5.1. Introduction

Quinoline alkaloids represent the major class of heterocycles occurring widely in nature and possess interesting pharmacological activities.\textsuperscript{1,2} Currently, there is a renaissance of interest in search of novel biologically active compounds due to a dramatic and alarming increase in the incidence of bacterial infections resistant to most common antibiotics.

The plant family \textit{Rutaceae}, comprises about one hundred and fifty genera with sixteen hundred species\textsuperscript{3} and found to be a rich source of remarkable varieties of natural products like alkaloids\textsuperscript{4}, coumarins\textsuperscript{5}, flavanoids\textsuperscript{6}, limonoids\textsuperscript{7} etc. The alkaloids isolated from the \textit{Rutaceous} plants are of diverse structural types\textsuperscript{8} like quinolines, furoquinolines, pyranoquinolines, acridines, pyrrolidines, oxazoles, dimeric quinolines etc.

Several reviews\textsuperscript{9-29} have appeared on the chemistry as well as the pharmacological properties of these alkaloids. Subsequent to those reviews there are reports on antitumour\textsuperscript{30,31} (Ptelefolonium), growth inhibition\textsuperscript{30,31} (Balfourodinium, Ptelefolonium), cytotoxic,\textsuperscript{31} hypothermic\textsuperscript{31} (Ptelefolonium), antibacterial\textsuperscript{32} (Vesprisinium), antimicrobial\textsuperscript{33} (Glycosolone), antifungal\textsuperscript{34} (Xanthobungalanine) and other interesting biological properties.\textsuperscript{35-37}

Since the work incorporated in this chapter is related to the synthesis of prenyl-, furo-, pyrano-, quinoline alkaloids, the discussion is confined to the chemistry of these alkaloids only.

The structures of the typical members of each group are given below.

(i) 3-Prenyl-2-quinolinones

\begin{center}
\includegraphics[width=0.2\textwidth]{1a.png}
\end{center}

\textit{e.g.} Atanine
(ii) 2-Isopropyl-2,3-dihydrofuro[2,3-\(b\)]quinolinones

\[
\begin{align*}
\text{e.g. Lunacrine} \\
\includegraphics[width=0.2\textwidth]{2a.png}
\end{align*}
\]

(iii) Pyrano[2,3-\(b\)]quinolinones

\[
\begin{align*}
\text{e.g. Khaplofoline} \\
\includegraphics[width=0.2\textwidth]{3a.png}
\end{align*}
\]

5.1.1. 3-Prenyl-2-quinolinone alkaloids

The alkaloids of these groups, isolated and characterized are listed in Table 5.1

\[
\begin{align*}
\includegraphics[width=0.5\textwidth]{1.png}
\end{align*}
\]

Table 5.1

<table>
<thead>
<tr>
<th>No</th>
<th>ALKALOID</th>
<th>(R_1)</th>
<th>(R_4)</th>
<th>(R_5)</th>
<th>(R_7)</th>
<th>(R_8)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Atanine (la)</td>
<td>H</td>
<td>OCH(_3)</td>
<td>H</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>2</td>
<td>N-Methylatanine (lb)</td>
<td>CH(_3)</td>
<td>OCH(_3)</td>
<td>H</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>3</td>
<td>Preskimmianine (lc)</td>
<td>H</td>
<td>OCH(_3)</td>
<td>H</td>
<td>OCH(_3)</td>
<td>OCH(_3)</td>
</tr>
<tr>
<td>4</td>
<td>N-Methylpreskimmianine (ld)</td>
<td>CH(_3)</td>
<td>OCH(_3)</td>
<td>H</td>
<td>OCH(_3)</td>
<td>OCH(_3)</td>
</tr>
<tr>
<td>5</td>
<td>Glycosolone</td>
<td>CH(_3)</td>
<td>OCH(_3)</td>
<td>H</td>
<td>H</td>
<td>OH</td>
</tr>
<tr>
<td>6</td>
<td>O-Methylglycosolone</td>
<td>CH(_3)</td>
<td>OCH(_3)</td>
<td>H</td>
<td>H</td>
<td>OCH(_3)</td>
</tr>
<tr>
<td>7</td>
<td>Glycophylone</td>
<td>CH(_3)</td>
<td>OH</td>
<td>H</td>
<td>H</td>
<td>OCH(_3)</td>
</tr>
<tr>
<td>8</td>
<td>Glycolonez</td>
<td>H</td>
<td>OCH(_3)</td>
<td>H</td>
<td>H</td>
<td>OCH(_3)</td>
</tr>
<tr>
<td>9</td>
<td>4-Demethyl-N-methylatanine (li)</td>
<td>CH(_3)</td>
<td>OH</td>
<td>H</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>10</td>
<td>N-Methylpremaculosidine (lj)</td>
<td>CH(_3)</td>
<td>OCH(_3)</td>
<td>OCH(_3)</td>
<td>H</td>
<td>OCH(_3)</td>
</tr>
<tr>
<td>11</td>
<td>7,8-Methylenedioxyatanine (lk)</td>
<td>H</td>
<td>OCH(_3)</td>
<td>H</td>
<td>-O-CH(_2)-</td>
<td></td>
</tr>
</tbody>
</table>
Even prior to isolation as natural products, 4-methoxy-3-prenyl-2-quinolinone (1a) was prepared\cite{25} in connection with the synthesis and biosynthesis of furoquinoline alkaloids. The prenyl quinolinones \textit{la-lr} have now been identified as constituents of the \textit{Rutaceous} plants. Atanine is the simplest alkaloid of this group and was isolated from \textit{Fagara Xanthoxyloides} Lam.\cite{38} The structure of atanine was proved to be 1a on the basis of

(i) Its spectral data,
(ii) Its ready reduction to 4-methoxy-3(3'-methylbutyl)-2-quinolinone\cite{39} (6)
(iii) Its conversion to dihydroflindersine\cite{50} (7) on heating with HI
The first synthesis of atanine (1a) was due to Grundon et al.\textsuperscript{40,41} who used it as the key precursor for the synthesis of platydesmine. The method involved heating a mixture of aniline and diethyl(3'-methylbut-2'-enyl)malonate (4) in boiling diphenyl ether to give 5\textsuperscript{42} which on methylation with diazomethane afforded 1a. Alkaloids 1b,\textsuperscript{43} 1c,\textsuperscript{44} 1d,\textsuperscript{45} 1f,\textsuperscript{46} 1j\textsuperscript{47} and 1k\textsuperscript{48} (Table 5.1) were synthesized likewise using 4 and appropriately substituted anilines.

