CHAPTER V

THERMAL AND PHOTO CONVERSIONS OF MAHANIMBINE
From the stem bark of *Murraya koenigii*, Dutta and coworkers\(^1,2\) isolated two alkaloids. These were named as curryanine and curryangine and assigned structures I and II respectively.

Popli and coworkers\(^3\) later reported three new alkaloids from the leaves of the same plant. Two of these, cyclomahanimbine and mahanimbidine had physical data identical with curryanine and curryangine respectively. However, while Dutta and coworkers proposed structure I for curryanine, Popli and coworkers preferred structure III for cyclomahanimbine. For mahanimbidine, the latter group also proposed structure II, same as that for curryangine.
Chakraborty and coworkers also isolated two alkaloids, murrayazolidine\textsuperscript{4} and murrayazoline\textsuperscript{5} from the stem bark. They assigned structures I and II respectively for the new alkaloids, identical with those for curryanine and curryangine.

In an extensive study of the alkaloidal content of \textit{Murraya koenigii} seven alkaloids (including five reported in the earlier chapter) have been isolated, in this laboratory, from the leaves and seeds of this plant. In spite of careful investigation, however, none of the alkaloids mentioned in the previous paragraph could be detected in the plant. In the present work, these alkaloids were obtained in a different way, i.e. by the action of heat on mahanimbine. The investigations reported here are on these thermal products.
Curryanine

Curryanine, C_{23}H_{26}NO, m.p. 137° was isolated by Dutta and coworkers\(^1\) from the stem bark of \textit{Murraya koenigii}. An alkaloid presumably identical with the above but called cyclomahanimbine, m.p. 146° was isolated from the leaves by Fopli and coworkers\(^3\). Chakraborty and coworkers\(^4\) isolated murrayazolidine m.p. 137°, (\(\alpha\))\(_D^\circ + 26° (\text{CHCl}_3)\) from the bark. They assigned for it the same structure as of curryanine.

In the present work a compound, m.p. 137°, was obtained by heating mahanimbine in a evacuated sealed tube at 200° for six hours. Direct comparison of the IR spectra\(^8\) showed it to be identical with curryanine and cyclomahanimbine. The thermal product was also optically inactive.

The presence of a carbazole ring in curryanine (cyclomahanimbine, murrayazolidine and the thermal product) was deduced from its UV spectrum (Fig. 41) which was similar to 2-methoxy carbazole (Fig. 2). The IR band at 3450 cm\(^{-1}\) (Fig. 42) revealed that the NH group of the carbazole was unsubstituted.

Curryanine on catalytic reduction with palladised charcoal gave a dihydro derivative, indicating the presence
of a double bond. The UV spectrum of the dihydroderivative (Fig. 43) which was similar to the starting compound, showed that the double bond was not conjugated to the carbazole ring.

Although curryanine and cyclomahanimbine were apparently identical, their NMR spectra and those of their dihydro derivative had been interpreted, in some respects, in different ways by Dutta et al and Popli et al and two different structures I and III assigned to the alkaloid.

Interpretation of the NMR (CCl₄) spectrum of curryanine and its dihydro derivative by Dutta and coworkers.

This may be summarized as follows:

**Curryanine**:

1.36 (6H, bs) -gem dimethyl group on carbon carrying oxygen.
2.33 (3H, s) -aromatic methyl
3.11 (1H, complex m) -benzylic methine
4.72 (2H, with further splitting) - C=CH₂
7.63 (1H, s) C-4 proton
7.88 (1H, m) C-5 proton

**Dihydro curryanine**

0.57 (3H, J=5.5Hz) H - C - CH₃
The dihydro derivative had no signal at 4.72 $\delta$.

The new methyl group was then arising by the reduction of the $-C=CH_2$ group.

