70.45; H, 4.64; N, 13.13; S, 7.54 %.

25b: Colorless (yield 60 %), m. p. 190 °C, ν_{max} / cm^{-1} (KBr) 3566, 3450 (NH), 1650 (CO); ^1H NMR (DMSO) δ = 2.55(t, 2H, CH_2), δ = 3.55(q,

3H, CH_3), δ = 7.3-8.6 (m, 14H, aromatic)and δ = 11.0 (s, 1H, NH); m/z 424 (Calcd for $C_{25}H_{20}N_4OS$: C, 70.73; H, 4.75; N, 13.20; S, 7.55 %. Found: C, 70.52; H, 4.62; N, 13.01; S, 7.12 %.

25c: Colorless (yield 66 %), m. p. 235 °C, ν_{max} / cm^{-1} (KBr) 3540, 3450 (NH), 1655 (CO); ^{1}H NMR (DMSO) δ = 7.1-9.5 (m, 19H, aromatic), δ = 10.5 (s, 1H, NH), δ = 11.0 (s, 1H, NH); m/z 455 (Calcd for $C_{29}H_{21}N_5O$: C, 76.47; H, 4.65; N, 15.37; %. Found: C, 76.21; H, 4.33; N, 15.25; %.

25d: Colorless (yield 70 %), m. p. 200 °C, ν_{max} / cm^{-1} (KBr) 3500, 3410 (NH), 1640 (CO); ^{1}H NMR (DMSO) δ = 2.5 (s, 3H, SCH_3), δ = 7.1-9.0 (m, 13H, aromatic), δ = 10.5 (s, 1H, NH), m/z 424 (Calcd for $C_{25}H_{20}N_4OS$: C, 70.73; H, 4.75; N, 13.20; S7.55 %. Found: C, 70.47; H, 4.90; N, 13.55; S 7.72 %.

25e: Colorless (yield 55 %), m. p. 195 °C, ν_{max} / cm^{-1} (KBr) 3544, 3421 (NH), 1665 (CO); ^{1}H NMR (DMSO) δ = 2.33(t, 2H, CH_2), δ = 2.52(s, 3H, CH_3), δ = 3.65(q, 3H, CH_3), δ = 7.2-8.6 (m, 13H, aromatic)and δ = 11.0 (s, 1H, NH); m/z 438 (Calcd for $C_{26}H_{22}N_4OS$: C, 71.21; H, 5.06; N, 12.78; S, 7.31 %. Found: C, 71.65; H, 5.46; N, 12.54; S, 7.22 %.

25f: Colorless (yield 70 %), m. p. 240 °C, ν_{max} / cm^{-1} (KBr) 3550, 3470 (NH), 1660 (CO); ^{1}H NMR (DMSO) δ = 2.48 (s, 3H, CH_3), δ = 7.0-9.0 (m, 18H, aromatic), δ = 9.6 (s, 1H, NH), δ = 10.20 (s, 1H, NH); m/z 469 (Calcd for $C_{30}H_{23}N_5O$: C, 76.74; H, 4.94; N, 14.92; %. Found: C, 76.54; H, 4.66; N, 14.74; %.

25g: Colorless (yield 65 %), m. p. 180 °C, ν_{max} / cm^{-1} (KBr) 3565, 3414 (NH), 1655 (CO); ^{1}H NMR (DMSO) δ = 2.44 (s, 3H, SCH_3), δ = 7.0-8.5 (m, 13H, aromatic)and δ = 10.33 (s, 1H, NH); m/z 444 (Calcd for $C_{24}H_{17}ClN_4OS$: C, 64.79; H, 3.85; N, 12.59; S, 7.21 %. Found: C, 64.54; H, 3.63; N, 12.44; S, 7.54 %.

25h: Colorless (yield 75 %), m. p. 225 °C, ν_{max} / cm^{-1} (KBr) 3545, 3420 (NH), 1645 (CO); ^{1}H NMR (DMSO) δ = 2.42(t, 2H, CH_2), δ = 3.50(q, 3H, CH_3), δ = 7.0-8.5 (m, 13H, aromatic); and δ = 10.1 (s, 1H, NH); m/z 458 (Calcd for $C_{25}H_{19}ClN_4OS$: C, 65.42; H, 4.17; N, 12.21; S, 6.99 %. Found: C, 65.66; H, 4.63; N, 12.45; S, 6.66 %.

25i: Colorless (yield 75 %), m. p. 250°C, 3523, 3430, 3410 (NH), 1630 (CO)

^{1}H NMR (DMSO) δ = 7.0-9.2(m, 18H, aromatic), δ = 10.1 (s, 1H, NH), δ = 10.8 (s, 1H, NH); m/z 489 (Calcd for $C_{29}H_{20}ClN_5O$: C, 71.09; H, 4.11; N, 14.29 %. Found: C, 70.87; H, 4.24; N, 14.53 %.

25j: Colorless (yield 70 %), m. p. 245 °C, ^{1}H NMR (DMSO) δ = 2.2 (s, 3H, CH_3), δ = 7.2-8.9 (m, 14H, aromatic); m/z 335 (Calcd for $C_{23}H_{17}N_3$: C, 82.36; H, 5.11; N, 12.53; %. Found: C, 82.55; H, 5.34; N, 12.47; %.
25k: Colorless (yield 71 %), m. p. 220°C, ^{1}H NMR (DMSO) δ = 7.0-8.5 (m, 14H, aromatic); m/z 355 (Calcd for $C_{22}H_{14}ClN_3$ C, 74.26; H, 3.97; N, 11.81; %. Found: C, 74.65; H, 4.21; N, 11.65 %.
25l: Colorless (yield 65 %), m. p. 190°C, ^{1}H NMR (DMSO) δ = 7.0-8.8 (m, 15H, aromatic); m/z 321 (Calcd for $C_{22}H_{15}N_3$: C, 82.22; H, 4.70; N, 13.08; %. Found: C, 82.00; H, 4.64; N, 13.11 %.
25m: Colorless (yield 60 %), m. p. 198 °C, ^{1}H NMR (DMSO) δ = 2.44 (s, 3H, CH_3), δ = 7.1-8.6 (m, 14H, aromatic); m/z 335 (Calcd for $C_{23}H_{17}N_3$: C, 82.36; H, 5.11; N, 12.53 %. Found: C, 82.22; H, 5.33; N, 12.23 %. .

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تشييد بعض مشتقات ٥-فنيل ازوثيازول و بيرازولو[٥,١-a] بيريميدين الجديدة

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تكاثف الاندول-٣-كربوكسالدهيد (١) مع الثيوسيمى كاربازيد (٢) يعطى ١-هيدرو-اندول-٣-كاربوكسالدهيد ثيوسيمى كاربازون (٤) الذى يتفاعل مع الهيدرازونيل هاليد (٧) لينتج ٥-اريل ازوثيازول (٩).

تم الحصول على بيرازولو[٥,١-a]بيريميدين (١٥) و كذلك ٧-(٢-نافثيل)بيرازولو[٥,١-a]بيراميدين (٢٣) من تفاعل ملح الصوديوم (٢-اوكسوسيكلو ألكيليدين)ميثانولات (١١) و ١-نافثيل-٣-هيدروكسى-٢-بروبين-١-اون (١٧) مع امينوبيرازول (١٠).

و لقد اثبات التراكيب الكيمائية للمركبات المشيدة الجديدة باستخدام التحليل العنصرى و الطيفى و الاشعة السينية للبلورة الواحدة بالاضافة الى استخدام الطرق الكيميائية كلما امكن ذلك.