The various methods adopted towards the synthesis of 3-prenyl-2-quinolinones are summarized in Scheme 5.1 and Scheme 5.2.

Scheme 5.1
5.1.2. 2-Isopropylfuroquinolinone alkaloids

*Rutaceae* plant is a rich source of furoquinoline alkaloids with an isopropyl side chain at C2-position. The various alkaloids of this group that have been isolated and characterized are listed in Table 5.2 and Table 5.3. Lunacrine, lunacine and platydesmine are typical examples.

![Diagram of alkaloid structure](image)

Table 5.2

<table>
<thead>
<tr>
<th>No</th>
<th>ALKALOID</th>
<th>R&lt;sub&gt;2&lt;/sub&gt;</th>
<th>R&lt;sub&gt;3&lt;/sub&gt;</th>
<th>R&lt;sub&gt;6&lt;/sub&gt;</th>
<th>R&lt;sub&gt;7&lt;/sub&gt;</th>
<th>R&lt;sub&gt;8&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Lunacrine</td>
<td>CH(CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>OCH&lt;sub&gt;3&lt;/sub&gt;</td>
</tr>
<tr>
<td>2</td>
<td>Lunine</td>
<td>CH(CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>H</td>
<td>H</td>
<td>-O-CH&lt;sub&gt;2&lt;/sub&gt;-O-</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Isoplatydesmine</td>
<td>C(OH)(CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Balfourodine</td>
<td>C(OH)(CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>OCH&lt;sub&gt;3&lt;/sub&gt;</td>
</tr>
<tr>
<td>5</td>
<td>Ribaline</td>
<td>C(OH)(CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>H</td>
<td>OH</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>6</td>
<td>Hydroxylunine</td>
<td>C(OH)(CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>H</td>
<td>H</td>
<td>-O-CH&lt;sub&gt;2&lt;/sub&gt;-O-</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Ptelefolone</td>
<td>C(CH&lt;sub&gt;3&lt;/sub&gt;)=CH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>H</td>
<td>OCH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>H</td>
<td>OCH&lt;sub&gt;3&lt;/sub&gt;</td>
</tr>
<tr>
<td>8</td>
<td>Ptelefolidone</td>
<td>C(CH&lt;sub&gt;3&lt;/sub&gt;)=CH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>H</td>
<td>H</td>
<td>-O-CH&lt;sub&gt;2&lt;/sub&gt;-O-</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Folisine</td>
<td>C(OH)CH&lt;sub&gt;3&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;OH</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Lemobiline</td>
<td>(CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>H</td>
<td>H</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>Ifflaiamine</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>(CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>H</td>
<td>H</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>Demethoxylunacrine</td>
<td>CH(CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td></td>
</tr>
</tbody>
</table>

The structure of lunacrine (2a), an iso-alkaloid was determined by chemical as well as by spectral methods. On heating lunacrine (2a) with alkali, an alcohol (9) was obtained which upon reaction with diazomethane afforded lunacridine (10). Lunacridine gave back lunacrine (2a) on acid treatment. Lunasine perchlorate 8a was also found to give lunacrine on treatment with LiBr in acetonitrile (Scheme 5.3).
Table 5.3

<table>
<thead>
<tr>
<th>No</th>
<th>ALKALOID</th>
<th>R₂</th>
<th>R₆</th>
<th>R₇</th>
<th>R₈</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Lunasine (8a)</td>
<td>CH(CH₃)₂</td>
<td>H</td>
<td>H</td>
<td>OCH₃</td>
</tr>
<tr>
<td>2</td>
<td>O-Methylluninium (8b)</td>
<td>CH(CH₃)₂</td>
<td>H</td>
<td>-O-CH₂-O-</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>N-Methylplatydesminium (8c)</td>
<td>C(OH)(CH₃)₂</td>
<td>H</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>4</td>
<td>O-Methylbalfourodinium (8d)</td>
<td>C(OH)(CH₃)₂</td>
<td>H</td>
<td>H</td>
<td>OCH₃</td>
</tr>
<tr>
<td>5</td>
<td>O-Methylhydroxyluninium (8e)</td>
<td>C(OH)(CH₃)₂</td>
<td>H</td>
<td>-O-CH₂-O-</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Ribalinium</td>
<td>C(OH)(CH₃)₂</td>
<td>OH</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>7</td>
<td>Ptteleatinium</td>
<td>C(OH)(CH₃)₂</td>
<td>H</td>
<td>H</td>
<td>OH</td>
</tr>
<tr>
<td>8</td>
<td>6-Methoxy-7,8-methylene dioxyplatydesminium</td>
<td>C(OH)(CH₃)₂</td>
<td>OCH₃</td>
<td>-O-CH₂-O-</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Veprisinium</td>
<td>C(OH)(CH₃)₂</td>
<td>H</td>
<td>OCH₃</td>
<td>OCH₃</td>
</tr>
<tr>
<td>10</td>
<td>6,8-Dimethoxyplatydesminium</td>
<td>C(OH)(CH₃)₂</td>
<td>OCH₃</td>
<td>H</td>
<td>OCH₃</td>
</tr>
<tr>
<td>11</td>
<td>O-Methylptelefolonium (8l)</td>
<td>C(CH₃)=CH₂</td>
<td>OCH₃</td>
<td>H</td>
<td>OCH₃</td>
</tr>
<tr>
<td>12</td>
<td>O-Methylptelefolidonium (8l)</td>
<td>C(CH₃)=CH₂</td>
<td>H</td>
<td>-O-CH₂-O-</td>
<td></td>
</tr>
</tbody>
</table>

Scheme 5.3

Kavitha C, 2002
Rajendra Prasad et al.\textsuperscript{60,61} have reported the synthesis of 2-isopropylfuro[2,3-b]quinoline (12) from 3-prenyl-2-quinolinones (11) and 3-vinyl-2-quinolinones (13) by Prevost reaction using iodine and mercuric oxide in acetic acid.