On the basis of the above data Dutta and coworkers proposed structure I for curryanine$^1$.

\begin{center}
\includegraphics[width=0.5\textwidth]{structure.png}
\end{center}

**Interpretation of the NMR (CCl$_4$) of cyclomahanimbine and its dihydro derivative by Popli and coworkers.**

This was as follows:

**Cyclomahanimbine**

1.36 (6H, bs)  
- overlapping methyl groups  
- one on carbon carrying oxygen and the other on olefinic carbon

2.30 (3H, s)  
- aromatic methyl

3.24 (1H, complex m)  
- benzylic methine

4.72 (2H, complex d)  
- $C=CH_2$
The assignments of the last three signals were similar to those of Dutta and coworkers. However the six proton broad singlet at 1.36 \( \delta \) was assigned to two overlapping methyl groups, one on a carbon carrying an oxygen, \((O-C-CH_3)\) and the other on a double bond, \((CH_2=CH_2)\). No specific reason\(^+\) had been given for the preference of this interpretation.

**Dihydrocyclomahanimbine**

The signal at 0.57 \( \delta \) \((3H, J = 5.5 \text{ Hz})\), in dihydrocyclomahanimbine, was assigned to one of the methyl groups in the newly formed isopropyl group.

Popli and coworkers then assigned structure III for cyclomahamibine.

\[
\text{III}
\]

\(^+\) This was presumably in analogy with compounds from Hashish series.\(^6\)
Chakraborty and coworkers interpreted the NMR of murrayazolidine in the same way as Dutta and coworkers had done for curryanine and proposed for the alkaloid a structure identical with I.

It was at this stage that we isolated a compound, m.p. 137°, as one of the thermal products of mahanimbine. The UV (Fig. 41) and IR (Fig. 42) spectra were identical with curryanine and cyclomahaninmine. The UV was further identical with that of 2-methoxy carbazole (Fig. 2) indicating the presence of an intact carbazole ring, carrying an (ether) oxygen function at 2 position. The IR spectrum had a band at 3450 cm⁻¹ due to NH group of the carbazole ring.

In our studies, the NMR of curryanine was determined with a 100 MHz spectrometer. In CDCl₃ (Fig. 44) this showed signals at 2.30 (3H, s, aromatic methyl), 3.22 (1H, m, benzylic methine), 4.64 (2H, d with J=5 Hz, C=CH₂), 7.38 (1H, s, C-4), 7.63 (1H, m, C-5) and 7.456 (1H, bs, disappeared with D₂O, NH). The above signals were similar to what had been seen with 60 MHz spectrometer. However, in the 100 MHz spectrum in place of one signal of six protons at 1.36 δ observed in the 60 MHz (CCl₄), two signals appeared at 1.32 and 1.36 δ (3H, each). These were presumably due to methyl groups attached to a sp² carbon or carbon atom carrying O or N atom.

† The UV, IR and Mass spectra are collectively presented at the end of the experimental.
FIG. 44 100 MHz NMR SPECTRUM (CDCl₃) OF CURRYANINE
FIG. 46: 100 MHz NMR SPECTRUM (CDCl₃) OF CURRYANINE
One of these was shorter in height and broader at half height. Dutta's structure, if correct should have given signals of equal intensities for the gem dimethyl group on the carbon carrying oxygen. On the other hand, Fopli's group structure in which the vinylic methyl should be further coupled to the vinylic proton, could explain the height difference observed.

In order to determine whether the methyl group was coupled to the vinyl proton, the latter was irradiated with the methyl frequency. Indeed a simplification of the olefinic proton signal at 4.64 $\delta$ was observed (Fig. 47). Additionally, when the methyl protons were irradiated with olefinic proton frequency, the height of the signal at 1.36 $\delta$ increased and now corresponded to the height of the other methyl signal at 1.32 $\delta$ (Fig. 48). This proved that the methyl group and the vinylic protons were mutually coupled and that the following group was present in the molecule.
**Fig. 47:** Methylene protons at 4.64 δ (Sweep width 500 Hz)

(A) Before irradiation (B) after irradiation with methyl signal

frequency at 136 Hz

**Fig. 48:** Methyl protons at 1.36 δ (Sweep width 500 Hz)

A) After irradiation (B) before irradiation with methylene proton

frequency at 464 Hz
It was mentioned that the benzylic methine had a signal at 3.22 $\delta$. Attempts were then made to determine the environment of the benzylic methine. For this the high field signals of the proton spectrum were irradiated with the benzylic methine frequency. No change was observed in the methyl signals. This showed that the methyl groups were not coupled to the benzylic proton (even by $W$ coupling). The only change observed was in the 1.84 and 2.42 $\delta$ region (Fig. 49). The signal position and intensity of the latter corresponded to one allylic proton. The benzylic proton was then coupled to an allylic proton. The presence of the following group was thus deduced.

