INTRODUCTION

The abundant fatty acids from natural sources, are recognized as a versatile group of chemicals in oleochemical industry. Since the past decades the utilization of fatty acids as agrichemicals find their way into industries not only in a simple acid or ester form but also through derivatization. The reactions of fatty acids are readily accepted to lead towards general perfection of the development and progress of organic chemistry.

The recent trend in technology of fats and fatty acids have given importance to such industrial processes as polymerization, oxidation and metathesis. Consequently fatty acids have increasingly been found usable as specific and characteristic base materials for the emerging organic chemical industry.

In recent years the attention of chemists has been diverted to synthesize oleochemicals from natural fats and oils due to ever increasing cost of petrochemicals. These fat derived chemicals are essential to a variety of industries such as coating, surfactants, plasticizers, lubricant additives, cosmetics, pharmaceuticals and organic pesticides.

The widespread occurrence of heterocyclic compounds in nature such as alkaloid, vitamin and variety of plant and
animal cell constituents is widely known. The current research in organic chemistry development and closely allied branches of biology is characterized by extensive investigation of physiologically active compounds encountered in the plant and animal world. The search for these active constituents which control the biological process of various systems has acted as powerful stimulus to the further development of chemistry of the heterocyclic compounds. A survey of literature reveals that long-chain fatty acids possessing a heterocyclic ring in the chain are a rarity in nature. Some long-chain substituted furanoid esters, however, have been reported to occur naturally.

Keeping in view the aforementioned importance of heterocyclic compounds, the azidirine, azirine, lactone, thiolactone, and phosphorus containing fatty acids have been synthesized from epoxy and hydroxy fatty acids.
CHAPTER - 3
THEORETICAL

Preparation of aziridines and azirines:

The saturated three membered heterocyclic nitrogen containing compounds (ethylenimine or aziridine or azacyclop propane or dimethyl enamine) are analogous to epoxy compounds\(^1,2\). Several general methods for the synthesis of aziridines have been described\(^3\). A few widely used methods are: Gabriel synthesis\(^13\), Nitrene addition to unsaturated compounds\(^16\), from alcohol\(^4\), ketoximes\(^5\) and from epoxides\(^6,7\) etc. First successful preparation of aziridines has been reported in Gabriel synthesis in which vinyl halides reacted with simple amines\(^3\) which was further cyclized to give aziridines\(^8\).

Short chain alpha, beta, dihalogen carbonyl compound on reaction with amines gave aziridines\(^11-13\). Gabriel synthesis was successfully applied for the synthesis of fatty aziridines in our laboratory\(^9,10\) with methyl 2,3-dibromohexadecanoate and primary amines.

Mid chain fatty aziridines were also prepared by the addition of iodine-isocyanate (INCO) to the double bond followed by cyclization\(^14\). Aziridines have also been prepared by mild cyclization of 2-amino alcohol using
diphosphorus tetraiodide. Aziridines were prepared via nitrene intermediates. There are various methods for generation of nitrenes. Only few are mentioned here.

(a) By oxidation:

Oxidation of 1,1-disubstituted hydrazines using leadtetraacetate (LTA) as oxidant gave nitrene in very smooth manner which can be trapped by olefins. Unsaturated fatty compound on reaction with N-aminophthalimide in presence of LTA gave aziridines.

Anderson et al. have observed that nitrene, generated by LTA oxidation may be stable enough to the olefinic compounds.

(b) By alpha elimination:

Base induced alpha elimination under certain condition leads to the generation of nitrene intermediates.

Fatty ester and amides of chloroformic acids isocyanate and isothiocyanate afforded aziridines. N, N-dibromobenzene sulphonamide was cyclized in presence of enolic ester yielded aziridines. Recently Atkinson et al. reacted isoquinolzoline with olefin to yield aziridines in presence of LTA. The product yield was improved when it was carried out in presence of trifluoroacetic acid (TFA).
Aziridines were also prepared by lithium aluminium hydride (LAH) reduction of oximes. When beta naphthyl propan-2-one oxime was reduced by LAH, it gave a mixture of syn and anti isomers.