Sekar and Rajendra Prasad\textsuperscript{62} also reported the synthesis of lunacrine (2a) and demethoxy-lunacrine (18) as depicted below.
The various methods of synthesizing 2-isopropylfuroquinoline alkaloids are outlined in Scheme 5.4 and Scheme 5.5.

**Scheme 5.4**

**Ref. 63**

![Chemical structure](image1)

**Ref. 64**

![Chemical structure](image2)

**Ref. 41**

![Chemical structure](image3)

**Ref. 65**

![Chemical structure](image4)

**Ref. 25**

![Chemical structure](image5)
5.1.3. 2,2-Dimethylpyran[2,3-b]quinolinone alkaloids

The 2,2-dimethylpyran[2,3-b]quinolines like khaplofoline (3a) and geibalansine (19a) also occur in the Rutaceous plants. The alkaloids of this group are listed in Table 5.4.

Table 5.4

<table>
<thead>
<tr>
<th>No</th>
<th>ALKALOID</th>
<th>R</th>
<th>R₃</th>
<th>R₆</th>
<th>R₇</th>
<th>R₈</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Khaplofoline</td>
<td>(3a)</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>2</td>
<td>N-Methylkhaplofoline</td>
<td>(3b)</td>
<td>CH₃</td>
<td>H</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>3</td>
<td>Ribalinine</td>
<td>(3c)</td>
<td>CH₃</td>
<td>OH</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>4</td>
<td>Ribalinidine</td>
<td>(3d)</td>
<td>CH₃</td>
<td>OH</td>
<td>OH</td>
<td>H</td>
</tr>
<tr>
<td>5</td>
<td>Isobalfourodine</td>
<td>(3e)</td>
<td>CH₃</td>
<td>OH</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>6</td>
<td>Neohydroxylunine</td>
<td>(3f)</td>
<td>CH₃</td>
<td>OH</td>
<td>H</td>
<td>-O-CH₂-O-</td>
</tr>
<tr>
<td>7</td>
<td>Haplobucharine</td>
<td>(3g)</td>
<td>‘a’</td>
<td>H</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>8</td>
<td>Ribalinine acetate</td>
<td>(3h)</td>
<td>CH₃</td>
<td>OAc</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>9</td>
<td>Isobalfourodine acetate</td>
<td>(3i)</td>
<td>CH₃</td>
<td>OAc</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>10</td>
<td>Geibalansine</td>
<td>(19a)</td>
<td>-</td>
<td>OH</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>11</td>
<td>O-Acetylgeibalansine</td>
<td>(19b)</td>
<td>-</td>
<td>OAc</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>12</td>
<td>Pteleflorine</td>
<td>(19c)</td>
<td>-</td>
<td>OH</td>
<td>H</td>
<td>-O-CH₂-O-</td>
</tr>
</tbody>
</table>

'B':

Bowman and Grundon⁴² synthesized khaplofoline (3a), which involved the acid catalysed cyclisation of 4-hydroxy-3-prenyl-2-quinolinone (5). But the major product obtained was the angular isomer dihydroflindersine (7). Bayerman and Rooda⁶⁶ also achieved the synthesis of khaplofoline (3a) utilising α-anilinocarbonyl-γ-lactone (20) as the starting point.
Rajendra Prasad and his coworkers\textsuperscript{9} have reported the synthesis of khaplofoline (3a) from 4-hydroxy-3-prenyl-2-quinolinone (5). Reaction of 5 with iodine and silver acetate in gla acetic acid gave iodopyranoquinolinone (21), which was then converted into khaplofoline (3a) on treatment with pyridine followed by reduction.

The various methods of synthesizing these groups of alkaloids are outlined in Scheme 5.6.
5.2. Results and Discussion

Based on the above facts, it is evident that the prenyl-, furo- and pyrano- quinoline alkaloids of *Rutaceae*, constitute an important group of natural products. The major synthetic route directed towards the construction of pyrano- and 2-isopropylfuro- quinoline alkaloids involves the preparation and exploitation of precursors namely, 3-prenyl-2-quinolinones (11) and 3-(3'-methylbut-1'-enyl)-2-quinolinones (13). Among, these two precursors, the 3-prenyl-2-quinolinones (11) have been recognized as synthetic as well as biosynthetic precursors for the production of furo- and pyrano- quinoline systems.