![Chemical structure](image)

The NMR evidence then led to the following part structure for curryanine.

![Chemical structure](image)
Figure 49: Methylene protons at 1.846 and allylic protons at 2.426 (sweep width 500 Hz)
A) After irradiation
B) Before irradiation
with benzylic proton frequency at 322 Hz
**Fig. 50**: Benzylic proton at $3.22 \delta$ (sweep width 500 Hz)

A) After irradiation (B) before
irradiation with 184 Hz

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**Fig. 51**: Benzylic proton at $3.22 \delta$
(sweep width 500 Hz)

(A) After irradiation (B) before
irradiation with allylic proton
frequency at 242 Hz
Curryanine had no other methyl group. The part structure was then expanded to III.

III

Popli and coworkers had derived the same structure for cyclomahanimbine. As was noted earlier their evidence was not adequate. The authors had derived their structure presumably in analogy with observations on the Hashish compounds.

Structure III of curryanine contains a 1:3 fusion of rings D and E. This must be cis and diaxial on chair structure for ring E. This was in agreement with the narrow signal (3.22 δ, $W_H=5$ Hz) observed for the benzylic proton in the NMR spectrum (CDCl₃) of the compound (Fig. 46).  

+ There was no compelling evidence why ring E should have the boat structure.
On the chair structure for ring E, the isopropenyl group was assigned the equatorial conformation because the allylic proton (at 2.42 δ) present on the same carbon atom showed broad signal pattern (Fig. 46) which undoubtedly included axial axial coupling. The allylic proton then had the axial conformation and the isopropenyl group the equatorial.

The stereostructure of curryanine was then as shown below.

Curryangine

Curryangine, C_{23}H_{25}NO, m.p. 260° was isolated by Dutta and coworkers from the stem bark. Subsequently it was isolated by Popli and coworkers from the leaves and was named mahanimbidine. Chakraborty and coworkers isolated the alkaloid from stem bark. All the workers mentioned above, reported no optical activity for this compound.

Curryangine had been obtained in this laboratory by heating (+) mahanimbine in an evacuated sealed tube.
The compound was identical with the specimen obtained by Dutta and by Popli. The UV spectrum (Fig. 54)† suggested that it had a carbazole ring with an oxygen function at 2 position. The IR (Fig. 55) showed that both -OH and -NH groups were absent in the molecule.

The NMR (CDCl₃) spectrum of curryangine (Fig. 56) showed three singlets at 1.27 (3H), 1.43 (3H) and 1.90 (3H). These were the methyl groups on a carbon carrying some electronegative atom such as oxygen or nitrogen. The fourth singlet was at 2.33 (3H) which was the aromatic methyl. The benzylic methine appeared at 3.33 (1H).

The spectral data was consistent with two structures for the alkaloid. Dutta and Popli both had favoured structure II for the molecule, although structure IV was equally possible.

† UV, IR and Mass spectra are collectively presented at the end of the experimental.
It was indeed difficult to choose between these two structures on the basis of spectral data alone and the issue was finally resolved in favour of structure II, only by X-ray analysis of murrayazoline.

**Formation of curryanine and curryangine by the action of heat on mahanimbine**

Both Dutta and Fopli have reported that mahanimbine is very susceptible to acid and can be converted into cyclic products very easily. Their mechanism for conversion of mahanimbine to curryanine (=cyclo-mahanimbine) and curryangine (=mahanimbidine) are illustrated in Chart I.

In mechanism 2 and 3 the asymmetric center is not affected. It was then surprising that the resulting curryanine (cyclomahanimbine) and curryangine (mahanimbidine) showed no optical activity.

**Action of Heat on mahanimbine**

When (+) mahanimbine was heated in an evacuated sealed tube, three products, varying with time and temperature were obtained. Thus at 150⁰, irrespective of the duration of heating, the only product obtained was racemic mahanimbine. On the other hand, heating at 200⁰ gave a mixture of

*This could be due to some coincidence (in both cases!)*
curryangine, curryanine and racemic mahanimbine. The proportion of curryangine and racemic mahanimbine were large in the initial stages but diminished with time. At the end of six hours curryanine was the only product. Evidently, racemic mahanimbine and curryangine were the initial products which were then transformed into curryanine.

