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Research Article

SYNTHESIS OF 6-{4-AMINO-N-[2-(DIETHYLAMINO)ETHYL]-O-ANISAMIDO-5-YL}-AMINO-2-THIO-3-SUBSTITUTEDAMINO,4-SUBSTITUTEDIMINO-1,3,5-THIADIZINES

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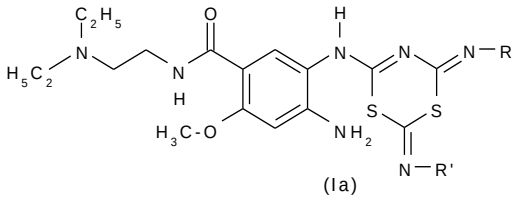
Abstract: Recently a novel series of 6-{4-amino-N-[2-(diethylamino)ethyl]-o-anisamido-5-yl}amino-2-substitutedimino-3-substituted-4-thio-1,3,5-thiadizines was successfully synthesized by the isomerisation of 4-{4-amino-N-[2-(diethylamino)ethyl]-o-anisamido-5-yl}-amino-2,6-disubstitutedimino-1,3,5-dithiazines by 5% aqueous sodiumbicarbonate in ethanol medium. The structures of all synthesized compounds were justified on the basis of chemical characteristics, elemental analysis and spectral studies.

Keywords:6-{4-amino-N-[2-(diethylamino)ethyl]-o-anisamido-5-yl}amino-2-sub-stitutedimino-3-substituted-4-thio-1,3,5-thiadizines, 4-{4-amino-N-[2-(diethylamino) ethyl]-o-anisamido-5-yl}-amino-2,6-disubstitutedimino-1,3,5-dithiazines, 5% aqueous sodium bicarbonate in ethanol medium.

Introduction:

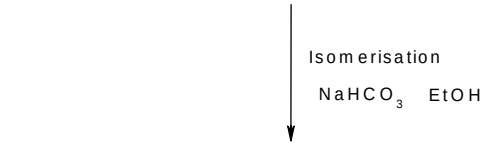
The literature survey reveals that the thiourea and its derivaties having 1,3,5-thiadiazine nucles enhanced pharmaceutical, agricultural and industrial values[1]. So, the medicines containing thiadiazines nucles are now used extensively in medical, biomedical and biotechnological faculties. It has been shown to posses industrial[2-3], fungicidal insecticidal[4-5], medicinal[6] values. The synthetic applications of N-aryl/alkyisocynodichlorides[7] have been investigated and shown to have enough potential in the synthesis of nitrogen and sulphur containing heterocyclic compounds, thus with an aim to synthesize 1,3,5-thiadiazine, reaction of N-aryl/alkylisocynodichlorides[7] have been carried out with different 1,3-bis(N-substitutedamidinothiocarbamido)thiourea (1) in 1:2 molar ratios.

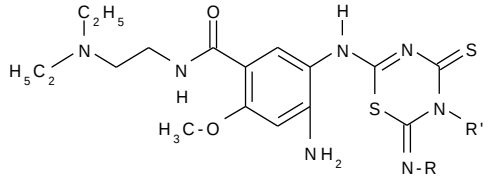
Hence it was thought interesting to synthesize 6-{4-amino-N-[2-(diethylamino)ethyl]-o-anisamido-5-yl}-amino-2-substitutedimino-3-substituted-4-thio-1,3,5-thiadia-zines by the isomerisation of 4-{4-amino-N-[2-(diethylamino)ethyl-o-anisamido-5-yl}-amino-2,6-disubstitutedimino-1,3,5-dithiazines in 5% ethanolic sodium bicarobonate solution. The tentative reaction for the formation of products is depicted below.



(Ia)

4-{4-Amino-N-[2-(diethylamino)-ethyl]-o-anisamido-5-yl}-amino-2-substitutedimino-6-substitutedimino-1,3,5-dithiazine





(IIa)

6-{4-Amino-N-[2-(diethylamino)-ethyl]-o-anisamido-5-yl}-amino-2-substitutedimino-3-substituted-4-thio-1,3,5-thiadiazine

Where R= H, allyl, t-butyl, phenyl, p-chlorophenyl.

R'=t-butyl, phenyl, p-chlorophenyl, ethyl, methyl, o-tolyl, m-tolyl, p-tolyl.