![Image of molecular structures](image)

\[ R_1 = \text{H, CH}_3, \text{OCH}_3, \text{Ph} \]
\[ R = \text{H, CH}_3, \text{Cl} \]

Although, many preparative methods were available in the literature towards the synthesis of 3-prenyl-2-quinolinones (11), it suffers from some limitations like low yield accessibility, and often attended by the formation of C,C-, C,O- and O- prenylated products. It is still challenging to explore new and simple synthetic methods for furo- and pyrano- quinolines, particularly for 3-prenyl-2-quinolinones (11) - stable intermediates to derive many naturally occurring quinoline alkaloids.\textsuperscript{52,77}

Earlier workers from our laboratory accomplished the synthesis of several 3-prenyl-2-quinolinones (15) along with the vinyl isomers 13, starting from 2-quinolinone-3-acetic acid derivatives (23).\textsuperscript{51} The synthetic sequence involved the condensation of 2-quinolinone-3-acetic acid with isobutyraldehyde in presence of acetic anhydride, sodium acetate and acetic acid to yield butyraldine-lactones (24), which were then hydrolyzed to give 3(1'-carboxy-3'-methylbut-1'-enyl)-2-quinolinones (25). The acid 25 on
Studies in Heterocycles

decarboxylation with copper powder in diphenyl ether under severe condition gave a mixture of 3-prenyl-2-quinolinones (11) and 3-(3'-methylbut-1'-enyl)-2-quinolinones (13).

\[
\begin{align*}
\text{R}_1 &= \text{H, CH}_3, \text{OCH}_3 \\
\text{R} &= \text{H, CH}_3, \text{Cl}
\end{align*}
\]

Since the 3-prenyl-2-quinolinones (11) were obtained in low yield along with the vinylquinolinones (13) in major yield, an alternative method of de-C-prenylation reaction using sodium hydrogen telluride has proved to be a fairly neat one. The overall yield realized of these alkaloids were only 15-35 %, the reason being that the method employed for deriving the precursor diprenylquinolinone (27) (from 2,4-dihydroxy quinoline (26) and isopropyl bromide in presence of sodium hydroxide)\(^{78}\) was not quite productive and often attended by unwanted side reactions.\(^{68,79}\)

It was felt that any methodology that would provide an alternative convenient access to the prenylquinolinone precursor or its synthetic equivalent make the Piozzi's technique more expedient and widely applicable.\(^{80}\) Recently, Sekar and Rajendra Prasad \(^{62}\)
showed the decarboxylation reaction of 3(1'-carboxy-3'-methylbut-1'-enyl)-2-quinolinone (25) with PPA, which, led to a new product 3,4-dihydro-2,2-dimethyl-2H-pyrano[2,3-b]quinoline and the possible intermediate, 3-prenyl-2-quinolinone (11) was not isolated.

5.2.1. 2-Isopropylfuro[2,3-b]quinoline, Prenylquinolinones and pyrano[2,3-b]quinolines from vinylcarboxylic acids

Hence, we envisaged to find out one-pot synthetic route for deriving furo[2,3-b]quinoline, pyrano[2,3-b]quinoline alkaloids from 3(1'-carboxy-3'-methylbut-1'-enyl)-2-quinolinones (25)

To realize our objective, 4-methyl-3(1'-carboxy-3'-methylbut-1'-enyl)-2-quinolinone (25a) (Scheme 5.7) was decarboxylated by refluxing with ethanolamine at 170°C for 15 min. The excess ethanolamine was then removed under reduced pressure and the resulting product was subjected to Prevost reaction with iocine and yellow mercury(II)oxide in acetic acid at room temperature. After work up, it showed a single spot on tlc and the product was obtained as yellow crystals (mp 80°C) in 73% yield and identified as 2-isopropyl-4-methylfuro[2,3-h]quinoline (12a) on the basis of its spectral characteristics. The elemental analysis, C 79.90%, H 06.70%, N 06.26% agreed well with the proposed molecular formula C_{15}H_{15}NO. The IR spectrum showed absorption at 1600 cm^{-1} for C=N stretching frequency. The ^1H NMR spectrum (Fig 1) showed the following assignable signals.

(i) a ‘6H’ doublet at δ 1.15 with J = 6.5 Hz (-CH(CH₃)₂)
(ii) a’3H’ singlet at δ 2.45 (C₄-CH₃)
(iii) a’1H’ multiplet at δ 3.15 (-CH(CH₃)₂)
(iv) a’1H’ singlet at δ 6.65 (C₃-H)
(v) a ‘4H’ aromatic envelop at δ 7.40-8.05 (C₅-H, C₆-H, C₇-H and C₈-H)

The physical and spectral properties were consistent with an authentic sample of 4-methyl-2-isopropylfuro[2,3-b]quinoline (12a) in all respects (mp, mmp, co TLC, superimpossable IR spectra and ^1H NMR spectra).
Fig 1. $^1$H NMR spectrum of 4-methyl-2-isopropylfuro[2,3-$b$]quinoline (12a)
In order to confirm whether the reaction proceeded via through 4-methyl-3-prenyl-2-quinolinone (11a) or through the vinyl isomer (13a), the intermediate formed during the course of the reaction was isolated and characterized. 4-Methyl-3(1'-carboxy-3'-methylbut-1'-enyl)-2-quinolinone (25a) was treated with ethanolamine at 170°C for 15 min. After work up it showed a single spot on tlc, melting at 213°C. Its IR spectrum showed amide carbonyl and NH stretching frequencies at 1660 cm\(^{-1}\) and at 3000 cm\(^{-1}\) respectively. The \(^1\)H NMR spectrum (Fig 2) showed two singlets at \(\delta\) 1.67 and at \(\delta\) 1.69 for gem dimethyl protons. The methyl protons at C\(_4\) carbon resonate at \(\delta\) 2.48 as a singlet. The methylene protons signals of a prenyl group attached to C\(_3\) carbon atom appeared as a doublet at \(\delta\) 3.52 (\(J = 7.00\) Hz). A triplet corresponds to -CH\(_2\)-CH appeared at \(\delta\) 5.12 with \(J = 7.00\) Hz. The C\(_5\) and C\(_8\) aromatic protons resonated as two doublets at \(\delta\) 7.32 and at \(\delta\) 7.69 respectively with \(J = 7.00\) Hz. The C\(_6\) and C\(_7\) aromatic protons resonate as two triplets at \(\delta\) 7.20 and at \(\delta\) 7.44 respectively with \(J = 7.00\) Hz. The NH proton appeared as a singlet at \(\delta\) 11.49. From the above mentioned spectral data the product was attested to be 4-methyl-3-prenyl-2-quinolinone (11a) and not the vinyl isomer (13a). Hence the reaction proceeded through the intermediate 4-methyl-3-prenyl-2-quinolinone (11a) (Scheme 5.8).
Fig 2. $^1$H NMR spectrum of 4-methyl-3-prenyl-2-quinolinone (11a)
The decarboxylation reaction realized with 4-methyl-3(1'-carboxy-3'-methylbut-1'-enyl)-2-quinolinone (25a) can be mechanistically viewed as proceeding through the initial abstraction of the carboxylic proton by amino group of ethanolamine to give the carboxylate ion (I) followed by successive decarboxylation, protonation and isomerisation to give the 4-methyl-3-prenyl-2-quinolinone (15a) as a single product in quantitative yield (Scheme 5.9).
On similar treatment, the other 3(1'-carboxy-3'-methylbut-1'-enyl)-2-quinolinone derivatives (25b-f) gave the corresponding 4-methyl-2-isopropylfuro[2,3-b]quinolines (12b-f) (Scheme 5.10) and their physical and spectral data were found to be identical with the authentic samples.51