A new one step synthesis of aziridines was developed in which oxiranes are simply treated with sodium salt of an N-substituted phosphoric ester in high boiling solvent. Apple and Halstenberg reported the conversion of epoxides into oxazophospholidines. The five membered heterocyclic compound underwent a special Wittig reaction to give aziridine.

However, the reactions of aziridines i.e. alkylation and silylation with butyl lithium followed by methyl iodide gave alkyl derivative and silyl derivative. Lithium -L-aziridine -2- carboxylate was synthesised from N-trityl-L-aziridine carboxylic acid benzyl ester by the treatment with trifluoroacetic acid. Several acyl aziridine -2- carboxylic acid esters were synthesized in good yield. Aziridine carboxylate with hydrazine at -50°C gave simple aziridine product. N-Hydroxyimidazoline obtained by treating aziridine with oxime and triethylamine hydrogenchloride.

Ethylenimine and its derivatives are potent pharmacological agents. The toxic effects of ethylenimine itself involve vesication of the skin, irritation of eyes,
reduction of white cell count and internal inflammation. Aziridines are highly active compounds and are used as insect chemo-sterilents, antimicrobials and important pharmaceuticals.
Azirine:

Several methods of preparation of azirines are reported from various processes. When irradiation of triazides gave azirine molecule and then new bi-2H-azirine compound was synthesised from diazides\textsuperscript{36}. Again chloroderivatives of acid on reaction with sodium azide and then thermolysis in boiling methanol gave azirine\textsuperscript{37} compounds. Acetylenic acid was reacted with HN\textsubscript{3} in acetic acid at room temperature gave azirine\textsuperscript{38}. A very simple reaction of cyanoderivatives with simple amines yielded azirines\textsuperscript{39}. Various imidazoles were reported by rearrangement in acid\textsuperscript{41} and base\textsuperscript{40} of azirines.
DISCUSSION

Reaction of methyl undec-10-enoate (1) with 3-amino-2-methyl-4-oxoquinazoline:

Reaction of methyl undec-10-enoate (1) with 3-amino-2-methyl-4-oxoquinazoline in presence of lead tetracetate (LTA) in dichloromethane afforded a brown oil which on purification gave solid compound (2) melting at 55°.

\[
\begin{align*}
\text{LTA} \\
\text{CH}_2 = \text{CH} - R + Y - \text{NH}_2 \rightarrow \text{CH}_2 - \text{CH} - R \\
\ (1) \\
\rightarrow \text{N} \\
\end{align*}
\]

\[R = (\text{CH}_2)_8 - \text{COOCH}_3\]

\[Y = \text{ } \]

Characterization of Product (2):

Elemental analysis of product(2) corresponded to formula C_{21}H_{29}O_3N_3. The IR spectrum exhibited characteristic band at 1725 for ester carbonyl, 1695 for ring carbonyl and sharp bands at 1605 and 775 for quinazoline unsaturation. A weak band at 1210 for C - N bond. The absorption band at 835 cm^{-1} showed the presence of aziridine moiety. Its NMR spectrum showed two multiplets at $\delta$ 8.2 and 7.6 for four quinazoline ring protons, a sharp singlet at 3.6 integrating
for three ester protons and at 2.7 for methyl protons and broad multiplet at 2.67 - 2.38 for three protons of aziridine ring. Methylene protons alpha to ester carbonyl and aziridine ring were appeared as a multiplets at 2.3 and 2.15 respectively. On the basis of analytical and spectral data, product (2) was characterized as methyl N - (2'-methyl - 4'-oxo -3'-quinazolinyl) - 10,11-epiminoundecanoate.