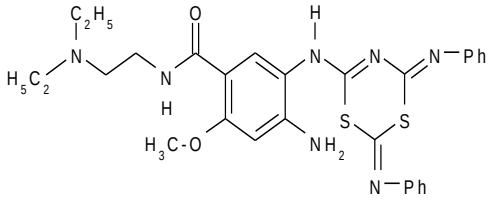
Synthesis of 6-{4-amino-N-[2-(diethylamino)ethyl]-o-anisamido-5-yl}-amino-2-phenylimino-3-phenyl-4-thio-

1,3,5-thiadiazine

4-{4-Amino-N-[2-(diethylamino)ethyl]-o-anisamido-5-yl}-amino-2-phenylimnio-6-phenylimino-1,3,5-dithiazine was successfully isomerised in 5% aqueous sodium bicarbonate ethanolic solution by refluxing for 5 minutes on water bath. During heating the reactants went into the solvent. After distillation of excess solvent orange crystals were isolated. It was recrystalised from glacial acetic acid to obtain 6-{4-amino-N-[2-(diethylamino)ethyl]-o-anisamido-5-yl}-amino-2-phenylimino-3-phenyl-4-thio-1,3,5-thiadiazine (IXa12), yield 92%, m.p. 280˚C.

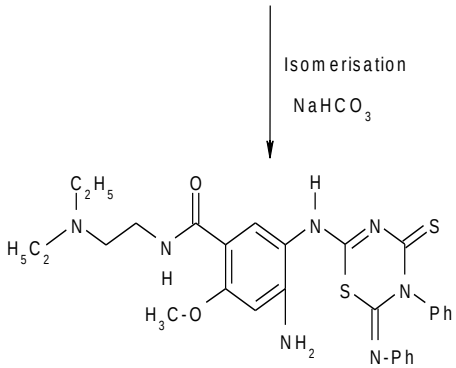
The probable reaction and mechanism for the formation of this compound, it may be depicted below

Reaction



(Ia)

4-{4-Amino-N-[2-(diethylamino)-ethyl]-o-anisamido-5-yl}-amino-2-phenylimino-6-phenylimino-1,3,5-dithiazine



(IIa)

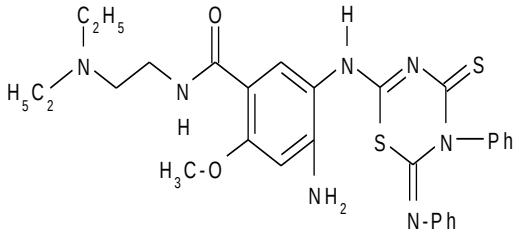
6-{4-Amino-N-[2-(diethylamino)-ethyl]-o-anisamido-5-yl}-amino-2-phenylamino-3-phenyl-4-thio-1,3,5-thiadiazine

Properties:

It is pale yellow crystalline solid having m.p. 280˚C. It gave positive test for nitrogen and sulphur. It does not desulphurized when boiled with sodium plumbite solution which clearly indicates that sulphur is not free and gets cyclised[8-9]. It was soluble in benzene, acetic acid, DMF and DMSO. **Elemental analysis**: This result of elemental analysis is gives Carbon[59.82%(found),60.52%(calculated)], Hydrogen[06.93%(found),05.73%(calculated)],Nitrogen[16.50 %(found),17.04%(calculated)],Sulphur[10.66%(found),11.13 %(calculated)]. From the analytical data the molecular formula was found to be $C_{29}H_{33}N_7O_2S_2$. **IR Spectrum**: The IR spectrum of compound was carried out in KBr pellets, the important absorption are correlated as (cm^{-1}) 3398.60 N-H Stretching, 2927.14 C-H(Ar)stretching, 1647.15 C=O stretching, 1339.15 C-N stretching, 1158.80 C=S stretching, 0764.25 Monosubstituted benzene.

PMR Spectrum: The PMR spectrum of compound was carried out in $CDCl_3$ and DMSO-d_6. This spectrum distinctly displayed the signals due to Ar-H protons at δ 8.4000 ppm, –NH proton at δ 5.5170-5.0193 ppm, NH_2 protons at δ 4.9492-4.6144 ppm, -OCH_3 protons at δ 3.6492-3.0654 ppm, CH_2 protons at δ 2.5175-2.4996 ppm, N-CH_3 protons at δ 1.2352 ppm.

From the above properties and spectral analysis of the compound was assigned the structure as 6-{4-amino-N-[2-(diethylamino)ethyl]-o-anisamido-5-yl}-amino-2-phenylimino-3-phenyl-4-thio-1,3,5-thiadiazine.