Scheme 5.10

Thus, we have developed a high yield one-pot synthesis of 2-isopropylfuro[2,3-d]quinolines (12) of them, 5-methoxy-2-isopropylfuro[2,3-b]quinoline (12e) was a readily available precursor for the synthesis of lunacrine (2a). It is worthy to note that ethanolamine was found to be the good choice of reagent for the conversion of 3(1'-carboxy-3'-methylbut-1'-enyl)-2-quinolinones (25) to 3-prenyl-2-quinolinones (11).

In continuation of this study, 4-methoxy-3(1'-carboxy-3'-methylbut-1'-enyl)-2-quinolinone (25e) was treated with ethanolamine, followed by Prevost reaction with iodine, silver acetate and acetic acid at room temperature to afford 3-acetoxy-3,4-dihydro-2,2-dimethyl-5-methoxy-2H-pyrano[2,3-b]quinoline (28). The product was found to be
identical in all respects (mp, mmp, IR, NMR) with the one derived by the earlier reported method.81 (Scheme 5.11).

Scheme 5.11

Next phase of our work was to cyclise appropriately substituted 3(1'-carboxy-3'-methylbut-1'-enyl)-2-quinolinones (25) to 3,4-dihydro-2,2,5-trimethyl-2H-pyrano[2,3-b]quinolines (29). When 4-methyl-3(1'-carboxy-3'-methylbut-1'-enyl)-2-quinolinone (25a) was treated with ethanolamine, followed by cyclisation using a few drops of conc sulphuric acid in ethanol to afford 3,4-dihydro-2,2,5-trimethyl-2H-pyrano[2,3-b]quinoline (29a). Its IR spectrum showed absorptions at 1615 cm$^{-1}$ (C=C) and 1150 cm$^{-1}$ (C-O-C). The $^1$H NMR spectrum (Fig 3) showed the following signals.

(i) a ‘6H’ singlet at $\delta$ 1.50 (gem dimethyl proton)
(ii) two ‘2H’ triplets at $\delta$ 1.95 and at $\delta$ 2.96 with $J = 7.00$ Hz (C$_3$-H$_2$ and C$_4$-H$_2$)
(iii) a‘3H’ singlet at $\delta$ 2.45 (C$_5$-CH$_3$)
(iv) a ‘4H’ aromatic envelop at $\delta$ 7.20-7.90 (C$_6$-H, C$_7$-H, C$_8$-H and C$_9$-H)

The physical and spectral properties were exactly corresponded to those reported earlier$^{82}$. Similar procedure was adopted for the synthesis of its derivatives (29b-f) from (25b-f) (Scheme 5.12). Of all the products 5-methoxy-3,4-dihydro-2,2-dimethyl-2H-pyrano[2,3-b]quinoline (29e) was a readily available precursor for the synthesis of khaplofoline (3a). Evidently our endeavor proved to be an easier on account of number of steps involved and the yield.

Scheme 5.12
Fig 3. $^1$H NMR spectrum of 3,4-dihydro-2,2,5-trimethyl-$2H$-pyano[2,3-$b$]quinoline (29a)
Experimental section

Preparation of 3(1'-carboxy-3'-methylbut-1'-enyl)-2-quinolinone (25)

These compounds were prepared by the procedure cited in the literature.51

Synthesis of 2-isopropylfuro[2,3-b]quinolines (12)

The 3(1'-carboxy-3'-methylbut-1'-enyl)-2-quinolinone (25, 0.001 mol) was refluxed with ethanolamine (2 mL) at 170°C. The course of the reaction was followed by tlc analysis of silica gel with petroleum ether-ethyl acetate as solvent system. The reaction was completed within 15 min. After completion of the reaction excess ethanolamine was distilled off under reduced pressure and the crude product was dissolved in glacial acetic acid (15 mL), yellow mercuric oxide (0.001 mol) was added and the suspension was stirred well at room temperature. To the stirred mixture, powdered iodine (0.001 mol) was added in portions over a period of 1 h. After the addition stirring was continued for 12 h. The precipitated mercuric iodide was filtered off, and the filtrate was diluted with water and extracted with chloroform. The chloroform extract was successively washed with dil solutions of sodium bicarbonate, sodium thiosulphate and finally with water and dried. The residue obtained by evaporation of solvent was placed on neutral alumina column and eluted with petroleum ether-ethyl acetate mixture. The solid obtained after evaporation of the solvent was recrystallised with petroleum ether-ethyl acetate to give 12 as colourless needles.
2-Isopropyl-4-methylfuro[2,3-\textit{b}]quinoline (12a)

4-Methyl-3(1'-carboxy-3'-methylbut-1'-enyl)-2-quinolinone (25a)

Yield : 0.271 g (0.001 mol)

Mp : 80°C (Lit mp \(^{60}\) 78-79°C)

