Synthesis of New 2,7-Dihydroxy Naphthalene Heterocyclic Derivatives
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Abstract
In this work was the ester compound (1) has been prepared by treating 2,7-
dihydroxynaphthalene with ethyl bromoacetate. The ester (1) reaction with
hydrazine hydrate (98%) and afford hydrazide (2). Then the reaction of hydrazide (2)
with phenyl isothiocyanate gave the compound (3). The azomethines (4-7) were
prepared from corresponding aldehydes or ketones and hydrazide compound(2).
Reaction of compounds (4-7) with mercaptaoacetic acid led to
azomethine group open giving a compounds (8-11). On other hand treatment of
compounds (4-7) with 2,4-dinitrobenzoyl chloride gave the compounds (12-15).
The dissolve of the compound (3) in the solution of NaOH (2N) and neutralized
with dilute HCl gave a compound (16).

As well as reaction compound (3) with carbon disulfide and KOH gave the
Potassium salt (17). The dissolve Potassium salt (17) in water and acidification gave
the compound (18). On other hand, the dissolve Potassium salt (17) with water on
treatment with hydrazine gave the compound (19).

Introduction
Naphthalene and its derivatives has clinical effect. It causes hemolysis
with subsequanent blocking of renal tubules, vomiting and Headunche (1,2).
Schiff bases have widely reported to be biologically versatile compounds having anti fungal, herbicidal and plant growth
regulating properties (3,4). Derivatives of 1,3,4-oxadiazole and 1,3,4-triazole have also been found to possess a wide spectrum of pharmacological, medical and biological

activities (4,5,6).
MATERIALS AND METHODS

Melting points were determined in open capillary tubes on a Gallenkamp melting point apparatus and are uncorrected.

The IR spectra (KBr disc were recorded with Shimadzu -2N, FT IR - 8400S. UV spectra were recorded on Varian,UV-Vis spectrophptometer using absolute ethanol as solvent.

Synthesis of ethyl{[7-(2-ethoxy-2-oxoethoxy)-2-naphthyl]oxy} acetate (1) [7]

To a solution of 2,7-dihydroxynaphthalene (0.01 mole) in 50 ml of absolute ethanol and (0.02 mole) of potassium carbonate, ethyl bromoacetate (0.02 mole) was added and the reaction mixture was refluxed for 3hrs. on cooling, the precipitate formed was filtered off, washed with water and recrystallized from aqueous ethanol to give compound(1).

Synthesis of 2- {{[7-(2-hydrazone-2-oxoethoxy) -2- naphthyl] oxy} aceto hydrazide (2) [7]

A mixture of compound (1) 0.01mole and hydrazine hydrate (25 ml) was refluxed for 4hrs. on cooling, the solid, the product was filtered and recrystallized from ethanol to give a compound (2).

Synthesis of 2- {[(7-oxo N`-(phenylcarbonothioyl) acetohyrazinyl -2- naphthyl) oxy] -N`-(phenylcarbonothioyl)acetohydrazide Compound (3) [7]

To a suspension of compound (2) (0.01 mole) in dry benzene (30 ml), phenylisothiocyanate (0.024 mole) was added and the reaction mixture was refluxed for (5hrs.) on cooling, the solid obtained was filtered and recrystallized from chloroform.

Synthesis of Schiff bases (4-7) [8]

General procedure

To stirring solution of compound (2) (0.01 mole) in absolute ethanol (15 ml), appropriate aldehyde or ketone (0.02 mole) was added, the mixture was refluxed for (3hrs.) and cooled to room temperature. The precipitate was filtered and recrystallized from ethanol.

Synthesis of N-(2,2-dimethyl-4-oxo-1,3-thiazolidin-3-yl)-2-[(7-N-(2,2-dimethyl - 4-oxo-1,3thiazolidin-3-yl)-2-oxoacetamide-2-naphthyl)oxy] acetamide(8-11) [9]

A mixture of an appropriate azomethine derivative (4-7)(0.01) and mercapto acetic acid (2mole ), in dry toluene (30 ml), was heated under reflux for (5hrs.) The solvent was then distilled in vacuo and the
obtained crude product was oily, so it purified by column chromatography along silica gel and xylene as eluent. The precipitate was filtered and recrystallized from xylene.

