In this study, the azo groups of 2-aryl/alkylamino-5-[p-(1’-phenyl-3’,5’-dimethyl-4’-pyrazolylazo)-phenyl]-1,3,4-thiadiazoles which were previously prepared by us were reduced with hydrazine hydrate without a catalyst in ethanol and the following compounds were obtained: 2-n-propylamino-5-(p-aminophenyl)-1,3,4-thiadiazole (I), 2-n-buthylamino-5-(p-aminophenyl)-1,3,4-thiadiazole (II), 2-cyclohexylamino-5-(p-aminophenyl)-1,3,4-thiadiazole (III), 2-phenethylamino-5-(p-aminophenyl)-1,3,4-thiadiazole (IV), 2-phenylamino-5-(p-aminophenyl)-1,3,4-thiadiazole (V). The structures of these substances were elucidated using UV, IR and NMR spectral methods besides elementary analysis.

ÖZET

Bu çalışmada, daha önce tarafından hazırlanmış olan 2-aril/alkil-1’-amino-5-[p-1’-fenil-3’-5’-dimetil-4’-pirazolylazo]-fenil]-1,3,4-thiadiazollerin, azo grubu katalizörsüz olarak etanollü ortamda hidrazin nitroğluinouslar.
INTRODUCTION

We have previously reported (1) the synthesis and spectroscopic analysis of 1, 3, 4-thiadiazoles with azo groups. It is known that hydrazine hydrate reduces the azo groups to amino groups in the presence of a catalyst (2). We had observed that hydrazine hydrate also reduced the azo group without a catalyst (3-5).

Owing to our interest in the synthesis of 2-alkyl/aryl amino-5-(p-aminophenyl)-1, 3, 4-thiadiazoles, we attempted to prepare it by reductive cleavage with hydrazine hydrate.

EXPERIMENTAL

Melting points were taken on apparatus Buchi (Flawil/Schweiz) and are uncorrected. UV spectra were obtained with a 25 Model Beckman recording spectrophotometer. IR spectra were recorded on a Perkin-Elmer 577 Spectrophotometer in KBr. NMR spectra were recorded on a Varian A 60 D instrument using TMS as an internal standard.

General method for the preparation of the compounds

A mixture of the azo compound (0.0025 mol), hydrazine hydrate (3 ml of 99 %) and ethanol (30-40 ml) was stirred for 30 45 min at 60-65 °C. Excess ethanol was removed by distillation, when the water was added to the solution, white or pale yellow crystalline product was obtained and recrystallized from aqueous ethanol (1:1).

2-n Propylamino-5-(p-aminophenyl)-1, 3, 4-thiadiazole (I)

The substance was prepared according to the general method
from 1.03 g of 2-allylamino-5-[p-(1'-phenyl-3', 5'-dimethyl-4'-pyrazolylazo)phenyl]-1, 3, 4-thiadiazole (Pale yellow needles).

2 2-N-Butylamino-5 (p-aminophenyl)-1, 3, 4-thiadiazole (II)

The substance was prepared according to the general method from 1.07 g of 2-n-buthylamino-5-[p-(1'-phenyl-3', 5'-dimethyl-4'-pyrazolylazo)phenyl]-1, 3, 4-thiadiazole (White needles).

2 Cyclohexylamino-5 (p-aminophenyl)-1, 3, 4-thiadiazole (III)

The substance was prepared according to the general method from 1.14 g of 2-cyclohexylamino-5-[p-(1'-phenyl-3', 5'-dimethyl-4'-pyrazolylazo)phenyl]-1, 3, 4-thiadiazole (White needles).

2 Phenethylamino-5 (p-aminophenyl)-1, 3, 4-thiadiazole (IV)

The substance was prepared according to the general method from 1.2 g of 2-phenethylamino-5-[p-(1'-phenyl-3', 5'-dimethyl-4'-pyrazolylazo)phenyl]-1, 3, 4-thiadiazole (White needles).

2-Phenyl-5 (p-aminophenyl) 1, 3, 4-thiadiazole (V)

The substance was prepared according to the general method from 1.12 g of 2-phenylamino-5-[1'-phenyl-3', 5'-dimethyl-4'-pyrazolylazo)phenyl]-1, 3, 4-thiadiazole (White needles).

RESULTS and DISCUSSION

In our previous paper, 4-aminopyrazole derivatives were prepared by reducing the azopyrazole derivatives with hydrazine hydrate without a catalyst in ethanol (3-5). This method provides an easy hydrogenolysis with good yield without the need of the usual hydrogenation equipment. The aromatic amines have been isolated in high purity.

