CHAPTER - IV

1,3-DIPOLAR CYCLOADDITION REACTIONS: SYNTHESIS OF TRIAZOLYLINDOLES AND THEIR DERIVATIVES

INTRODUCTION
In contrast to the very large number of special methods applicable to syntheses in the heterocyclic series, relatively few general methods are available. The 1,3-dipolar addition offers a remarkably wide range of utility in the synthesis of five membered heterocycles. Here "1,3-dipole" which can only be represented by zwitterionic octet resonance structure, combines in a cycloaddition with a multiple bond system, the "dipolarophile" to form an uncharged five membered ring. Numerous examples of this reaction were known.

Cycloadditions can be classified according to the number of new σ-bonds formed or according to the size of the ring which is formed. In the most frequent case, two reactants unite to form the cyclic compound, creating two new σ-bonds at the expense of two π-bonds. The thermal or photochemical formation of cyclobutanes from alkenes and the Diel's-Alder synthesis are two important cycloadditions in which 4- and 6-membered rings are produced respectively. A 1,3-dipole, a-b-c, must be defined, such that atom 'a' possesses an electron sextet, i.e. an incomplete valence shell combined with a positive formal charge, and that atom 'c', the negatively charged center, has an unshared electron pair. Combination of such a 1,3-dipole with a multiple bond system d-e, termed the dipolarophile, is referred to as 1,3-dipolar cycloaddition. The two components coalesce by means of cyclic electron displacement with extinction of the formal charges to give a 5-membered ring. The dipolarophile may be double or triple bond.

In the azides, the 1,3-system is composed entirely of nitrogen atoms. The first preparation of organic azide was effected in 1864 by P. Griess. The fact that three adjoining nitrogen atoms could yield a stable system was a
A fascinating phenomenon and is probably responsible for the early development of azide chemistry. In 1925, Hendricks and Pauling\textsuperscript{391} showed that the azide ion in sodium and potassium azides had a linear configuration and possessed a center of symmetry. Later\textsuperscript{392,393,394}, it was shown that in organic compounds, the azido group was linear but did not possess a center of symmetry like the azide ion. Methyl azide\textsuperscript{395} was investigated by electron diffraction measurements and the data showed that the azide group was linear, with the methyl group at an angle of about 120°C to the line through the azide group, and on the basis of the adjacent charge rule, the two resonance structures favoured are given below -

\[
\begin{array}{c}
\text{H}_2\text{C}\\
\text{N} \\
\text{N} \\
\text{N} \\
\text{N} \\
\end{array}
\]

Azides are considered as very important compounds due to both their industrial as well as biological applications\textsuperscript{396}. Azide derivatives have been used in rubber vulcanisation, polymer cross linking, dyes, tire cored adhesives, foaming of plastics, pharmaceuticals, pesticides and herbicides. Many azides show magnetic properties\textsuperscript{397-400}. The chemistry of azides thus attracted the attention of many chemists since many of these compounds play a role in organic chemistry\textsuperscript{401-402}. One of the more useful synthetic application of azides is the preparation of 1,2,3-triazoles via 1,3-dipolar cycloaddition reaction of azides with substituted acetylenic compounds\textsuperscript{403-408}. 1,2,3-Triazole moiety is a substructure of a number of biologically active compounds\textsuperscript{404}. A number of their derivatives found diverse uses in synthetic 330, analytical, medicinal (muscarinic receptor ligand 331), pharmaceutical, agrochemical and photographic chemistry and in other applications as corrosion inhibitors, dye stuffs, fluorescent whiteners 332, asymmetric dihydroxylation catalysts and photosensitizers 333.
Michael reported the preparation of 1-phenyl-1,2,3-triazole-4,5-dicarboxylic ester from phenyl azide and dimethylacetylene dicarboxylate.
Kirmse and Homer\textsuperscript{410} reported the triazole derivatives of the type 335 and 336.