Synthesis of 2,7-\{di[N-(1-chloro-1-methylethyl) -N’-glycoloyl -2,4-dinitro benzohydrazide] naphthalene\} (12-15) [8]

To a stirring solution of an appropriate (4-7) (0.005 mole) in dry benzene (15 ml), 2,4-dinitrobenzoyl chloride (0.01 mole) in dry benzene (10 ml) was added dropwise, the mixture reaction was refluxed for (1 hr.), after cooling, the precipitate was filtered and recrystallized from benzene.

Synthesis of 2,7-di[(5-methoxy)-1,3,4-triazole-2(3H)-thion] naphthalene (16) [7]

Compound (3) (0.01 mole) was dissolved in NaOH (20 ml, 2N) and heated on a water bath for (2 hrs.), cooled and the reaction mixture filtered, and the filtrate neutralized with dilute HCl. The precipitate obtained was filtered and crystallized from ethanol.

Synthesis of 2,7-di[(5-methoxy)-1,3,4-oxadiazole-1-phenyl-2(3H)-thion] naphthalene (18) [7]

Potassium salt (17) was prepared by refluxing hydrazide derivative (2) (0.01 mole) and carbon disulphide (0.03 mole) in absolute ethanol containing KOH (0.03 mole) on a water bath for (1 hr.) The solvent was removed and the solid salt which had been formed, dissolved in water (10 ml), cooled and acidified with HCl. The precipitate was filtered off, washed with water and recrystallized from ethanol – CHCl3.

Synthesis of 2,7-di [(5-methoxy)-1,3,4-triazole -1- amino -2(3H) -thion] naphthalene (19) [7]

Compound (3) (0.01 mole) and carbon disulphide (0.03 mole) in ethanol (25 ml) containing KOH (0.03 mole) were reflux on a water bath for (1 hr.). The solvent was removed and the residue was dissolved in water (10 ml) and then treated with hydrazine hydrate (0.04 mole, 98%) and refluxed for (4 hrs.). The contents were cooled, diluted with water and acidified with HCl. The precipitate was collected by filtration, washed with water, dried and recrystallized from ethanol.

This paper reports the synthesis of some new 2,7-dihydroxy naphthalene compounds.
\[ \text{H}_2\text{N-NH-C-CH}_2\text{-O-CH}_2\text{-C-NH-NH} \]

\[ \text{O} \]

\[ \text{R-CH} \]

\[ \text{O} \]

\[ \text{N-NH-C-CH}_2\text{-O-CH}_2\text{-C-NH-N} \]

\[ \text{O} \]

\[ \text{R} \]

\[ \text{R} \]

\[ \text{HSCH}_2\text{COOH} \]

\[ \text{NO}_2 \]

\[ \text{NO}_2 \]

\[ \text{CODCI} \]

\[ \text{C=NH-NH-C-CH}_2\text{-O-CH}_2\text{-C-NH-N} \]

\[ \text{O} \]

\[ \text{R} \]

\[ \text{R} \]

\[ \text{R} \]

\[ \text{R} \]

\[ \text{S} \]

\[ \text{S} \]

\[ \text{S} \]

\[ \text{S} \]

\[ \text{CS}_2 / \text{KOH} \]

\[ \text{K-S-C-S-NH-C-CH}_2\text{-O-CH}_2\text{-C-NH-NH-C-SK} \]

\[ \text{O} \]

\[ \text{N NH} \]

\[ \text{O} \]

\[ \text{HN N} \]

\[ \text{S} \]

\[ \text{CH}_2\text{-O-CH}_2\text{-S} \]

\[ \text{Ph} \]

\[ \text{HCl} \]

\[ \text{N} \]

\[ \text{N NH} \]

\[ \text{N} \]

\[ \text{HN N} \]

\[ \text{S} \]

\[ \text{CH}_2\text{-O-CH}_2\text{-S} \]

\[ \text{N} \]

\[ \text{HN N} \]

\[ \text{S} \]

\[ \text{Ch}_2\text{-O-CH}_2\text{-S} \]

\[ \text{Ph} \]

