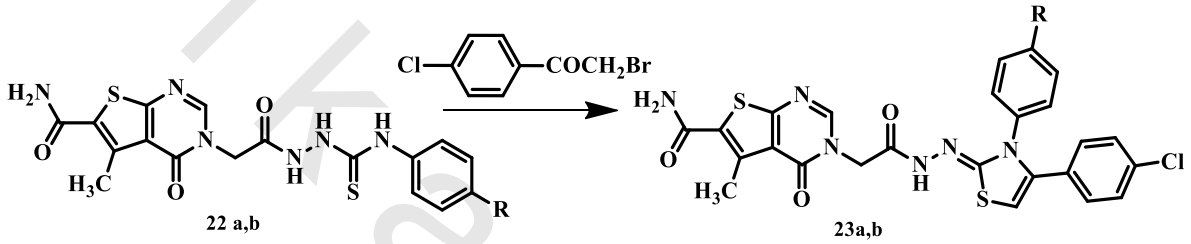
^{1}H-NMR spectrum of **22a** lacked the hydrazide NH_2 signal and showed two D_2O exchangeable singlets, one integrated for two protons corresponding to –NH-C=S and –NH-R at 9.92 ppm and the other integrated for one proton corresponding to –NH-C=O at 10.59 ppm in addition to the signals of other protons of the thienopyrimidine nucleus and 4-chlorophenyl moiety appeared at their expected chemical shifts.

EIMS for **22a** Showed [$M^{+\bullet}$+2] at m/z 452, [$M^{+\bullet}$] at m/z 450 and the base peak at m/z 227 and 55.

EIMS for **22b** Showed [$M^{+\bullet}$] at m/z 446 and the base peak at m/z 379 and 227.

3-{2-[2-(4-(4-chlorophenyl)-3-(4-substituted phenyl)thiazol-2(3*H*)-ylidene) hydrazinyl]-2-oxoethyl}-5-methyl-4-oxo-3,4-dihydrothieno[2,3-*d*]pyrimidine-6-carboxamides 23a,b



In the present study the title compounds were obtained by treating the thiosemicarbazides **22a,b** with 4-chlorophenacyl bromide in absolute ethanol and anhydrous sodium acetate adopting the described method reported by Rida *et al* [(100)].

IR spectra of **23a,b** lacked N–C=S stretching absorption bands and showed NH, amide C=O, C=N, C=C and C-S-C at their expected frequencies.

^{1}H-NMR of **23a** lacked the two NH signals characteristic for the substituted thiosemicarbazide precursor. They showed two singlets one deuterium exchangeable corresponding to –NH-N= proton and the other corresponding to deshielded thiazoline-C_5-proton at 10.37 and 6.60 ppm, respectively. Other protons were observed within their expected chemical shifts.

EIMS for **23a** Showed [$M^{+\bullet}$+4] at m/z 588, [$M^{+\bullet}$+2] at m/z 586, [$M^{+\bullet}$] at m/z 584 and the base peak at m/z 57.

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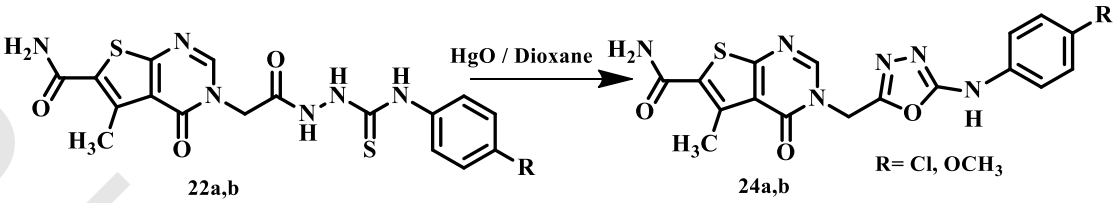
3-{[5-(4-Substituted phenylamino)-1,3,4-oxadiazol-2-yl]methyl}-5-methyl-4-oxo-3,4-dihydrothieno[2,3-*d*]pyrimidine-6-carboxamides 24a,b



22a,b 24a,b

5-Substituted amino-1,3,4-oxadiazoles were reported to be prepared by cyclodesulphurization of substituted thiosemicarbazides using mercuric oxide [101], dicyclohexylcarbodimide [102], bromine in chloroform [103] or iodine/potassium iodide in aqueous sodium hydroxide [104].