\begin{align*}
335 & \quad 336 \\
\begin{array}{c}
\text{H}_2\text{C}_6 \\
\text{C} = \text{C} \\
\text{H}
\end{array} & \quad \begin{array}{c}
\text{H} \\
\text{C} = \text{C} \\
\text{Ph}
\end{array}
\end{align*}

Sheehan and Robinson\textsuperscript{411} have reported the synthesis of triazole derivatives of the type 337 and 338.

\begin{align*}
337 & \quad 338 \\
\begin{array}{c}
(\text{H}_2\text{C}_2\text{O})_2\text{HC} \\
\text{C} = \text{C} \\
\text{H}
\end{array} & \quad \begin{array}{c}
\text{H} \\
\text{C} = \text{C} \\
\text{CH(OC}_2\text{H}_2)\text{)}_2
\end{array}
\end{align*}

Erichomovitch \textit{et. al}\textsuperscript{2} have reported the synthesis of triazolopyridazine 339.

339
Sasaki and coworkers\textsuperscript{413} have synthesised triazole derivative of the type 340.

\[
\begin{array}{c}
\text{R}_1 \\
\text{R}_2 \\
\text{H}_3\text{COOC} \\
\text{\textcolor{white}{C}} \\
\text{COOCH}_3
\end{array}
\]

340

Henkel and Weygand\textsuperscript{414} reported the synthesis of 341.

\[
\begin{array}{c}
\text{(H}_2\text{C}_2\text{O})_2\text{HC} \\
\text{\textcolor{white}{C}} \\
\text{C}_\text{12H}_2\text{5}
\end{array}
\]

341

Michael \textit{et.al}\textsuperscript{415} synthesised compound 342.

\[
\begin{array}{c}
\text{C}_6\text{H}_5 \\
\text{H}_3\text{C}_6 \\
\text{\textcolor{white}{C}} \\
\text{H}_2\text{C}_2\text{OOC} \\
\text{CONH}_2
\end{array}
\]

342

Miglarese\textsuperscript{416} reported the synthesis of compound 343.

\[
\begin{array}{c}
\text{CONH}_2 \\
\text{H}_2\text{COOC} \\
\text{H}_2\text{COOC}
\end{array}
\]

343
Maiorana and associates\textsuperscript{417} reported the triazole derivatives 344 and 345.

\[ \text{Ar} = \text{Ph, C}_6\text{H}_4 - \text{NO}_2(4) \]

Tolman \textit{et. al}\textsuperscript{418} synthesised the compound 346.

L’Abbe and coworkers\textsuperscript{419} synthesised triazole derivatives 347, 348 and 349.

\[ \text{R} = \text{SO}_2\text{C}_6\text{H}_5, \text{SO}_2\text{C}_6\text{H}_4\text{-NO}_2(4) \]
Gonzalez and associates\textsuperscript{420} synthesised triazole derivatives of the type \textbf{350}, \textbf{351} and \textbf{352}. 

\textbf{350} 

\textbf{351}
Aebli et al.\textsuperscript{421} reported the triazolylstyryl triazoles 353 as fluorescent whiteners.

Claussen\textsuperscript{422} reported triazole derivative 354 as intermediates for dyes and fluorescent brighteners.

Denzel and Hoehn\textsuperscript{423} synthesised triazolopyridines 355 as tranquilizing, antiasthmatic, antiinflammatory agents.

R = CH\textsubscript{2}CHMe\textsubscript{2}, H, Et, \( R_1 = Bu, R = R' = H \)
Auricchio and associates\textsuperscript{424} synthesised arylsulfonamido-1,2,3-triazoles 356 and 357.

\begin{align*}
\text{R} & = \text{Ph, } C_6H_4\text{-Me (p), } C_6H_4\text{-Br (p), } C_6H_4\text{-NO}_2 (p)
\end{align*}

Abu Orabi and coworkers\textsuperscript{425} synthesised triazole derivatives 358.

\begin{align*}
y & = \text{H, 4-OCH}_3, 3\text{-OCH}_3, 4\text{-CH}_3, 2\text{-CH}_3, 3\text{CH}_3, 4\text{-NO}_2, 3\text{-NO}_2, 2\text{-NO}_2, 4\text{-Cl}, 3\text{-Cl, 2-Cl, 4-Br, 3-Br, 2-Br}
\end{align*}

Melani and associates\textsuperscript{426} have synthesised 5H-1,2,3-triazolo[5,1-c][1,4]benzodiazepine 359.