\[ \text{N} \]

\[ \text{HN N} \]

\[ \text{S} \]

\[ \text{Ch}_2\text{-O-CH}_2\text{-S} \]

\[ \text{N} \]

\[ \text{HN N} \]

\[ \text{S} \]

\[ \text{Ch}_2\text{-O-CH}_2\text{-S} \]

\[ \text{Ar} \cdot \text{N} \]

\[ \text{N} \]

\[ \text{N} \]

\[ \text{Br OCH}_3 \]

\[ \text{R} \cdot \text{CH} \cdot \text{H} \]

\[ \text{Ar} = 2,4 \cdot \text{di (NO)}_2 \cdot \text{C}_6\text{H}_3 - \]

\[ \text{18} \]

\[ \text{19} \]

\[ \text{12-15} \]

\[ \text{16} \]

\[ \text{17} \]

\[ \text{8-11} \]

\[ \text{3} \]

\[ \text{4-7} \]

\[ \text{1} \]

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RESULTS AND DISCUSSION

The reaction of the 2,7-dihydroxy naphthalene with ethyl bromoacetate in absolute ethanol gave a compound (1) \(\text{Table (1)}\). The formation of this compound was indicated by presence in their IR spectra of the carbonyl group \((\text{C}=\text{O})\) at 1761 cm\(^{-1}\) combined with the disappearance of the OH stretching band. UV-spectra of compound (1) mostly showed intense maxima at 324 nm and 236 nm which belonged to \(\text{n} \rightarrow \pi^*\) and \(\pi \rightarrow \pi^*\) transition respectively. A compound (1) which was then reacted with hydrazine hydrate (98%) to afford the compound (2). IR spectra showed the carbonyl group \((\text{C}=\text{O})\) stretching bond at 1690 cm\(^{-1}\) combined with appearance of \((\text{NH}_2)\) bands at 3398, 3279 cm\(^{-1}\). UV. Spectra of compound (2) mostly showed intense maxima at 233 nm and 308 which belonged to \(\pi \rightarrow \pi^*\) and \(\text{n} \rightarrow \pi^*\) transitions respectively.

As well as treatment the compound (2) with phenylisothiocyanate in dry benzene to gave a compound (3). IR spectra shows the carbonyl group \((\text{C}=\text{O})\) stretching band at 1660 cm\(^{-1}\) \((\text{N-H})\) stretching band at 3320,3210 cm\(^{-1}\). UV spectra showed intense maxima at 325 and 237 nm belonged to \(\text{n} \rightarrow \pi^*\) and \(\pi \rightarrow \pi^*\) respectively.

The condensation of compound (2) with difference aldehydes or ketones in absolute ethanol gave the Schiff bases (4-7) (Table 2). The formation of these Schiff bases was indicated by the presence in their IR spectra of the azomethine \((\text{CH}=\text{N})\) stretching band at 1604-1688 cm\(^{-1}\) combined with the disappearance of the \(\text{NH}_2\) stretching bands. UV spectra of Schiff bases mostly showed two intense maxima at 333-352 nm and 206-247 nm which belonged to \(\text{n} \rightarrow \pi^*\) and \(\pi \rightarrow \pi^*\) transitions respectively. Schiff bases (4-7) which were then cyclo condensed with mercapto acetic acid in dry toluene to afford the thiazolidine-4-ones (8-11) (table 3). IR spectra showed the carbonyl group \((\text{C}=\text{O})\) stretching band at 1640-1697 cm\(^{-1}\) combined with the disappearance of the azomethine \((\text{CH}=\text{N})\) bands.

UV spectra of (8-11) compounds mostly showed two intense maxima at 277-280 nm and 205-247 nm which belonged to \(\text{n} \rightarrow \pi^*\) and \(\pi \rightarrow \pi^*\) transitions respectively.

However treatment of Schiff bases (4-7) with acid chloride results in the formation of (12-15) (Table 4) in which the two groups (\(\text{Cl}\) and \(\text{ArCO}\)) were introduced in the same step of the reaction. This reaction was followed by disappearance of absorption bands of \((\text{CH}=\text{N})\) in the 1604-1688 cm\(^{-1}\) and 1680-1695,760-780 cm\(^{-1}\) which were attributed to \((\text{C}=\text{O})\) and \((\text{C-Cl})\) respectively. UV. spectra of (12-15) compounds showed two intense maxima at 336-340 nm and 204-
236nm due to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$.