An attractive mechanism for the formation of racemic mahanimbine at 150° would be as follows:

![Chemical Reaction Diagram]
Besides reverting back to racemic mahanimbine, other pathways of transformation are also available for the intermediate V. These could occur at higher temperature ($200^\circ$). Two of the possible pathways are as shown in Chart II.

Pathway I would have curryanine formed first, which could then get converted to curryangine. Actually it was found that in the pyrolysis experiments curryanine was the end product. Indeed curryanine itself after prolonged heating either alone or with a variety of catalysts like pyridine, adipic acid, p-toluene sulphonic acid, diethyl amine, benzoic acid gave no curryangine and remained essentially unchanged. On the other hand, curryangine on heating at $200^\circ$ in an evacuated sealed tube, was converted to curryanine. The above experiment would presumably rule out pathway I.

Pathway II was in agreement with the observed results in the thermolysis experiment, i.e. the formation of curryanine as the end product. Attempts were then made to trap the intermediates V and VI.

When (+) mahanimbine was heated with 2,4 dinitrophenyl-hydrazine, aniline, p-toluidine or p-anisidine, it was hoped that compounds corresponding to incorporation of these amines in mahanimbine, as shown below, would be obtained (Chart II A)
CHART II

Pathway I

Non concerted

Pathway II

V
However, the only compound formed at 150° was (+) mahanimbine and at 200° curryanine.

The above experiment could be interpreted to mean that either intermediate $V$ was not formed or that as soon as it was formed, it was converted to the phenol VI. Attempts were then made to trap the phenolic intermediate. (+) Mahanimbine was heated in evacuated sealed tubes with acetic anhydride and pyridine. At 150° an acetyl derivative, m.p. 76° was obtained. This had an IR band (Fig. 59)\textsuperscript{†} at 1700 cm\textsuperscript{-1}, and hence was N-acetyl mahanimbine, rather than the O-acetyl derivative of the pyran ring opened compound (O-acetyl derivative would have IR band at 1750 cm\textsuperscript{-1}). The

\textsuperscript{†} UV, IR are presented at the end of the experimental.
NMR (CDCl₃) of the new compound (Fig. 60) was consistent with the N-acetyl structure (N-CO-CH₃ at 2.53 δ).

In an attempt to convert the N-acetyl derivative into the known N-ethyl derivative by the lithium aluminium hydride reduction, deacetylation occurred to give racemic mahanimbine. The mechanism of the deacetylation could be as shown below:

![Mechanism of deacetylation](image)

The acetaldehyde formed could not be identified as it would be further reduced to ethyl alcohol.

The above reaction indicated that N-acetylation was a more facile process than the pyran ring opening reaction at 150°. The acetylation experiments were then repeated.
FIG. 60: 60 MHz NMR SPECTRUM (CDCl₃) OF N-ACETYL MAHANIMBINE
at 200°. Here, however, only a mixture of compounds was obtained, from which only N-acetyl mahanimbine could be obtained in lesser yields.

The trapping experiments with (+) mahanimbine having failed, similar experiments were initiated with N-methyl mahanimbine. Since this lacked the free -NH group, it was hoped that the enolisation would not occur and the intermediate ketone of structure VII would react with the amines to give compounds of type (VIII).
When N-methyl mahanimbine was heated at 200° with aniline or p-toluidine the only compound obtained, in 70% yield, was N-methyl curranine. The structure of the latter was established by direct comparison with a sample obtained by methylation of curranine (IR spectrum Fig. 61, NMR in CDCl₃ Fig. 62). It was obvious that VII was still getting converted to the enolate ion IX which was then cyclising as shown below:
FIG. 61: IR SPECTRUM OF N-METHYL CURRYANINE
FIG. 62: 60 MHZ NMR SPECTRUM (CDCl₃) OF N-METHYL CURRYANINE
Attempts were then made to trap the phenolate ion with acetic anhydride. When N-methyl mahanimbine was heated with acetic anhydride and pyridine, a fluorescent compound, relatively unstable, was obtained. The compound was destroyed within two hours. Its IR (Fig. 63) showed a band at 1750 cm$^{-1}$ characteristic of phenol acetate. The NMR (CDCl$_3$) had (Fig. 64) a singlet at 2.36 $\delta$, beside the one due to aromatic methyl at 2.30 $\delta$. These were in agreement with a phenol acetate structure for the compound. The NMR also had bands at 1.83 and 1.65 $\delta$, indicating two methyl groups on double bonds. The methyl group attached to the nitrogen of the carbazole ring was seen at 4.00 $\delta$. Attempts to characterise this compound have so far not succeeded. But from the spectral data it must be concluded$^+$ that the pyran ring has opened up and the phenolate ion converted into the acetyl derivative.