The structure was further strengthened by mass spectrum by showing molecular ion peak at m/z 371(10) along with the structure revealing peak at m/z 357 (M - CH₂, 10)(scheme - I). The alpha cleavage of the aziridine ring moiety showed a fragment ion peak at m/z 200 (10). The beta cleavage of the ring showed ion peak at m/z 215 (22). The mass ion peak at m/z 211(25) observed by the loss of quinazoline moiety with hydrogen from molecular ion and at m/z 186 (35) after the loss of (CH₂)₈ COOCH₃ from m/z 357. Other characteristic ion peaks were observed at m/z 340 (M- OCH₃, 15), 312 (M- COOCH₃, 10), 298 (M - CH₂COOCH₃, 30), 284 (M - CH₂CH₂COOCH₃,10), 256[M - (CH₂)₄ - COOCH₃, 20], 161 (M - C₁₂H₂₀O₂N,35) and 160(M - C₁₂H₂₁O₂N,100).

Reaction of methyl octadec - 9(Z) - enoate (3) with 3-amino-2-methyl -4-oxoquinazoline:

Reaction of methyl octadec - 9 (Z) - enoate (3) with 3-amino-2-methyl -4-oxoquinazoline in presence of LTA in
R = (CH₂)₈ COOCH₃

SCHEME I
dichloromethane gave an oily product which was chromatographed over silica gel column to yield an oily product (4).

\[
R - CH = CH - R' + Y - NH_2 \xrightarrow{LTA, CH_2Cl_2} R - CH - CH - R' \quad (4)
\]

\[
R = CH_3 - (CH_2)_7, \quad R' = (CH_2)_7 - COOCH_3, \quad Y = \text{quinazolyl}
\]

Characterization of Product (4):

The elemental analysis of product (4) corresponded to formula C_{28}H_{43}N_{3}O_{3}. The IR spectrum gave bands at 1680 for ring carbonyl function and 1600, 775 cm\(^{-1}\) for unsaturation of quinazoline ring. The other characteristic bands at 1230 and 1665 showed N - N and C - N bonds stretching respectively. A weak absorption band for cis aziridine ring appeared at 830. The NMR spectrum displayed important signals at 8.0 and 7.43 as multiplets for quinazoline ring protons and other at 2.75 as a multiplet for aziridine ring protons (in part merged with sharp singlet of methyl protons of quinazoline ring at 2.6). With the help of these, compound (4) was formulated as methyl N - (2' - methyl - 4' - oxo - 3' - quinazoliny1) 9 ,10-epiminooctadecanoate.
Additional support in favour of the structure (4) was obtained by the study of its mass spectrum. The mass spectrum showed molecular ion at m/z 469 (10) in scheme II. The other structure revealing peaks are at m/z 356 (70) and 312 (10) for alpha cleavage of the aziridine ring. After breaking of aziridine ring moiety the peaks were observed at m/z 343 (10) and 170 (10) which support the azidine ring. The only ring peak was obtained at m/z 199 (10) besides other usual ion peaks at m/z 410 (M-COOCH₃, 10), 396 (M-CH₂COOCH₃, 10), 370 (10) and 326 (10) for beta cleavages and 110 (M - 359, 100).

Reaction of methyl hexadec-2 (E) enoate (5) with 3-amino-2-methyl-4-oxoquinazoline:

Methyl hexadec-2 (E) enoate (5) when stirred with 3-amino-2-methyl-4-oxoquinazoline in presence of LTA under similar conditions as described earlier gave an oily product which was chromatographed over silica gel column yielded solid product (6) melting at 35°.

Characterization of Product (6)

Elemental analysis of product resembled to formula C₂₆H₃₉N₃O₃. The IR spectrum exhibited characteristic

\[ \text{R-CH = CH} \rightarrow \text{R-CH - CH - R'} \]

\[ \text{CH₂Cl₂} \]

\[ \text{N-Y} \]

(5) (6)
SCHEME - II
bands at 1735 and 1695 cm\(^{-1}\) for ester and ring carbonyl respectively and 1600, 775 for unsaturation of quinazoline ring along with 1225 and 1185 cm\(^{-1}\) for N-N and C-N bond respectively. IR spectrum also showed a characteristic absorption at 875 cm\(^{-1}\) for \textit{trans} aziridine \(^{14}\). The NMR spectrum exhibited a multiplet at \(\delta 1.75\) for C-4 methylene protons alpha to aziridine, a sharp singlet at 2.7 for methyl protons, a multiplet at 2.9 for C-3 aziridine and 3.2 for C-2 aziridine protons. On the basis of above spectral data compound (6) was formulated as methyl N-(2'-methyl -4'-oxo-3'-quinazolyl) - 2, 3 - epiminohexadecanoate.

