fore depend to a lesser extent on the character of the hybridization of the ring nitrogen atom, can be considered to be more expedient. The coincidence of \( \delta(5-\text{CH}) \) in the PMR spectra of tautomeric Ia and model derivatives IIa (Table 2) indicates the amine structure of 2-arylamino-5,6-dihydro-4H-1,3-thiazines Ia.

It follows from the PMR spectra of TFA solutions of I-III that bases I-III are protonated at the nitrogen atom attached to the C=N double bond, but the positive charge is delocalized over the amidine system. The coincidence of the chemical shifts of the signals of all of the methylene groups of I-III (Table 2) indicates an identical structure for the resulting cations. At the same time, on passing from the bases to the cations the weak-field shifts of the signals of these groups (\( \Delta \delta \text{CH}_2 \)) of amine models II and substituted I are found to be close and differ markedly from the corresponding values of models of imine structure III, and the differences between the \( \Delta \delta \text{CH}_2 \) values of the latter (III) and the \( \Delta \delta \text{CH}_2 \) values of tautomeric derivatives I are close to the differences in the chemical shifts of the methylene groups of bases II and III (Table 2). This once again indicates that aryl- and alkylaminothiazines Ia and Ib exist in the amine form.

**LITERATURE CITED**


**SYNTHESIS OF 2-HYDRAZINO- AND 2-AMINO-1,3,4-THIADIAZINES CONTAINING POLYHYDRIC PHENOL RESIDUES IN THE 5 POSITION**


2-Hydrazino-1,3,4-thiadiazines containing polyhydric phenol residues in the 5 position were obtained by reaction of 3,4-dihydroxy-, 2,5-dihydroxy-, and 2,3,4-trihydroxyphenacyl \( \omega \)-halides with thiocarbohydrazide. 2-Amino-1,3,4-thiadiazines were obtained by reaction of 3,4-dihydroxy- and 2,5-dihydroxyphenacyl \( \omega \)-halides with thiosemicarbazide in acidic and alcoholic media. In contrast to the dihydroxy derivatives, 2,3,4-trihydroxyphenacyl halide forms a 2-amino derivative only in strongly acidic media, whereas the isomeric thiazole compound with a hydrazine group in the 2 position of the thiazole ring is formed in alcoholic media.

In order to obtain new inhibitor-antioxidants we synthesized a series of 2-hydrazino- and 2-amino-1,3,4-thiadiazines containing polyhydric phenol (pyrocatechol, hydroquinone, and pyrogallol) residues in the 5 position.


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### TABLE 1. 2-Hydrazino- and 2-Amino-1,3,4-Thiadiazines Containing Polyhydric Phenol Residues in the 5 Position

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ar</th>
<th>X</th>
<th>mp, °C*</th>
<th>Empirical formula</th>
<th>Found, %</th>
<th>Calculated, %</th>
<th>UV spectra, λmax (ε · 10^4)</th>
<th>Yield, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>3,4-(OH)₂C₆H₄</td>
<td>NH₃H₂</td>
<td>183–186</td>
<td>C₉H₈N₄O₂S</td>
<td>45.1</td>
<td>4.4</td>
<td>23.2  13.3</td>
<td>222* 327 (1.6)</td>
</tr>
<tr>
<td>II</td>
<td>2,5-(OH)₂C₆H₄</td>
<td>NH₃H₂</td>
<td>175–176</td>
<td>C₉H₈N₄O₂S</td>
<td>42.6</td>
<td>4.7</td>
<td>21.9  12.2</td>
<td>238* 359 (1.2)</td>
</tr>
<tr>
<td>III</td>
<td>2,3,4-(OH)₃C₆H₃</td>
<td>NH₃H₂</td>
<td>203–204</td>
<td>C₉H₈N₄O₄S</td>
<td>45.0</td>
<td>4.1</td>
<td>21.8  12.5</td>
<td>218* 333 (1.1)</td>
</tr>
<tr>
<td>IV</td>
<td>3,4-(OH)₂C₆H₄</td>
<td>NH₂</td>
<td>194–195</td>
<td>C₉H₈N₂O₂S</td>
<td>48.3</td>
<td>4.1</td>
<td>18.6  14.3</td>
<td>238* 331 (1.7)</td>
</tr>
<tr>
<td>V</td>
<td>2,5-(OH)₂C₆H₄</td>
<td>NH₂</td>
<td>196–197</td>
<td>C₉H₈N₂O₄S</td>
<td>48.5</td>
<td>4.1</td>
<td>18.7  14.5</td>
<td>250 (1.2)  367 (1.0)</td>
</tr>
<tr>
<td>VI</td>
<td>2,3,4-(OH)₃C₆H₃</td>
<td>NH₂</td>
<td>185–186</td>
<td>C₉H₈N₂O₄S</td>
<td>44.7</td>
<td>3.8</td>
<td>17.6  13.6</td>
<td>217 (2.0)  344 (1.5)</td>
</tr>
</tbody>
</table>

*All of the substances melted with decomposition.
†The maximum was expressed as a shoulder.

**Fig. 1.** PMR spectra (in CF₃COOH): A) 2-hydrazino-5-(3,4-dihydroxyphenyl)-1,3,4-thiadiazine (I); B) 2-hydrazino-4-(2,3,4-trihydroxyphenyl)thiazole (IX).

**Fig. 2.** UV spectra (in ethanol): 1) 2-hydrazino-5-(2,3,4-trihydroxyphenyl)-1,3,4-thiadiazine (III); 2) 2-amino-5-(2,3,4-trihydroxyphenyl)-1,3,4-thiadiazine (VI); 3) 2-hydrazino-4-(2,3,4-trihydroxyphenyl)thiazole (IX); 4) 2-hydrazino-4-phenylthiazole (VIII).