(IIa)

6-{4-Amino-N-[2-(diethylamino)-ethyl]-o-anisamido-5-yl}-amino-2-phenylamino-3-phenyl-4-thio-1,3,5-thiadiazine

Similarly, 4-{4-amino-N-[2-(diethylamino)ethyl]-o-anisamido-5-yl}-amino-2-phenylimnio-6-methylimino-1,3,5-dithiazine **(Ib),** 4-{4-amino-N-[2-(diethylamino) ethyl]-o-anisamido-5-yl}-amino-2-phenylimnio-6-t-butylimino-1,3,5-dithiazine **(Ic),** 4-{4-amino-N-[2-(diethylamino)ethyl]-o-anisamido-5-yl}-amino-2-phenyl-imnio-6-p-chlorophenylimino-1,3,5-dithiazine **(Id) ,**4-{4-amino-N-[2-(diethylamino)ethyl]-o-anisamido-5-yl}-amino-2-phenylimnio-6-o-tolylimino-1,3,5-dithiazine **(Ie),** 4-{4-amino-N-[2-(diethylamino)ethyl]-o-anisamido-5-yl}-amino-2-phenyl-imnio-6-m-tolylimino-1,3,5-dithiazine **(If),** 4-{4-amino-N-[2-(diethylamino)ethyl]-o-anisamido-5-yl}-amino-2-phenylimnio-6-p-tolylimino-1,3,5-dithiazine **(Ig)** were isomerized by 5% aqueous sodium carbonate in ethanol solution by above mentioned method to isolate 6-{4-amino-N-[2-(diethylamino)ethyl]-o-anisamido-5-yl}-amino-2-methylimino-3-phenyl-4-thio-1,3,5-thiadiazine**(IXa17),** 6-{4-amino-N-[2-(diethylamino)ethyl]-o-anisamido-5-yl}-amino-2-t-butylimino-3-phenyl-4-thio-1,3,5-thiadiazine **(IIb),** 6-{4-amino-N-[2-(diethyl-amino)ethyl]-o-anisamido-5-yl}-amino-2-p-chloro-phenylimino-3-phenyl-4-thio-1,3,5-thiadiazine **(IIc),**6-{4-amino-N-[2-(diethylamino)ethyl]-o-anisamido-5-yl}-amino-2-o-tolylimino-3-phenyl-4-thio-1,3,5-thiadiazine **(IId),** 6-{4-amino-N-[2-(diethylamino) ethyl]-o-anisamido-5-yl}-amino-2-m-tolylimino-3-phenyl-4-thio-1,3,5-thiadiazine **(IIe),** 6-{4-amino-N-[2-(diethylamino)ethyl]-o-anisamido-5-yl}-amino-2-p-tolylimino-3-phenyl-4-thio-1,3,5-thiadiazine **(IIf)** respectively and enlisted in **Table No. VI-1.**

Table No. VI-1.

Sr. No.	Compd. No	6-{4-Amino-N-[2-(diethylamino)ethyl]-o-anisamido-5-yl}-amino-2-**substitut- edimino**-3-**substituted**-4-thio-1,3,5-thiadiazine	Yield (%)	m.pt. (^{0}C)
1	**(IIb)**	6-{4-Amino-N-[2-(diethylamino)ethyl]-o-anisamido-5-yl}-amino-2-**methylim- ino**-3-**phenyl**-4-thio-1,3,5-thiadiazine	95	272
2	**(IIc)**	6-{4-Amino-N-[2-(diethylamino)ethyl]-o-anisamido-5-yl}-amino-2-**t-butylim- ino**-3-**phenyl**-4-thio-1,3,5-thiadiazine	84	275
3	**(IId)**	6-{4-Amino-N-[2-(diethylamino)ethyl]-o-anisamido-5-yl}-amino-2-**p-chloro phenylimino**-3-**phenyl**-4-thio-1,3,5-thiadiazine	91	290
4	**(IIe)**	6-{4-Amino-N-[2-(diethylamino)ethyl]-o-anisamido-5-yl}-amino-2-**o-tolylim- ino**-3-**phenyl**-4-thio-1,3,5-thiadiazine	87	292
5	**(IIf)**	6-{4-Amino-N-[2-(diethylamino)ethyl]-o-anisamido-5-yl}-amino-2-**m-tolylim- ino**-3-**phenyl**-4-thio-1,3,5-thiadiazine	93	295
6	**(IIg)**	6-{4-Amino-N-[2-(diethylamino)ethyl]-o-anisamido-5-yl}-amino-2-**p-tolylim- ino**-3-**phenyl**-4-thio-1,3,5-thiadiazine	95	300

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