$^+$ A possible structure for the new compound can be as follows.
**Fig. 63**: IR spectrum of the product obtained by heating N-methyl mahanimbine and acetic anhydride at 200° in a sealed tube.
FIG. 64: 60 MHz NMR SPECTRUM (CDCl₃) OF THE PRODUCT OBTAINED BY HEATING N-METHYL MAHANIMBINE AND ACETIC ANHYDRIDE AT 200° IN A SEALED TUBE
Summary of the thermal reactions of mahanimbine

It must be concluded at this stage that the thermal products obtained from mahanimbine are formed through breaking of the pyran ring and loss of optical activity. Possible intermediates in all the heating experiments could be the ring opened enolate ions VI and IX, which could then cyclise in different ways, leading to optically inactive compounds. Phenols (corresponding to the enolate ions VI and IX), probably, would also be formed under acid catalysed conditions. It was then not improbable that curryanine (cyclomahanimbine) and curryangine (mahanimbidine, murrayazoline) do not occur as such in the plant but are artefacts, actually formed from mahanimbine during work up due to heating or prolonged contact with acids. The latter hypothesis would explain the optical inactivity of these compounds.

Photoproduction

The ease with which (+) mahanimbine got converted to curryanine and curryangine was seen in the previous section. It was thought that similar products could be obtained photolytically. Photochemical ring opening of the pyran rings have indeed been reported.

The photolysis was carried out twice. In the first reaction from 3 g of mahanimbine only 0.030 g of a compound,
m.p. 178° was obtained. In the second reaction, in order to see whether the reaction involved the optically active center, the reaction was stopped half way and the unreacted mahanimbine examined for its optical activity. The latter was found to be optically inactive.

The compound m.p. 178° obtained in the first experiment has not yet been characterised by determination of its molecular weight by Mass spectrum or by elemental analysis. However its UV (Fig. 65) and NMR spectra (in CDCl₃, Fig. 66, in DMSO, Fig. 67) had been taken. This was similar to curryanine in the aromatic region. Thus in CDCl₃, the mutually deshielded aromatic protons at C-4 and C-5 appeared at 7.68 and 7.92 δ and the NH at 7.78 δ. The aromatic methyl group was observed at 2.3 δ and the olefinic protons as two doublets at 4.86 and 4.95 δ. Seven protons remained scattered between 1.14 and 2.8 δ.

There were two major differences in the NMR of curryanine and the photoproduct. In the latter, the benzylic proton appeared as a doublet (J=13Hz) at 3.35 δ further split into fine structure. The large coupling constant suggested that this proton had an axial conformation with another neighbouring axial proton. The second difference was in the signal of the high field methyl groups at 1.05 and 1.46 δ. These were singlets with same heights. When the high field
Fig. 65: UV Spectrum of the product of photolysis of (+)-mahanimbine.
FIG. 66 100 MHz NMR Spectrum (CDCl₃) of the Product of Photolysis of (+) Mahanimbine
FIG. 67: 100 MHZ NMR SPECTRUM (DMSO-d₆) OF THE PRODUCT OF PHOTOLYSIS OF (+) MAHANIMEINE
proton signals were irradiated with the benzylic proton absorption frequency, three protons, one at 2.08 \( \delta \) and two in the 2.64-2.74 \( \delta \) region were sharpened (Fig. 66). This indicated that three protons were adjoining to the benzylic proton. A possible structure for the photoproduct was XI, earlier assigned to curryanine by Dutta and coworkers.