IR (KBr) [\(\nu_{\text{max}} \text{ cm}^{-1}\)] : 2915, 1600

\(^1\)H NMR (CDCl\(_3\)) [\(\delta \text{ ppm}\)]

(Fig 1)

1.15 (d, 6H, -CH(CH\(_3\))\(_2\) J = 6.5 Hz), 2.45 (s, 3H, C\(_3\)-CH\(_3\)), 3.15 (m, 1H, -CH(CH\(_3\))\(_2\)), 6.65 (s, 1H, C\(_3\)-H), 7.40-8.05 (m, 4H, aromatic-H)

Analysis (C\(_{15}\)H\(_{15}\)NO) Calcd

Calcd : C, 79.97; H, 06.71; N, 06.21 %

Found : C, 79.90; H, 06.70; N, 06.26 %

2-Isopropylfuro[2,3-\textit{b}]quinoline (12b)

3(1'-Carboxy-3'-methylbut-1'-enyl)-2-quinolinone (25b)

Yield : 0.257 g (0.001 mol)

Mp : 93-94°C (Lit mp \(^{60}\) 93-94°C)

2-Isopropyl-6-methylfuro[2,3-\textit{b}]quinoline (12c)

6-Methyl-3(1'-Carboxy-3'-methylbut-1'-enyl)-2-quinolinone (25c)

Yield : 0.271 g (0.001 mol)

Mp : 109°C (Lit mp \(^{60}\) 108-110°C)

5,8-Dimethyl-2-isopropylfuro[2,3-\textit{b}]quinoline (12d)

5,8-Dimethyl-3(1'-carboxy-3'-methylbut-1'-enyl)-2-quinolinone (25d)

Yield : 0.285 g (0.001 mol)

Mp : 110°C (Lit mp \(^{60}\) 110-112°C)

2-Isopropyl-4-methoxyfuro[2,3-\textit{b}]quinoline (12e)

4-Methoxy-3(1'-carboxy-3'-methylbut-1'-enyl)-2-quinolinone (25e)

Yield : 0.287 g (0.001 mol)

Mp : 105-106°C (Lit mp \(^{60}\) 105-106°C)
6-Chloro-2-isopropyl-4-phenylfuro[2,3-b]quinoline (12f)

6-Chloro-4-phenyl-3(1'-carboxy-3'-methylbut-1'-enyl)-2-quinolinone (25f)
Yield: 0.245 g (76%)
Mp: 136°C (Lit mp 60 136-137°C)

Synthesis of 3-prenyl-2-quinolinones (11)

3(1'-Carboxy-3'-methylbut-1'-enyl)-2-quinolinone (25, 0.01 mol) was refluxed with ethanolamine (4 mL) at 170°C for 15 min. The excess ethanolamine was distilled off and brown solution was cooled, poured into crushed ice, extracted using ethyl acetate and the combined organic layers were dried over anhydrous sodium sulphate, distilled off the solvent and chromatographed using 95:5 petroleum ether-ethyl acetate mixture to give 3-prenyl-2-quinolinone (11) as colourless crystals.

4-Methyl-3-prenyl-2-quinolinone (11a)

4-Methyl-3(1'-carboxy-3'-methylbut-1'-enyl)-2-quinolinone (25a)
Yield: 1.771 g (78%)
Mp: 213°C (Lit mp 51 213-214°C)
IR (KBr) [v max cm⁻¹]: 3000, 1660

1H NMR (CDCl₃) [δ ppm] (Fig 2):
1.67 and 1.69 (2 s, 6H, C(CH₃)₂), 2.48 (s, 3H, C₄-CH₃), 3.52 (d, 2H, -CH₂, J = 7.00 Hz), 5.12 (t, 1H, -CH₂-CH=, J = 7.00 Hz), 7.32 (d, 1H, C₅-H, J = 7.00 Hz), 7.20 (t, 1H, C₆-H, J = 7.00 Hz), 7.69 (d, 1H, C₇-H, J = 7.00 Hz), 7.44 (t, 1H, C₇-H, J = 7.00 Hz), 11.49 (s, 1H, NH)

Analysis (C₁₅H₁₇NO) Calcd: C, 79.26; H, 07.54; N, 06.16%
Found: C, 79.22; H, 07.46; N, 06.25%

3-Prenyl-2-quinolinone (11b)

3(1'-Carboxy-3'-methylbut-1'-enyl)-2-quinolinone (25b)
Yield: 1.67 g (77%)
Mp: 155°C (Lit mp 51 154-155°C)
IR (KBr) [v max cm⁻¹]: 2955, 1650
6-Methyl-3-prenyl-2-quinolinone (11c)

6-Methyl-3(1'-carboxy-3'-methylbut-1'-enyl)-2-quinolinone (25c)
Yield: 2.71 g (0.01 mol)
Mp: 1.85 g (82%)
IR (KBr) [\( \nu_{\text{max}} \text{ cm}^{-1} \)]: 115-117°C (Lit mp51 115-117°C)
\[^1\text{H} \text{NMR} (\text{CDCl}_3) [\delta \text{ ppm}]\] (Fig 4): 1.94 (s, 6H, C(CH3)2), 3.70 (d, 2H, -CH2, J = 7.00 Hz), 5.73 (t, 1H, -CH2-CH=, J = 7.00 Hz), 7.50-7.90 (m, 5H, C5-H, C6-H, C7-H, C8-H, C4-H), 11.49 (s, 1H, NH)
Analysis (C14H15NO) Calcd: C, 78.62; H, 07.16; N, 06.42%
Found: C, 78.84; H, 07.09; N, 06.57%

5,8-Dimethyl-3-prenyl-2-quinolinone (11d)