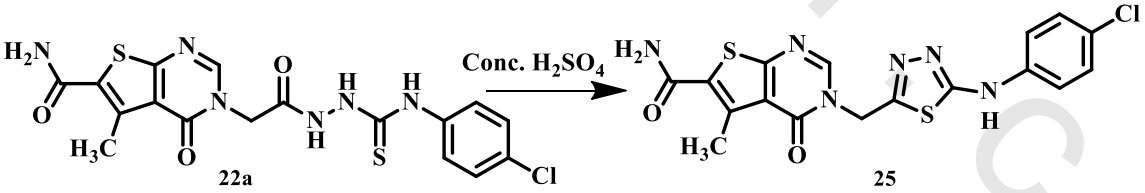
In the present investigation oxadiazole derivatives **24a,b** were prepared from **22a,b** derivatives using mercuric oxide in dry dioxane.

IR spectra of **24a,b** indicated the absence of N–C=S absorption bands .It showed absorption bands due to NH, amide C=O, C=N and C-S-C in addition to C–O–C absorption bands of the oxadiazole ring.

^{1}H-NMR of **24a** lacked the two NH signals characteristic for substituted thiosemicarbazide precursors. They showed one deuterium exchangeable singlet at 10.68 ppm corresponding to NH proton. In addition, signals for other thienopyrimidine and aromatic protons appeared at their expected chemical shifts.

EIMS for **24a** Showed [$M^{+\bullet}$+2] at m/z 418, [$M^{+\bullet}$] at m/z 416 and the base peak at m/z 57.

3-{[5-(4-Chlorophenylamino)-1,3,4-thiadiazol-2-yl]methyl}-5-methyl-4-oxo-3,4-dihydrothieno[2,3-*d*]pyrimidine-6-carboxamide 25



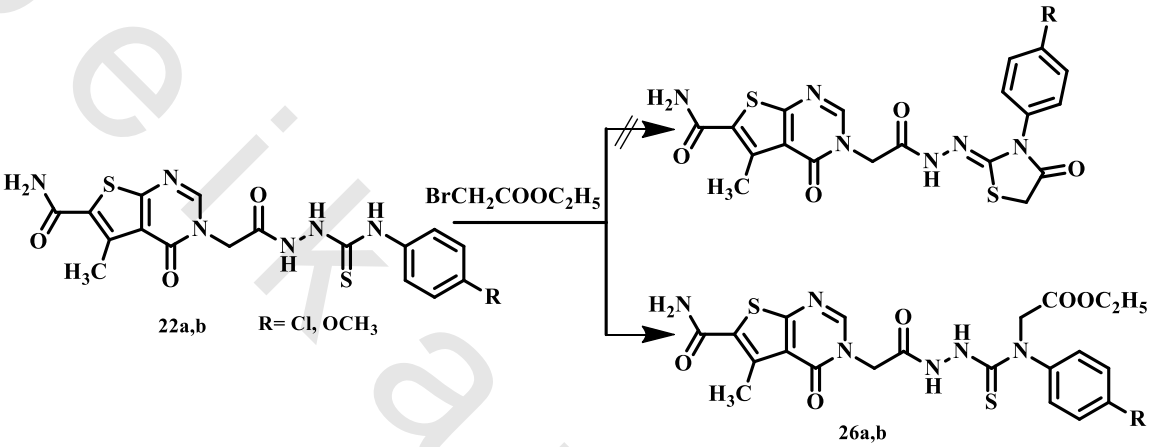
22a 25

The title compound was prepared by cyclization of thiosemeicarbazide **22a** by stirring with cold sulphuric acid adopting the reaction conditions reported by Pintillie *et al* [105].