The photo product could be represented by stereostructures A, B or C. The observed coupling pattern of the benzylic proton (one large and two small couplings) would favour stereostructure C.
The isolation of racemic mahanimbine half way in that photolysis suggests as in the thermolysis experiment, in this reaction also the pyran ring has opened up. The mechanism of formation of photocurryanine is probably as follows:-
Racemic mahanimbine: (+) Mahanimbine (0.05 g) was heated at 150° for one hr in a tube, sealed under 1 mm pressure. The colourless gummy product was collected and crystallised from pet-ether. The solid (0.03 g, 60%), m.p. 76° (α)D 0° (CHCl₃) was identical with (+) mahanimbine (TLC, mixed m.p., IR superposable, Fig. 68), synthesised by an unambiguous route in this laboratory².

Attempted racemisation at lower temperature

(+ ) Mahanimbine (0.05 g) was taken in tubes sealed with and without vacuum. The tubes were heated on a waterbath at 98° for 2 hr. The product in both cases was crystallised from pet-ether and had m.p. 94-5°. M.p., mixed m.p. and IR spectrum remained unchanged.

Thermal conversion of (+) Mahanimbine

(+ ) Mahanimbine (0.2 g) was heated at 200° in a tube sealed under 1 mm pressure for 3 hr. The product was a green transparent mass which on TLC showed three major spots. This was then chromatographed over 30 parts silica gel in pet.ether. Following are the details of the chromatography of the product obtained from five batches.
FIG. 68: IR SPECTRUM OF MAHANIMBINE

--- Racemic

--- Natural product
The product (1 g) was loaded on silica gel (30 g) column (inner diameter 1.2 cm; height of the column 15 cm) and eluted with solvents indicated. Fractions (50 ml each) were collected and followed by TLC. The mixture was then separated into pools:

<table>
<thead>
<tr>
<th>Pool</th>
<th>Solvent</th>
<th>Fraction Nos.</th>
<th>Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Pet ether</td>
<td>1-4</td>
<td>-</td>
</tr>
<tr>
<td>B</td>
<td>Pet ether</td>
<td>5-8</td>
<td>0.2 g</td>
</tr>
<tr>
<td>C</td>
<td>Pet ether</td>
<td>9-14</td>
<td>0.35 g</td>
</tr>
<tr>
<td>D</td>
<td>Pet ether</td>
<td>15-20</td>
<td>0.02 g</td>
</tr>
<tr>
<td>E</td>
<td>Benzene</td>
<td>21</td>
<td>0.2 g</td>
</tr>
<tr>
<td>F</td>
<td>Benzene :</td>
<td>22</td>
<td>0.07 g</td>
</tr>
<tr>
<td></td>
<td>MeOH</td>
<td>95 : 5</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Total</td>
</tr>
</tbody>
</table>

Pool B: This, on evaporation of the solvent, gave a white crystalline solid, which on crystallisation from n-hexane gave white needles (0.20 g, 20%), m.p. 137°. Direct comparison with curryanine (m.p., mixed m.p., IR superposable) and cyclomahanimbine (IR superposable except for minor details) proved that all of these were identical.
Pool C: Even though this was a solid, the range in the m.p. suggested that it was a mixture. It was then treated with hot n-hexane (10 ml). A white crystalline compound insoluble in the solvent was obtained. The supernatant liquid was decanted and the solid washed once with hot n-hexane (5 ml), dried in vacuum and crystallised from benzene to give white cubes (0.035 g, 3.5 %) m.p. 260°. Comparison of this compound (m.p., mixed m.p. superposable IR) with curryangine and mahanimbidine proved that all of these were identical.

The decanted liquid on evaporation of the solvent, yielded a solid (0.2 g, total yield 40 %), m.p. 137°, identical (TLC, m.p., IR) in every respect with curryanine isolated from Pool B.

Pool D: This was a colourless gummy liquid which, on addition of n-hexane (10 ml), scratching and cooling, afforded a white fluffy solid (0.01 g, 1%). It had m.p. 76°. The TLC indicated that it could be (+) mahanimbine. Superposable IR and optical rotation (α)D 0°(CHCl₃), confirmed this.