5,8-Dimethyl-3(1'-carboxy-3'-methylbut-1'-enyl)-2-quinolinone (25d)
Yield: 2.85 g (0.01 mol)
Mp: 2.05 g (85%)
IR (KBr) [\( \nu_{\text{max}} \text{ cm}^{-1} \)]: 126-127°C (Lit mp81 126-127°C)
\[^1\text{H} \text{NMR} (\text{CDCl}_3) [\delta \text{ ppm}]\] : 1.50 and 1.60 (2 s, 6H, C(CH3)2), 2.30 (s, 3H, C6-CH3), 3.35 (d, 2H, -CH2 J = 7.00 Hz), 5.20 (t, 1H, -CH2-CH=), 7.00-7.60 (m, 4H, C4-H, C5-H, C7-H, C8-H), 12.9 (b s, 1H, NH)
Analysis (C16H19NO) Calcd: C, 79.63; H, 07.45; N, 06.58%
Found: C, 79.66; H, 07.82; N, 05.84%

4-Methoxy-3-prenyl-2-quinolinone (11e)

4-Methoxy-3(1'-carboxy-3'-methylbut-1'-enyl)-2-quinolinone (25e)
Yield: 2.87 g (0.01 mol)
\[^1\text{H} \text{NMR} (\text{CDCl}_3) [\delta \text{ ppm}]\] : 1.77 g (73%)
Analysis (C16H19NO) Calcd: C, 79.66; H, 07.82; N, 05.84%

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Mp : 133°C (Lit mp51 132-134°C)
IR (KBr) [v max cm⁻¹] : 2998, 1651
¹H NMR (CDCl₃) [δ ppm] : 1.65 and 1.85 (2 s, 6H, C(CH₃)₂), 3.4 (d, 2H, -CH₂, J = 7.00 Hz), 3.80 (s, 3H, OCH₃), 5.32 (t, 1H, -CH₂-CH=, J = 7.00 Hz), 6.90-7.60 (m, 4H, C₅-H, C₆-H, C₇-H, C₈-H), 7.70 (d, 1H, C₇-H, J = 7.00 Hz)

Analysis (C₁₅H₁₇NO₂) Calcd : C, 74.04; H, 07.04; N, 05.75%
Found : C, 74.13; H, 07.25; N, 05.63%

6-Chloro-4-phenyl-3-prenyl-2-quinolinone (Ilf)

6-Chloro-4-phenyl-3(1'-carboxy-3'-methylbut-1'-enyl)-2-quinolinone (25f)

Yield : 3.67 g (0.01 mol)
Mp : 3.67 g (0.01 mol)
IR (KBr) [v max cm⁻¹] : 2.45 g (75%) 1660, 1380, 1355
¹H NMR (CDCl₃) [δ ppm] : 1.50 and 1.70 (2 s, 6H, C(CH₃)₂), 3.32 (d, 2H, -CH₂, J = 7.00 Hz), 5.29 (t, 1H, -CH₂-CH=, J = 7.00 Hz), 6.90-8.20 (m, 8H, C₅-H, C₇-H, C₉-H and 5 phenyllic-H), 12.03 (b s, 1H, NH)

Analysis (C₂₀H₁₈NOC₁) Calcd : C, 74.18; H, 05.60; N, 04.32%
Found : C, 74.23; H, 05.52; N, 04.25%

Synthesis of 3-acetoxy-3,4-dihydro-2,2-dimethyl-5-methoxy-2H-pyrano[2,3-b]quinoline (28)

The 3(1'-carboxy-3'-methylbut-1'-enyl)-2-quinolinone (25, 0.001 mol) was refluxed with ethanolamine (2 mL) at 170°C. The course of the reaction was followed by tlc analysis of silica gel with petroleum ether-ethyl acetate as solvent system. The reaction was completed within 15 min. After completion of the reaction excess ethanolamine was distilled off under reduced pressure and the crude product was dissolved in glacial acetic acid (15 mL) and to that silver acetate (0.167 g) was added and the suspension was stirred well at room temperature. To the stirred mixture was added portion wise, well-powdered iodine (0.001 mol) during a course of 1 h. After the addition, stirring was continued for further 1 h. Sodium chloride was added and the inorganic salts were filtered and washed with chloroform. The filtrate together with washing was diluted with water and extracted with chloroform. The extract was successively washed with water, dilute sodium thiosulphate

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solution and finally with water. The dried extract was evaporated and the residue obtained was placed over a column of neutral alumina. Elution with benzene-ethyl acetate furnished 28 as colourless crystals. The IR, $^1$H NMR and elemental analyses of this compound were identical with that of an authentic sample of 3-acetoxy-3,4-dihydro-2,2-dimethyl-5-methoxy-$2H$-pyrano[2,3-b]quinoline (28).

3-Acetoxy-3,4-dihydro-2,2-dimethyl-5-methoxy-$2H$-pyrano[2,3-b]quinoline (28)

4-Methoxy-3(1'-carboxy-3'-methylbut-1'-enyl)-2-quinolinone (25e)

Yield : 0.211 g (70%)
Mp : 136°C (Lit mp $^{81}$ 136-137°C)

Synthesis of 3,4-dihydro-2,2-dimethyl-$2H$-pyrano[2,3-b]quinolines (29)

The 3(1'-carboxy-3'-methylbut-1'-enyl)-2-quinolinone (25, 0.001 mol) was refluxed with ethanolamine (2 mL) at 170°C for 15 min. The course of the reaction was followed by tlc analysis of silica gel with petroleum ether-ethyl acetate as solvent system. The reaction was completed within 15 min. After completion of the reaction excess ethanolamine was distilled off under reduced pressure and the crude product was dissolved in ethanol (5 mL), added a few drops of sulphuric acid and refluxed in the water bath for 2h. The solution was concentrated to a small bulk and poured into ice water. The precipitated product was collected by filtration and recrystallised from ethanol to yield 3,4-dihydro-2,2-dimethyl-$2H$-pyrano[2,3-b]quinolines (29) as fine crystals.