IR spectrum of **25** was characterized by the absence of N–C=S stretching absorption band, it showed the usual absorption bands due to NH, amide C=O, C=N, C=C and C-S-C functions.

^{1}H-NMR of 25 lacked the two NH signals characteristic for substituted thiosemicarbazide precursors. They showed one deuterium exchangeable singlet at 10.45 ppm corresponding to –NH proton. In addition, signals for other protons appeared at their expected chemical shifts.

Ethyl 2-[*N*^{1}-(2-(6-carbamoyl-5-methyl-4-oxo-3,4-dihydrothieno[2,3-*d*]pyrimidin-3-yl)acetyl)-*N*^{4}-(4-substituted phenyl)thiosemicarbazide-*N*^{4}-yl]acetates 26a,b



In the present investigation, it was designed to prepare thiazolidenone derivatives by heating **22a,b** with ethyl bromoacetate in absolute ethanol according to the reported procedure used for synthesis of similar compounds [100]. However, the separated products were found to be the opened chain compounds **26a,b** rather than the cyclized derivatives and that was confirmed by the following analyses:

IR spectra of **26a,b** showed N–C=S stretching absorption bands and absorption band of C=O of ester group at 1736 and 1734 cm^{-1} in addition to NH, amide C=O, C=N, C=C, C-S-C and C-O-C at their expected frequencies.

^{1}H-NMR spectrum of **26a** lacked one NH proton of the starting thiosemicarbazide and showed triplet and quartet at 1.16 and 4.09 ppm assigned for the ethyl ester group. All the other aliphatic and aromatic protons were observed within the expected regions.

EIMS for **26a** Showed [$M^{+\bullet}$+2] at m/z 538, [$M^{+\bullet}$] at m/z 536 and the base peak at m/z 111.

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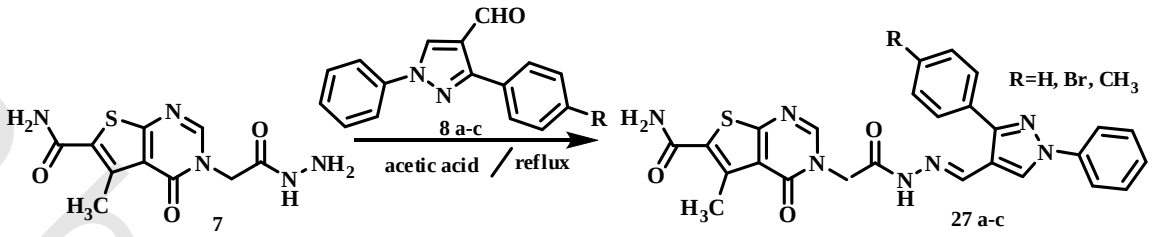
3-{2-[2-((3-Aryl-1-phenyl-1*H*-pyrazol-4-yl)methylene)hydrazinyl]-2-oxoethyl}-5-methyl-4-oxo-3,4-dihydrothieno[2,3-*d*]pyrimidine-6-carboxamides 27 a-c



The title compounds were synthesized following the same procedure for the preparation of compounds **9a-c** by the reaction of acid hydrazide **7** with different substituted pyrazole carbaldehydes in glacial acetic acid.

IR spectra of compounds **27a-c** showed absorption bands due to NH, amide C=O, C=N, C=C and C-S-C at their expected frequencies.

^{1}H-NMR spectrum of **27a** lacked the upfield D_2O exchangeable singlet assigned for the NH_2 protons of the hydrazide moiety, the =CH appeared as two singlets at 8.19 and 8.33 ppm each integrated for half proton indicating mixture of trans and cis isomers. In addition to the pyrazolyl-C_5-H appeared as a singlet at 9.05 ppm and the –NH–N= proton observed as two singlets at 11.61 and 11.74 ppm each integrated for half proton. Other aliphatic and aromatic protons were observed within their expected chemical shifts.

EIMS for **27a** Showed [$M^{+\bullet}$] at m/z 511 and the base peak at m/z 73.

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