Pool E: This was greenish yellow gummy mass which could not be obtained in crystalline form.
Attempts to Optimise the Yield of the Cyclised Products

1. (+) Mahanimbine (0.05 g) was heated at 200\(^\circ\) for 6, 24 and 36 hr in paraffin bath. TLC indicated that most of the product was curranine. This was confirmed by isolating only curranine from the reaction mixture. No other product could be obtained.

2. (+) Mahanimbine (0.05 g) was heated in separate tubes sealed under vacuum in Wood's metal bath at 200\(^\circ\), 250\(^\circ\) and 300\(^\circ\) for 1 hr. TLC indicated the presence of only curranine, curraninge and (+) mahanimbine.

3. (+) Mahanimbine (0.05 g) was heated at 200\(^\circ\), 250\(^\circ\) and 300\(^\circ\) for 3 hr in oil bath. TLC indicated that it was a mixture of curranine, curraninge and racemic mahanimbine.

Attempted cyclisations of (+) mahanimbine in different solvents

(+ ) Mahanimbine (0.01 g) was heated in sealed tubes (i) in diethyl aniline (0.5 ml) containing benzoic acid (0.001 g), (ii) in p-cymene (0.1 ml) and (iii) in pyridine (0.5 ml) for 12 hr at 200\(^\circ\). In each case the product was a dark brown mass. TLC indicated that they were all very complex mixtures.
Attempted acid catalysed cyclisations of (+) mahanimbine

1. (+) Mahanimbine (0.05 g) and adipic acid (0.005 g) were refluxed in benzene (5 ml) for 2 hr. TLC indicated that no change had occurred.

2. (+) Mahanimbine (0.026 g) and p-toluene sulphonic acid (0.001 g) were heated in benzene (5 ml) as well as in methanol (5 ml) for 4 hr. TLC showed that while most of the mahanimbine remained unreacted, a spot corresponding to curryangine has started appearing.

Attempted conversions of curryanine to curryangine

1. Curryanine (0.01 g), in tubes sealed under vacuum, was heated (i) at 200° and (ii) at 300° for 6 hr. TLC indicated no change.

2. Curryanine (0.01 g) was added to a hot solution of p-toluene sulphonlic acid (0.001 g) (i) in benzene (5 ml) and (ii) in chloroform (5 ml), refluxed for 2 hr. TLC indicated no change.

Conversion of curryangine to curryanine

Curryangine (0.1 g) was heated in a tube, sealed under vacuum, at 200° for 2 hr. TLC showed a mixture of three compounds. The major compound corresponded to curryanine. Column chromatography of the mixture over silica gel and elution with pet ether gave a solid
(0.04 g, 40 %) which was crystallised from n-hexane to give needles, m.p. 137°, identical in every respect with curryanine (m.p., mixed m.p., superposable IR, Fig. 69).

Attempts to trap the intermediate (V) in the heating experiments.

1. (+) Mahanimbine (0.05 g) was heated at 150° for 2 hr in three different tubes (i) with 2,4 dinitrophenylhydrazine (0.6 g), (ii) with aniline (0.5 ml) and (iii) with p-anisidine (0.5 g). TLC indicated that no change had occurred. The mixture on column chromatography yielded (+) mahanimbine, m.p. 76°, identical in every respect (TLC, mixed m.p. IR) with (+) mahanimbine isolated earlier.

2. The same experiment was repeated, but the heating was done at 200° for 4 hr. While the product with 2,4 dinitrophenylhydrazine was found to be very complex on TLC, the one with p-anisidine showed spots corresponding to curryanine and curryangine and that with aniline a spot corresponding to curryanine. The product obtained in the last case on chromatography gave curryanine identical in every respect (m.p., mixed m.p., IR) with authentic sample.
Fig. 69: IR spectrum of curryanine
--- Obtained by heating curryangine.
--- Obtained by heating (+) mahanimbine.
Attempts to trap the intermediate (VI) in the heating experiments

(+) Mahanimbine (0.3 g) was heated at 150° for 4 hr, in a tube sealed under vacuum, with acetic anhydride (0.5 ml). The product was poured on ice and extracted with ether (2 x 10 ml). The ether layer was washed with water, dried over Na₂SO₄ and the solvent removed. The dark yellow residue obtained was loaded on a silica gel column and eluted with pet ether. The pet ether eluate gave N-acetyl mahanimbine (0.06 g, 17 %), m.p. 76°.