Further support for the structure of (6) was obtained from its mass spectral data which is in agreement with the elemental formula. Molecular ion at \(m/z\) 441 (10) was observed. The other important peaks were observed at \(m/z\) 442 (\(M+1, 10\)) and 440 (\(M-1, 10\)) (Scheme - III).

The two characteristic fragment ions \(m/z\) 382 (20) and 258 (10) showed the presence of ring at C\(_2\) - C\(_3\) position. These can be shown to arise by the cleavages between C\(_1\) - C\(_2\) and C\(_3\) - C\(_4\) respectively. Fragment ion \(m/z\) 258 on further fragmentation gave ion at \(m/z\) 199 (10).
\[
\begin{align*}
\text{CH}_3 - (\text{CH}_2)_{12} - C = N^+ - H, & \quad \text{HN}^+ = C - \text{COOCH}_3 \\
m/z 210 & \quad m/z 86
\end{align*}
\]

Fragment ions at \(m/z\) 210 (10) and 86(92) originate from molecular ion via transannular fragmentation with one hydrogen transfer. They are of considerable significance to locate the position of ring at \(C_2 - C_3\).

\[
\begin{align*}
\text{HN}^+ = \text{CH} - \text{COOCH}_3, & \quad \text{N}^+ = \text{CH} - \text{COOCH}_3 \\
m/z 246 & \quad m/z 245
\end{align*}
\]

The fragment ion \(m/z\) 299(\(M - C_{10}H_{22}\), 20) constitute the peak of the spectrum arises from gamma cleavage to the ring. The rearranged fragments at \(m/z\) 246 (10) and 245 (10) from \(m/z\) 299 (15) support much towards confirmation of the presence of aziridine ring at \(C_2 - C_3\).

The fragmentation at \(m/z\) 272 (60) is a fairly strong peak and descends from the molecular ion peak via McLafferty rearrangement. The \(m/z\) 272 loses mass units 31 and 30 to give the fragments ions at \(m/z\) 241 (10) and 242 (10) respectively.
SCHEME - III
Reaction of methyl 12-hydroxyoctadec-9 (Z) - enoate (7) with 3-amino-2-methyl-4-oxoquinazoline

When methyl 12-hydroxyoctadec-9 (Z) - enoate (7) stirred with 3-amino-2-methyl-4-oxoquinazoline and LTA in dichloromethane as described earlier yielded an oily product which on purification by silica gel column chromatography furnished a liquid product (8).

\[
\begin{align*}
&\text{LTA} \\
&\text{R} - \text{CH} = \text{CH} - \text{R}^+\text{NH}_2 \quad \text{CH}_2\text{Cl}_2 \quad \text{CH}_2\text{NH} - \text{R}^+\text{NH}_2 \\
&(7) \quad (8)
\end{align*}
\]

\[
R = \text{CH}_2 - \text{CH(OH)} - (\text{CH}_2)_5 - \text{CH}_3
\]

\[
R' = (\text{CH}_2)_7 - \text{COOCH}_3
\]

Characterization of Product (8)

The elemental analysis of product (8) corresponded to formula C\text{28}H_{\text{43}}N\text{3}O\text{4}. IR spectrum showed bands at 3350 for hydroxyl group, 1680 for ring carbonyl, 1605 and 785 cm\text{1} for quinazoline unsaturation along with 1205 and 1175 cm\text{1} for N-N and C-N' bond respectively. One more characteristic band observed at 835 cm\text{1} for cis-aziridine\text{14} ring. The NMR spectrum contained characteristic signals at 8 8.12 and 7.4 as multiplets for
quinazoline ring protons and other at 4.4 multiplet for one methine (CHO) proton, sharp singlet at 2.64 for ring methyl protons and D2O exchangeable hydroxy proton observed at 2.64. On the basis of above spectral data compound (8) was considered as methyl 12 - hydroxy N - (2'- methyl - 4' - oxo - 3' - quinazolinyl) - cis- 9, 10 - epiminoctadecanoate.