3,4-Dihydro-2,2,5-trimethyl-$2H$-pyrano[2,3-b]quinoline (29a)

4-Methyl-3(1'-carboxy-3'-methylbut-1'-enyl)-2-quinolinone (25a)

Yield : 0.271 g (0.001 mol)
Mp : 0.172 g (60%)
IR (KBr) [$\nu_{\text{max}}$ cm$^{-1}$] : 1615, 1150
$^1$H NMR (CDCl$_3$) [$\delta$ ppm] (Fig 3)

Analysis (C$_{15}$H$_{17}$NO) Calcd : C, 79.91; H, 07.95; N, 06.13%
Found : C, 79.32; H, 07.64; N, 06.18%

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3,4-Dihydro-2,2-dimethyl-2'H-pyrano[2,3-b]quinoline (29b)

3(1'-Carboxy-3'-methylbut-1'-enyl)-2-quinolinone (25b)

Yield: 0.257 g (0.001 mol)

Mp: 94°C (Lit mp82 94-96°C)

IR (KBr) [v max cm⁻¹]: 1610, 1150

¹H NMR (CDCl₃) [δ ppm] (Fig 5): 1.50 (s, 6H, C(CH₃)₂), 1.86 (t, 2H, C₃-H₂, J = 7.00 Hz), 2.93 (t, 2H, C₄-H₂, J = 7.00 Hz), 7.92 (s, 1H, C₅-H), 7.20-7.90 (m, 4H, C₆-CH₃ and C₉-H)

Analysis (C₁₄H₁₅NO) Calcd: C, 78.47; H, 07.26; N, 06.54%

Found: C, 78.65; H, 07.22; N, 06.48%

3,4-Dihydro-2,2,7-trimethyl-2'H-pyrano[2,3-b]quinoline (29c)

6-Methyl-3(1'-carboxy-3'-methylbut-1'-enyl)-2-quinolinone (25c)

Yield: 0.271 g (0.001 mol)

Mp: 148-150°C (Lit mp81 150-151°C)

IR (KBr) [v max cm⁻¹]: 1610, 1150

¹H NMR (CDCl₃) [δ ppm]: 1.50 (s, 6H, C(CH₃)₂), 1.90 (t, 2H, C₃-H₂, J = 7.00 Hz), 2.50 (s, 3H, C₇-CH₃), 3.00 (t, 2H, C₄-CH₂, J = 7.00 Hz), 7.30-7.90 (m, 4H, C₅-H, C₇-H, C₉-H, C₉-H)

Analysis (C₁₅H₁₇NO) Calcd: C, 79.91; H, 07.95; N, 06.13%

Found: C, 79.18; H, 07.44; N, 06.14%

3,4-Dihydro-2,2,6,9-tetramethyl-2'H-pyrano[2,3-b]quinoline (29d)

5,8-Dimethyl-3(1'-carboxy-3'-methylbut-1'-enyl)-2-quinolinone (25d)

Yield: 0.285 g (0.001 mol)

Mp: 123-125°C (Lit mp83 123-125°C)

IR (KBr) [v max cm⁻¹]: 1615, 1155

¹H NMR (CDCl₃) [δ ppm]: 1.45 (s, 6H, C(CH₃)₂), 2.00 (t, 2H, C₇-H₂, J = 7 Hz), 3.00 (s, 2H, C₄-H₂, J = 7.00 Hz), 2.50 and 2.65 (2s, 6H, C₆-CH₃ and C₉-CH₃), 7.00-8.00 (m, 3H, C₅-H, C₇-H, C₉-H, C₉-H)

Analysis (C₁₆H₁₉NO) Calcd: C, 79.30; H, 08.31; N, 05.77%

Found: C, 79.82; H, 08.10; N, 05.76%
3,4-Dihydro-2,2-dimethyl-5-methoxy-2H-pyran[2,3-b]quinoline (29e)

4-Methoxy-3(1'-carboxy-3'-methylbut-1'-enyl)-2-quinolinone (25e)

Yield: 0.287 g (0.001 mol)

Mp: 94-95°C (Lit81 mp 95-96°C)

IR (KBr) [v max cm⁻¹]: 1615, 1150

¹H NMR (CDCl₃) [δ ppm]: 1.43 (s, 6H, C(CH₃)₂), 1.79 (t, 2H, C₃-H₂, J = 7.00 Hz), 2.88 (t, 2H, C₄-CH₂, J = 7.00 Hz), 3.93 (s, 3H, C₅-OCH₃), 7.10-7.90 (m, 4H, C₆-H, C₇-H, C₈-H, C₉-H)

Analysis (C₁₅H₁₇NO₂) Calcd: C, 73.74; H, 07.42; N, 05.73%

Found: C, 74.10; H, 07.04; N, 05.75%

3,4-Dihydro-2,2-dimethyl-7-chloro-5-phenyl-2H-pyran[2,3-b]quinoline (29f)

6-Chloro-4-phenyl-3(1'-carboxy-3'-methylbut-1'-enyl)-2-quinolinone (25f)

Yield: 0.367 g (0.001 mol)

Mp: 161-162°C (Lit mp82 161-162°C)

IR (KBr) [v max cm⁻¹]: 1620, 1160

¹H NMR (CDCl₃) [δ ppm]: 1.50 (s, 6H, C(CH₃)₂), 1.85 (t, 2H, C₃-H₂, J = 7.00 Hz), 2.70 (t, 2H, C₄-CH₂, J = 7.00 Hz), 7.00-8.10 (m, 8H, C₆-H, C₇-H, C₈-H, 5 phenylc-H)

Analysis (C₂₀H₁₆NOCl) Calcd: C, 73.95; H, 05.95; N, 04.31%

Found: C, 73.36; H, 05.58; N, 04.38%
Fig. 4. $^1$H NMR spectrum of 3-prenyl-2-quinolinone (11a)
Fig 5. 'H NMR Spectrum of 3,4-dihydro-2,2-dimethyl-2//-pyrano[2,3-b]quinolone (29b)
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