Reduction of N-acetyl mahanimbine

A solution of N-acetyl mahanimbine (0.06 g) in dry ether (5 ml) was added slowly to a well stirred slurry of lithium aluminium hydride (0.02 g) in ether (5 ml). The mixture was stirred for 15 min. Usual work up gave a white solid (0.01 g, 17 %) which was crystallised from n-hexane to give white needles, m.p. 70°. Mass and IR spectra of the product were identical with those of racemic mahanimbine.

Methylation of (+) mahanimbine

(+ ) Mahanimbine was methylated by the known procedure with slight modification in the quantities of reactants. It was found that the reported quantity of dimethyl sulphate (0.5 ml) was not enough to methylate 0.5 g of mahanimbine completely. Hence mahanimbine (0.5 g) was shaken with dimethyl sulphate (1 ml), acetone (7 ml)
and NaOH (2 g in 4 ml of water) at room temperature. After standing for 2 hr the mixture was poured on ice. The solid obtained was filtered, dried and crystallised from n-hexane (10 ml) to give white crystals of N-methyl mahanimbine (0.45 g, 66 %) m.p. 112° (Reported m.p. 112°).

**Attempts to trap the intermediate (VIII)**

N-methyl mahanimbine (0.1 g) was heated at 200° for 3 hr in tubes sealed under vacuum (i) with aniline (0.5 ml) and (ii) with p-toluidine. TLC indicated that the starting compound had disappeared. The product on crystallisation from n-hexane (10 ml) yielded white needles of N-methyl curryanine (0.03 g, 30 %), m.p. 172°, (Reported m.p. for N-methyl cyclomahanimbine 169-70°).

**Trapping of intermediate (IX)**

N-methyl mahanimbine (0.02 g) was heated in a tube sealed under vacuum with acetic anhydride (0.1 ml) and pyridine (0.1 ml) for three hours. The product showed on TLC a fluorescent spot under UV. The complexity of the reaction mixtures was found to be the same even after prolonged heating. The mixture was loaded on two FLC plates and the fluorescent zone separated. This zone on extracting with acetone and removal of solvent under reduced pressure gave a gummy mass (0.016 g, 40 %).
The product was unstable and could not be characterised completely.

Photolysis of mahanimbine

1. (+) Mahanimbine (3 g) in benzene (200 ml) was irradiated for 3 hr with a 250 w high pressure mercury lamp in a pyrex well under nitrogen atmosphere. The reaction was followed by TLC every 0.5 hr. The irradiation was stopped when the spot corresponding to the starting material had vanished. After removing the solvent under reduced pressure, the orange gummy mass was loaded on silica gel column (60 g) in pet ether. Elution with pet ether yielded white needles (0.03 g, 1 %) m.p. 178°.

2. (+) Mahanimbine (3 g) was irradiated again in similar manner for 1.5 hr. Chromatography yielded racemic mahanimbine (0.5 g, 16 %), m.p. 76°, identical with authentic sample.

+ We are indebted to Dr. Sukh Dev of N.C.L., Poona-8 for allowing us to use this apparatus.
Fig. 41: UV Spectrum of curranine.
Fig. 43: UV Spectrum of Dihydrocurryanine
FIG. 52: IR SPECTRUM OF DIHYDROCURRYANINE
Figure 54: UV Spectrum of Curryangine
FIG. 55: IR SPECTRUM OF CURRYANGINE
Fig. 5: Mass Spectrum of curryangine.
**Fig. 58**: UV Spectrum of N-Acetyl Mahanimbine.
Fig. 59: IR Spectrum of N-Acetyl Mahanimbin
REFERENCES


8. Samples of curryanine and curryangine were furnished by Dr. M.S. Wadia and those of cyclomahanimbine and mahanimbine by Dr. R.S. Kapil. The author wishes to thank both of them for their assistance.