Mass spectrum of product (8) supported the structure. It did not show the molecular ion peak at m/z 485 but it showed ion peaks at m/z 455 (M - 30, 10), 454 (455 - H, 10). The alpha cleavages of either side at m/z 356 (30) and 298 (10) were observed (Scheme - IV). The ion peak for beta cleavage was also seen at m/z 370 (10). The transannular fragmentation showed ion peak at m/z 342(10) and 315 (10). The gamma cleavage ion peak was observed at m/z 400 (10) besides other at 241(10). The azirine ring moiety ion peak was observed at m/z 199(10) besides other usual peaks at m/z 280(298 - H2O, 10) and 212(370 - C9H6N2O, 80).

Reaction of methyl 9-hydroxy-octadec-12(Z)-enoate (9) with 3-amino - 2 - methyl - 4 - oxoquinazoline

A similar reaction of methyl 9 - hydroxy - octadec -12 (Z) - enoate (9) with 3-amino - 2 - methyl - 4 - oxoquinazoline and LTA in dichloromethane yielded an oily product. The oily product on purification by column chromatography gave a oily product(10).
Scheme IV

R = -(CH₂)₅CH₃

R' = -(CH₂)₇COOCH₃

m/z 485 (M⁺ absent)
Characterization of Product (10):

The elemental analysis of product (10) corresponded to molecular formula C_{28}H_{43}O_{4}N_{3}. In IR spectrum, band at 825 cm\(^{-1}\) showed incorporation of cis aziridine ring in the chain. Other bands observed were at 3350 for hydroxy group, 1680 cm\(^{-1}\) for ring carbonyl group, 1600 and 775 for quinazoline unsaturation ring and 1240 and 1190 for N - N and C - N respectively. The NMR spectrum contained characteristic peaks at 8 8.15 and 7.8 as multiplets for quinazoline unsaturation, others at 5.04 a multiplet for methine (-CH-O) proton, a sharp singlet at 2.7 for ring methyl protons, a D\(_2\)O exchangeable broad peak at 2.54 for hydroxy proton and a multiplet at 2.4 for aziridine ring protons. On the basis of elemental analysis, IR and NMR data the product (10) was characterised as methyl 9-hydroxy- N-(2'-methyl-4'-oxo-3'-quinazolinyl) - cis-12, 13-epiminoctadecanoate.
The mass spectrum of compound (10) did not exhibit molecular ion at m/z 485. Characteristic mass fragments arising from alpha cleavage of aziridine ring was at m/z 270 (10) and 414(10) established the position of ring at C -12 and C -13 carbon atoms. The transannular fragment ions appeared at m/z 401(15) and 258 (10). The other fragment ions observed at m/z 255(20), 215(20), 199(30) and 99(10) (Scheme-V).

Reaction of Methyl 10 - undecynoate (11) with 3-amino - 2 - methyl -4- oxoquinazoline.