Reid Walter and Joanni\textsuperscript{427} synthesised triazolo-annulated 8-azapurines 360.

\begin{align*}
\text{R} & = \text{PhCH}_2, 4\text{-ClCH}_4\text{CH}_2, 2, 4\text{-Cl}_2C_6H_4\text{CH}_2
\end{align*}
Wen-Fa et al.\textsuperscript{428} synthesised triazole derivative of the type 361.

\[ \text{361} \]

Tomislav and associates\textsuperscript{429} synthesised triazolopyridazine derivative 362.

\[ \text{362} \]

\begin{verbatim}
R^1  R^2
H    Me
H    Et
H    n-pr
H    n-Bu
Ph   Me
Ph   Et
Ph   n-pr
Ph   n-But
Ph   n-pentyl
\end{verbatim}
Chen Min and coworkers\textsuperscript{430} reported the synthesis of compounds 363.

\[
\begin{array}{c}
\text{COOC}_2\text{H}_5 \\
\text{NH-R} \\
\text{363}
\end{array}
\]

X = 3-F, 4-Cl, 3-Br, 4-CH\textsubscript{3}CO, 4-NO\textsubscript{2}, 3-NO\textsubscript{2}, 3-CF\textsubscript{3}; \\
R = \text{CH}_3\text{CO}, \text{CH}_3\text{CH}_2\text{CO}, \text{C}_6\text{H}_5\text{CO}, \text{ClCH}_2\text{CO}

Guerin and Miller\textsuperscript{431} have synthesised compound 364.

\[
\begin{array}{c}
\text{364}
\end{array}
\]

Chu Changhu and associates\textsuperscript{432} prepared triazole derivative 365.

\[
\begin{array}{c}
\text{365}
\end{array}
\]
Theocharis and Alexandrou\textsuperscript{433} have reported the synthesis and mass spectral data of 4,5-bis[ary1,3,4-oxadiazol-2-yl]-1-benzyl-1,2,3-triazoles \textit{366}. 

\begin{center}
\includegraphics{image.png}
\end{center}

\textit{366}
Present Work

Synthesis of 1,2,3-triazolylindole/benz(g)indole derivatives
The perusal of the earlier reports on 1,2,3-triazole derivatives, revealed that there are practically no reports on the synthesis of 1,2,3-triazolylindoles. Hence, it was thought of considerable interest to embark upon the synthesis of novel triazolylindoles via 1,3-dipolar cycloaddition reaction wherein the bioactive 1,2,3-triazole is linked to position -1 and position -2 of pharmacologically active indole moiety.

In the present investigation, 5-hydroxyindole 283 was reacted with methyl iodide in refluxing dry acetone in presence of anhydrous potassium carbonate to get the required 1-[2-hydroxyethyl]-3-ethoxycarbonyl-5-methoxy-2-methylindole 371. This 5-methoxyindole 371 was reacted with methane sulphonyl chloride in dry pyridine to produce 1-[2-mesylethyl]-3-ethoxycarbonyl-5-methoxyindole 372. This indole mesylate 372 was further reacted with sodium azide in refluxing dimethyl formamide to secure 1-[2-azidoethyl]-3-ethoxycarbonyl-5-methoxyindole 373. The indolylazide 373 was further reacted separately with dimethylacetylene dicarboxylate and ethyl propiolate in refluxing dry acetone to obtain 1-[4,5-dimethoxycarbonyl-1,2,3-triazol-1-yl]ethyl-3-ethoxycarbonyl-5-methoxy-2-methylindole 374 and 1-[5-ethoxycarbonyl-1,2,3-triazol-1-yl]ethyl-3-ethoxycarbonyl-5-methoxy-2-methylindole 375 respectively. The reaction of the azide 373 with ethyl propiolate was found to be regiospecific resulting in the formation of only one isomer 375 and not the other isomer 376.