In the present investigation, as shown in scheme 1, the treatment of 2-aryl/alkylamino-5-[p-(1'-phenyl-3', 5'-dimethyl-4'-pyrazolylazo)phenyl]-1, 3, 4-thiadiazoles with hydrazine hydrate resulted in the formation of two products.
When the reaction medium was diluted water, compounds I–V were obtained, and then when the mother liquor was extracted with chloroform, compound VI was also isolated.

**Introduction**

We have previously reported on the synthesis and spectral details of compounds I–V. The reaction of 1-amino-3(3'-aminopyridinyl)-2-propyl-5-(p-aminophenyl)-1,3,4-thiadiazole (I) with hydrazine hydrate in the presence of catalyst (3) has led to the isolation of compound VI. We have also previously reported on the synthesis and spectral details of compounds I–V. The reaction of 1-amino-3(3'-aminopyridinyl)-2-propyl-5-(p-aminophenyl)-1,3,4-thiadiazole (I) with hydrazine hydrate in the presence of catalyst (3) has led to the isolation of compound VI.

**Experimental**

The starting substance of I contains an allyl group. When the NMR spectrum of compound I was investigated, it was found that allyl group was also reduced with hydrazine hydrate to propyl group (Fig. 1).

![Fig. 1: NMR Spectrum of 2-n-Propylamino-5-(p-aminophenyl)-1,3,4-thiadiazole (I)](image-url)
The IR spectra of I, IV and V showed the characteristic bands of $-\text{NH}_2$ asymmetric and symmetric stretching vibration at 3320-3286 cm$^{-1}$ in addition to the other characteristic bands. The IR spectra of II and III contained water of crystallization not showed the characteristic band of $-\text{NH}_2$ stretching vibration. (Fig. 2 6).

The $-\text{NH}_2$ protons of I-V appeared as a broad singlet at $\delta$ 3.10-5.10 ppm. The other NMR spectral data are listed in Table II.
<table>
<thead>
<tr>
<th>Compound</th>
<th>U.V. (in ethanol)</th>
<th>N.M.R. (CDCl₃ + DMSO-TMS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V (Shoulder)</td>
<td>328 (4.400)</td>
<td>3.00 (6H, cyclohexyl); 1.03-3.70 (6H, CH₂, CH₃)</td>
</tr>
<tr>
<td>IV</td>
<td>325 (4.450)</td>
<td>0.98 (6H, cyclohexyl); 1.03-3.70 (6H, CH₂, CH₃)</td>
</tr>
<tr>
<td>III</td>
<td>327 (4.450)</td>
<td>3.09-4.0 (6H, peak: 2H-NH); 3.28 (6H, CH₂-NH); 5.00-5.20 (6H, peak: 2H-NH)</td>
</tr>
<tr>
<td>II</td>
<td>327 (4.430)</td>
<td>0.98 (6H, cyclohexyl); 1.03-3.70 (6H, CH₂, CH₃)</td>
</tr>
<tr>
<td>I</td>
<td>327 (4.430)</td>
<td>3.09-4.0 (6H, peak: 2H-NH); 3.28 (6H, CH₂-NH); 5.00-5.20 (6H, peak: 2H-NH)</td>
</tr>
</tbody>
</table>

Note: All values are in parts per million (ppm).
Fig. 4: IR Spectrum of 2-Cyclohexylamino-5-(p-aminophenyl)-1,3,4-thiadiazole (II).

Fig. 5: IR Spectrum of 2-Phenethylamino-5-(p-aminophenyl)-1,3,4-thiadiazole (IV).
SUMMARY

Asphodeline, Asphodelus, Eremurus and Anthericum are the four genera of the Liliaceae family belonging to the Asphodeloideae subfamily and Asphodelaceae tribe. Except for the last one, the others are known as cirić plants in Turkey. These four Turkish genera, since their morphological similarities and taxonomical relatives, are treated together in a research realized between 1976-1982. As a result, 14 species of Asphodeline, 2 species of Asphodelus, 2 species of Eremurus, and 2 species of Anthericum are found in Turkey. In this paper, a dichotomous key to the genera, general and introductory knowledge, distributional maps and vernacular names in Turkey, uses, chemical properties and cultivation of the species pertaining the mentioned genera are represented.

REFERENCES