Oxidation of 3-amino - 2 - methyl -4- oxoquinazoline in presence of methyl 10 - undecynoate (11) using LTA as an oxidant in dichloromethane at room temperature gave the product (12).

\[
\begin{align*}
\text{LTA} \\
R - C \equiv C - R' + \text{Y} & \text{NH}_2 \rightarrow R - C \equiv C - R' \text{Y} \\
\text{CH}_2\text{Cl}_2
\end{align*}
\]

(11) 

\begin{align*}
R &= H, & R' &= (\text{CH}_2)_8 - \text{COOCH}_3 \\
Y &= \begin{array}{c}
\text{O} \\
\text{N} \\
\text{N} \\
\text{CH}_3
\end{array}, & Y &= \begin{array}{c}
\text{O} \\
\text{N} \\
\text{H} \\
\text{CH}_3
\end{array}
\end{align*}

(12)
\[ R - CH = NH \quad m/z \ 99 \]

\[ \text{m/z 255} \]

\[ R - CH = NH \quad m/z \ 258 \]

\[ \text{m/z 270} \]

\[ \text{m/z 414} \]

\[ \text{m/z 401} \]

\[ \text{m/z 215} \]

\[ \text{m/z 485 (M}^+ \text{ absent)} \]

\[ R - CH - HC\quad \text{N}^+ \quad Y \]

\[ \text{m/z 270} \]

\[ \text{m/z 199} \]

\[ R = \text{CH}_3 (\text{CH}_2)_4 - \]

\[ R' = (\text{CH}_2)_7 \text{COOCH}_3 \]

\[ \text{SCHEME-V} \]
Characterization of the Product (12)

The product (12) was analysed for C\textsubscript{21}H\textsubscript{27}O\textsubscript{3}N\textsubscript{3}. Its IR spectrum showed a very characteristic sharp band at 1775 cm\textsuperscript{-1} owing to the highly strained carbon nitrogen double bond vibration of azirine ring.\textsuperscript{143} A broad band in the region of 1740 - 1680 cm\textsuperscript{-1} revealed the presence of carbonyl functions of ester and quinazoline groups. Bands at 1600, 1430, 1150 and 870 cm\textsuperscript{-1} accounted for the presence of benzene ring. The NMR spectrum gave a multiplet centred at \( \delta \) 8.9 showing long range coupling for vinylic proton of the ring (HC =C), a multiplet at \( \delta \) 7.7 - 7.3 for four aromatic protons, a singlet at 2.5 for three methyl protons and a multiplet at 2.0 for two methylene protons alpha to azirine ring. 

These spectral data revealed the structure of the product (12) as 2-(8" - carbomethoxy octyl) - 2' - (2" - methyl -4"-oxoquinazolinyl) - 2H - azirine. The possibility of the formation of isomer of (12), 3(8" - carbomethoxy octyl) 2 - (2" - methyl -4"-oxoquinazolinyl) - 2H - azirine was due to appearance of NMR signal around 4.65 as a weak multiplet for methine proton of ring (H - C - C). It is believed that 1H-azirine is formed first and then rearranges very rapidly to 2H - azirine. The rearrangement may be due to the high antiaromatic\textsuperscript{42-43} nature of 1H - azirine.
Mass spectrum further distinguished the two isomers more effectively (Scheme - VI). Mass spectrum of product (12) gave molecular ion peak at m/z 369 (10). The prominent fragment ions confirming the isomeric nature of (12) were observed at m/z 198 (15) (alpha cleavage to the ring) along with C - N cleavages showed the ion peak at m/z 210 (10) and 159 (8). Transannular fragmentation showed isomeric nature by getting ion peaks at m/z 342 (10), 198 (15) and 172 (10) besides other peaks at m/z 212 (30), 171 (80), and 157 (15).

Reaction of methyl 9 - undecynoate (13) with 3-amino-2-methyl-4-oxoquinazoline:

Oxidation of 3-amino-2-methyl-4-oxoquinazoline with methyl 9-undecynoate (13) in presence of LTA was carried out as described earlier. Column chromatographic resolution of the reaction mixture furnished product (14) as an inseparable isomeric mixture.
\[ \text{Scheme-VI} \]

\[ m/z \ 342 \]

\[ m/z \ 369 \ (M^+) \]
Characterization of the Product (14):