Thin layer chromatography using different solvent systems confirmed the presence of a sole product in the reaction. The product was believed to be triazole 375. This belief is based on the assumption that the attack of the nucleophilic nitrogen of the azide 367 on the electrophilic β-carbon of the unsaturated ester 368 is both sterically and electronically favoured and further, it is also based on assumption that cycloaddition reaction involves conjugate addition of the azide 367 to the michael acceptor 368 followed by cyclisation as depicted below.
Indolylazide 373 was also reacted with ethyl phenyl propiolate in refluxing dry acetone to yield a mixture of two isomeric products 1-[4-phenyl-5-ethoxycarbonyl-1,2,3-triazol-1-yl]ethyl-3-ethoxycarbonyl-5-methoxy-2-methylindole 378 and 1-[4-ethoxycarbonyl-5-phenyl-1,2,3-triazol-1-yl]ethyl-3-ethoxycarbonyl-5-methoxy-2-methylindole 377 as expected and revealed by thin layer chromatography. The product mixture was separated by column chromatography using silica gel column and benzene-ethyl acetate mixture as eluant. The triazole 377 was found to be the major product on the basis of steric considerations. It is in fact reported that addition of azides to unsymmetrical acetylenes tends mainly to give the isomer with the electron withdrawing or very bulky group at position-4\textsuperscript{434,435} [Scheme-31].
Scheme - 31

\[
\begin{align*}
\text{HO-} & \text{COOC}_2\text{H}_3 & \text{CH}_3 & \text{COOC}_2\text{H}_3 \\
\text{H}_3\text{C} & \text{C} & \text{C} & \text{C} \\
\text{CH}_2 & \text{OH} & \text{CH}_2 & \text{OH} \\
\text{283} & \text{371} & \text{375} & \text{376} & \text{377} & \text{378}
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3 & \text{I}, \text{K}_2\text{CO}_3, \text{KI, dry acetone} \\
\text{H}_2\text{CO-} & \text{COOC}_2\text{H}_3 \\
\text{N} & \text{CH} \\
\text{H}_2\text{C} & \text{C} & \text{C} \\
\text{CH}_2 & \text{OH} & \text{CH}_2 & \text{OH} \\
\text{373} & \text{372}
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3\text{SO}_2\text{Cl}, \text{dry pyridine} & \text{stir at RT} \\
\text{NaN}_3, \text{DMF} \\
\text{acetone,} \\
\triangle & \text{acetone,} \\
\text{H}_2\text{COOC} & \text{H}_3\text{C} & \text{C} & \text{C} & \text{COOC}_2\text{H}_3 \\
\text{Ph} & \text{H}_3\text{C} & \text{C} & \text{C} & \text{Ph} \\
\text{374} & \text{377} & \text{378}
\end{align*}
\]

223
1-[4,5-Dimethoxycarbonyl-1,2,3-triazol-1-yl]ethyl-3-ethoxycarbonyl-5-methoxy-2-methylindole 374 was reacted with hydrazine hydrate (99%) in refluxing ethanol in order to obtain the corresponding pyridazine derivative 379. But the actual product obtained was the dicarbohydrazide 381. In this reaction, the C3-ester group of indole did not react with hydrazine hydrate while the two carboxylate groups on 1,2,3-triazole ring only reacted with hydrazine hydrate to produce only the dicarbohydrazide 381 instead of the expected tricarbohydrazide 380 and this observation in conformity with our earlier reports. This dicarbohydrazide 381 was further reacted separately with acetonyl acetone and CS2/KOH to get the desired 1-[4,5-bis-(2,5-dimethylpyrrol-1-yl-)aminocarbonyl-1,2,3-triazol-1-yl]ethyl-3-ethoxycarbonyl-5-methoxy-2-methylindole 382 and 1-[4,5-bis-(5-mercapto-1,3,4-oxadiazol-2-yl)-1,2,3-triazol-1-yl]ethyl-3-ethoxycarbonyl-5-methoxy-2-methylindole 383 [Scheme-32].