The reaction was followed, the attack by the azomethine at the (C=O) of 2,4- dinitrobenzoyl chloride displacing the chloride as chloride anion forming, the iminiumcation. However, iminiumcation was unstable, so the Cl attached $-N=\overset{\cdot}{C}$ moiety and offered more stable covalently compounds (12-15).

Then, preparations compound (16) from compound (3) and solution of NaOH (2N) (table 5). The appearance of IR new absorption bands in general regions 3180 cm$^{-1}$ and 1590 cm$^{-1}$ were attentively belonged to (N-H) and (C=N) respectively. UV. spectra of compound (16) at 254 nm and 332 nm due to $n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$. Preparation compound (18) from potassium salt (17) was dissolved in water and acidified with HCl (table 5). IR spectrum of the absorption bands in 3146 cm$^{-1}$ and 1586 cm$^{-1}$ were attentively to (NH) and (C=N). UV. Spectra of compound (18) at 256 nm and 326 nm due to $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$.

Finally, Preparation compound (19) from potassium salt (17) was dissolved in water and hydrazine hydrate (98%) (table 5). IR spectra of above the absorption bands in 3386-3250 cm$^{-1}$, 3136 cm$^{-1}$ and 1605 cm$^{-1}$ due to (NH$_2$,NH) and (C=N). UV. spectra of compound (19) at 253 nm and due to $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$.

Table - 1: Properties of Compounds (1-3)

<table>
<thead>
<tr>
<th>Comp. No.</th>
<th>R O O R Comp.</th>
<th>M.P.</th>
<th>Yield %</th>
<th>C°</th>
<th>-C.H.N Analysis (%)</th>
<th>(Calc./Fou.) Spectral data</th>
<th>IR cm$^{-1}$</th>
<th>UV.$\lambda_{max}$ (EtOH)</th>
<th>Decomp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CH$_2$CO$_2$Et</td>
<td>Decomp.</td>
<td>201</td>
<td>87</td>
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<td></td>
<td>3180</td>
<td>254</td>
<td>201</td>
</tr>
<tr>
<td>R1</td>
<td>C</td>
<td>N</td>
<td>NH</td>
<td>NH</td>
<td>C</td>
<td>R</td>
<td></td>
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<tr>
<td>CH₂</td>
<td>O</td>
<td>O</td>
<td>CH₂</td>
<td>C</td>
<td>NH</td>
<td>N</td>
<td>C</td>
<td>R₁</td>
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</tr>
</tbody>
</table>

C(65.06/64.93)
N(0/0)
H(6.02/6.20)
324,310, 274,236
1761(C=O), 2945(C-Hor.), 1249(C-O-C), 1629(C=C), 2914(C-Hal.)
2
-CH₂CONHNH₂:
234-236
73
C(61.53/60.73)
N(20.51/20.62)
H(4.02/4.55)
308,233, 204,235
3398,3279(N-H), 3093(C-Hor), 1690(C=O), 1535(C=C or .), 2993(C-Hal.)
3
Hₐ C C
O
NH NH C
S
NH Ph
Decomp. 218
63 C(61.76/61.42)
N(15.44/15.61)
H(4.77/4.83)
S(11.76/11.90)
325,379, 205,237
3320,3210(NH), 1660(C=O), 3080(C-Hor), 1550(C=C)

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Table -2 : Properties of Schiff bases(4-7)
<table>
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<tr>
<th>Comp. No.</th>
<th>R</th>
<th>R₁</th>
<th>M.P.</th>
<th>C°</th>
<th>Yield %</th>
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</tbody>
</table>

**Spectra data**

**IR.**

**UV.λ<sub>max</sub> cm<sup>-1</sup>**

(εtOH)

1. **NCH₃**
   - 220-222
   - 67
   - 207,245,347
   - 3220(N-H),
   - 3050(C-Hor.),
   - 2970(C-Hal.),
   - 1697(C=O),
   - 1662(C=N)