Microanalysis for the product (14) gave as $C_{21}H_{27}O_{3}N_3$. IR spectrum of (14) also showed characteristic azirine ring vibration at $1770 \text{ cm}^{-1}$. It revealed other equally significant broad bands at 1745 and $1680 \text{ cm}^{-1}$ (carbonyl groups of ester and quinazoline ring respectively). Bands for the presence of benzene ring were observed at 1625, 1440, 1170 and $790 \text{ cm}^{-1}$. The appearance of NMR signals at $7.6$ - $7.3$ as a multiplet for four aromatic protons, $2.4$ a triplet for methylene protons alpha to azirine ring, merged in parts to the signal at $2.26$ for methylene protons alpha to ester carbonyl groups, $2.2$ a sharp singlet for methyl protons ($CH_3 - C - C -$), $2.03$ a singlet for methyl protons of ring and $1.4$ a singlet for methyl protons attached.
to azirine ring \(\text{CH}_3 - C - C -\) along with usual signals of fatty acid ester clearly established the formation of isomeric azirines (14) as 2 (3) - (7'' - carbomethoxyl heptyl) - 3 (2) - methyl -2- (2'' - methyl - 4'' - oxoquinazolinyl) 2H - azirine.

Mass spectrum of (14) further confirmed the isomeric nature of the product (Scheme - VII). It did not show the molecular ion peak at m/z 369. Characteristic alpha cleavage to the azirine ring were observed at m/z 212 (10) and 157 (10), 210 (80) and 159 (10) (C - N cleavage). The ion peaks at m/z 329 (10), 183 (20) and 41 (60) further confirmed the isomeric nature. The other ion peaks were observed at 211 (30), 196 (20), 187 (186 + H, 30), 156 (157 - H, 30 ), 137 (196-COOCH\(_3\),70), 124 (183 - COOCH\(_3\) , 30 and 54 (70).

Reaction of methyl 9 - octadecyanoate (15) with 3-amino-2-methyl-4-oxoquinazoline:

Oxidation of 3-amino-2-methyl-4-oxoquinazoline in presence of methyl 9 - octadecyanoate (15) and LTA afforded the product (16) as an isomeric mixture.
Scheme-VII

\[ \text{m/z 369 (M$^+$, absent)} \]

\[ \text{m/z 329} \]
The product (16) on elemental analysis gave composition $C_{28}H_{41}O_3N_3$ corresponding to its molecular weight. The IR spectrum of (16) showed a characteristic absorption band at 1775 cm$^{-1}$ for C = N stretching of azirine ring, 1740 and 1680 cm$^{-1}$ for ester and quinazoline carbonyl respectively and 1595, 1160 and 770 for aromatic ring. The NMR spectrum gave multiplets at 7.7 and 7.3 for quinazoline ring protons, 2.4 a triplet for methylene protons alpha to azirine ring and 2.1 a singlet for ring methyl protons. These spectral data coupled with the mechanistic consideration indicated the structure of product (16) as 2(3) - ( 7" - carbomethoxy heptyl) - 3 (2) - octyl 2 - (2" - methyl - 4" - oxoquinazolinyl) 2H - azirine.

Mass spectral fragmentation data gave further proof for the isomeric nature of (16). The mass spectrum of (16) did not exhibit molecular ion peak at m/z 467. It showed two alpha cleavage ions at m/z 354 (10) and 310 (20) and two beta fragment ions at 324 (32) and 143 (25). The fragment
ions at m/z 329 (10), 282(17), 140(30), 184(20) have further
confirmed the structure. Other fragment ions observed were
at m/z 308 (M - C₉H₇N₂O, 15), 295 (354 - COOCH₃, 40), 280 (282
- 2H, 15), 269 (329, C₂H₄O₂, 25) 212(20), 198 (10), 184 (M -
C₁₈H₁₆N₂O, 15), 154(184 - CH₂O, 10) and 140 (M-C₁₉H₂₃N₂O₃, 20)
(Scheme - VIII).
\[
\begin{align*}
\text{Y} &= \begin{array}{c}
\text{Scheme-VIII}
\end{array}
\end{align*}
\]