Quinolyl-nitro Ethylenes and Nitrostyryl-quinolines of Molluscicidal Activity

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Quinolyl-nitro Ethylenes, Styrylquinolines, \( p \)-Nitro-styrylquinolines, Molluscicidal Activity

For possible molluscicidal activity, 1-(4-quinolyl)-2-nitro ethylenes, 1-(4-quinolyl)-2-methyl-2-nitro ethylenes, 2-styryl, and 2-(p-nitro styryl)-quinolines were synthesized.

It has been reported that the nitro ethylenes exhibit antibacterial and antifungal activities [1], and \( \beta \)-nitrostyrenes found to have promising molluscicidal activity [2]. On the other hand styrylquinolines have been reported to be germicides [3] or to inhibit aerobic glycolysis [4].

In view of these findings, the nitro ethylenes 1 and 2 were synthesized to study their biological activity compared with different styrylquinolines (3) in an attempt to obtain a molluscicide of increased activity.

\[
\begin{align*}
\text{1, 2a: } & R = H \\
\text{b: } & R = \text{NO}_2 \\
\text{e: } & R = \text{Cl} \\
\text{3a: } & R = 5 \text{ Cl}; \ R' = \text{H} \\
\text{b: } & R = 5 \text{ Cl}; \ R' = \text{NO}_2 \\
\text{c: } & R = 6 \text{ Cl}; \ R' = \text{H} \\
\text{d: } & R = 6 \text{ Cl}; \ R' = \text{NO}_2 \\
\text{e: } & R = 7 \text{ Cl}; \ R' = \text{N0}_2 \\
\text{f: } & R = 7 \text{ Cl}; \ R' = \text{NO}_2 \\
\text{g: } & R = 8 \text{ NO}_2; \ R' = \text{Cl}
\end{align*}
\]

Synthesis of 1-(4-quinolyl)-2-nitro ethylenes (1) and 1-(4-quinolyl)-2-methyl-2-nitro ethylenes (2) was achieved by the reaction of the corresponding quinoline-4-carboxaldehydes with nitro methane and nitro ethane respectively, and synthesis of 2-styrylquinolines (3) was accomplished by the reaction of the substituted quinaldines with aromatic aldehydes in the presence of fused zinc chloride.

All compounds were tested as molluscicides against two kinds of bilharzia snails namely, Biomphalaria alexandrina and Bulinus truncatus, freshly collected from irrigation canals of the river Nile. Compounds 1b and 2b were the most active, and snails were killed at dilutions of 3–4 ppm.

Experimental

Melting points are uncorrected and were taken on Boetius melting point microscope.

Quinoline-4-carboxaldehydes and substituted quinaldines were prepared according to the reported methods.

1-(4-Quinolyl)-2-nitro ethylenes (1) and 1-(4-quinolyl)-2-methyl-2-nitro ethylenes (2)

To a solution of the quinoline-4-carboxaldehyde (0.01 mole) in 20 ml abs. EtOH, nitromethane or nitroethane (0.016 mole) was added. Butylamine (1 ml) was added as a catalyst. The reaction mixture was left overnight. The separated solid was collected and recrystallized from AcOEt or to inhibit aerobic glycolysis [4].

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Table. Preparation of compounds 1-3.

<table>
<thead>
<tr>
<th>Compound</th>
<th>m.p. [°C]</th>
<th>Yield [%]</th>
<th>Analysis [%]</th>
<th>C</th>
<th>H</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>173</td>
<td>46</td>
<td>C_{12}H_{12}N_{2}O_{2}</td>
<td>66.00</td>
<td>4.00</td>
<td>14.00</td>
</tr>
<tr>
<td>1b</td>
<td>197</td>
<td>45</td>
<td>C_{12}H_{12}N_{2}O_{2}</td>
<td>53.87</td>
<td>2.85</td>
<td>17.14</td>
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<tr>
<td>1c</td>
<td>162</td>
<td>42</td>
<td>C_{12}H_{12}Cl_{2}O_{2}</td>
<td>56.28</td>
<td>2.98</td>
<td>11.93</td>
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<tr>
<td>1d</td>
<td>2a</td>
<td>162</td>
<td>C_{12}H_{12}N_{2}O_{2}</td>
<td>65.60</td>
<td>4.22</td>
<td>13.08</td>
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<tr>
<td>1e</td>
<td>148</td>
<td>40</td>
<td>C_{12}H_{12}N_{2}O_{2}</td>
<td>55.60</td>
<td>3.47</td>
<td>16.21</td>
</tr>
<tr>
<td>1f</td>
<td>210</td>
<td>40</td>
<td>C_{12}H_{12}Cl_{2}O_{2}</td>
<td>57.90</td>
<td>3.62</td>
<td>11.26</td>
</tr>
<tr>
<td>1g</td>
<td>118</td>
<td>60</td>
<td>C_{12}H_{12}Cl_{2}O_{2}</td>
<td>65.67</td>
<td>4.51</td>
<td>5.26</td>
</tr>
<tr>
<td>2a</td>
<td>161</td>
<td>62</td>
<td>C_{12}H_{12}Cl_{2}O_{2}</td>
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<td>4.51</td>
<td>5.26</td>
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<tr>
<td>2b</td>
<td>172</td>
<td>65</td>
<td>C_{12}H_{12}Cl_{2}O_{2}</td>
<td>65.67</td>
<td>3.56</td>
<td>9.01</td>
</tr>
<tr>
<td>2c</td>
<td>145</td>
<td>62</td>
<td>C_{12}H_{12}Cl_{2}O_{2}</td>
<td>65.67</td>
<td>3.56</td>
<td>9.01</td>
</tr>
<tr>
<td>3a</td>
<td>128</td>
<td>58</td>
<td>C_{12}H_{12}Cl_{2}O_{2}</td>
<td>65.67</td>
<td>3.56</td>
<td>9.01</td>
</tr>
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</table>

Compounds 3a-g were crystallized from ethanol.