2. **NCH₃**
   - 213-215
   - 72
   - 206,243,343
   - 3232(N-H),
   - 3012(C-Hor),
   - 2912(C-Hal.),
   - 1688(C=O),
   - 1635(C=N)

3. **OCH₃**
   - 190-192
   - 52
   - 209,245,333
   - 3452(N-H),
   - 3045(C-Hor)
   - 2916(C-Hal.),
   - 1658(C=O),
   - 1604(C=N)

4. **Br**
   - 170-172
   - 82
   - 206,247,353
   - 3320(N-H),
   - 308(C-Hor),
   - 2910(C-Hal.),
   - 1660(C=O),
Table -3 : Properties of compounds (8-11)

<table>
<thead>
<tr>
<th>Comp. No.</th>
<th>R</th>
<th>R₁</th>
<th>M.P. (°C)</th>
<th>Yield (%)</th>
<th>Spectra data</th>
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<tbody>
<tr>
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<td></td>
<td></td>
<td></td>
<td>IR. cm⁻¹</td>
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<td>UV. λmax (EtOH)</td>
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<td>8</td>
<td>N</td>
<td>CH₃</td>
<td>192-194</td>
<td>54</td>
<td>205, 233, 277</td>
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<td></td>
<td></td>
<td></td>
<td>3240(N-H),</td>
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<td></td>
<td></td>
<td>1697(C=O),</td>
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<td>1688(C=O),</td>
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<td></td>
<td></td>
<td>3070(CH₂or.),</td>
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<td>2970(C-Hal.),</td>
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<td>1550(C=Cor.)</td>
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<tr>
<td>9</td>
<td>N</td>
<td>CH₃</td>
<td>205-207</td>
<td>42</td>
<td>206, 234, 279</td>
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<td>3270(N-H),</td>
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<td>1695(C=O),</td>
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<td></td>
<td>1650(C=O),</td>
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<td></td>
<td>3070(C-Hor.),</td>
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<td>10</td>
<td>OCH₃</td>
<td>H</td>
<td>Oily</td>
<td>38</td>
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205,244,280
3320(N-H),
1690(C=O),
1650(C=O),2050(C Hor.),
1590(C=Cor.)
11
Br
H
17-199
47
208,247,289
3290(N-H),1680(C=O),
1640(C=O),3060(C Hor.),
1560(C=Cor.)

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Table - 4 : Properties of compounds(12-15)

O CH₂ C N NH CH₂ O NH N
Cl
R C
Cl
R₁
R₂ R
C C
CH CH₃ ₃
O O

Comp. No.
R
R₁
M.P.
°C
Yield %

Spectra data
IR.
UV.λₘₐₓ cm⁻¹
(EtOH)
12
N
CH₃
250-252
67
206,233,336
3260(N-H),
1680(C=O),
1650(C=O),
760(C-Cl),
1390(NO₂)
3060(C-Hor.)
13
N
CH₃
240-242
55
207,231,338
3260(N-H),
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Table -5: Properties of compounds(16-19)

<table>
<thead>
<tr>
<th>Comp. No.</th>
<th>R</th>
<th>M.P. (°C)</th>
<th>Yield (%)</th>
<th>Spectra data</th>
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<td>IR. cm⁻¹</td>
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<td>UV.λ max (EtOH)</td>
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<td>16</td>
<td>N</td>
<td>227-229</td>
<td>55</td>
<td>207,254,290,332</td>
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<td>17</td>
<td>N</td>
<td></td>
<td>63</td>
<td>1690,1660(C=O)</td>
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<tr>
<td>18</td>
<td>NH</td>
<td></td>
<td>63</td>
<td>1395(NO₂)</td>
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<tr>
<td>19</td>
<td>S</td>
<td></td>
<td>63</td>
<td>3295(N-H)</td>
</tr>
</tbody>
</table>

O CH₂ R CH₂ O R

OCH₃
REFERENCES


6. Daoud, K.M. and Eisa, M.A., (Synthesis of some substituted 1,3,4-oxadiazoles, thiadiazoles and 1,2,4-triazoles from 4-Al Mustansiriya J. Sci Vol. 20, No 2, 2009