IR spectrum of 371 (Fig. 125) exhibited strong stretching band at 3399 cm⁻¹ due to alcoholic OH group and strong stretching band at 1653 cm⁻¹ due to C3-ester carbonyl. ¹H NMR spectrum of 371 (Fig. 126) displayed triplet (J = 7.1 Hz) at 1.45 δ due to C3-ester methyl protons. The C2-methyl protons resonated as singlet at 2.78 δ and multiplet ranging from 3.89 to 3.99 δ corresponded to C5-methoxy and CH₂-O-protons. Multiplet ranging from 4.26 to 4.38 δ belonged to C3-ester methylene, NCH₂ and hydroxyl protons. Doublet of doublet (J = 8.5 Hz and 2.5 Hz) at 6.87 δ was assigned to C6-proton. Doublet (J = 8.5 Hz) at 7.23 δ was related to C7-proton while another doublet (J = 2.5 Hz) at 7.66 δ was ascribed to C4 proton.
Scheme-32

H₂CO
XXX
■COOC,H
N₂H₄,H₂O
I I
H₂COOC COOCH₃
374
-xe
N CH,
H,C—CH:—
U
H₂CO
-X- XXX
O=C C=O
N-N H H
379
CONHNH₂
N CH₃
H,C—CH₂—N 'N
H,NHNOC CONHNH₂
380
H₂NHNOC CONHNH₂
381
CS₂/KOH
382
225
The IR spectrum of 372 (Fig. 127) displayed a strong stretching band at 1671 cm\(^{-1}\) due to C\(_3\)-ester carbonyl. Asymmetric and symmetric stretching bands of methyl sulphonyl group were observed at 1349 cm\(^{-1}\) and 1159 cm\(^{-1}\) respectively. \(^1\)H NMR spectrum of 372 (Fig. 128) displayed a triplet (J = 7.1 Hz) at 1.49 \(\delta\) due to C\(_1\)-ester methyl protons and a singlet at 2.70 \(\delta\) was accounted for C\(_2\)-methyl protons. Singlet at 2.80 \(\delta\) was attributed to mesyl methyl protons and another singlet at 3.90 \(\delta\) was due to C\(_5\)-methoxy protons. Multiplet ranging from 4.38 \(\delta\) to 4.49 \(\delta\) belonged to C\(_3\)-ester methylene and N-CH\(_2\)-CH\(_2\) protons. Doublet of doublet (J = 8.5 Hz and 2.5 Hz) at 6.92 \(\delta\) was assigned to C\(_6\)-proton. Doublet (J=8.5 Hz) at 7.20 \(\delta\) was accounted for C\(_7\) proton while another doublet (J= 2.5 Hz) at 7.69 \(\delta\) was ascribed to C\(_4\)-proton.

The IR spectrum of 373 (Fig. 129) exhibited strong stretching bands at 2122 cm\(^{-1}\) and 2091 cm\(^{-1}\) due to azide function and another strong stretching band at 1684 cm\(^{-1}\) assigned to C\(_3\)-ester carbonyl. \(^1\)H NMR spectrum of this sample 373 (Fig. 130) showed triplet (J = 7.1 Hz) at 1.47 \(\delta\) assigned to C\(_3\)-ester methyl protons. Singlet at 2.80 \(\delta\) belonged to C\(_2\)-methyl protons and triplet (J = 7.1 Hz) at 3.69 \(\delta\) was due to CH\(_2\)-N\(_3\). Singlet at 3.90 \(\delta\) was attributed to C\(_5\)-methoxy protons. Triplet (J=7.1 Hz) at 4.28 \(\delta\) was assigned to NCH\(_2\) protons while quartet (J= 7.1 Hz) at 4.43 \(\delta\) was ascribed to C\(_3\)-ester methylene. Doublet of doublet (J=8.5 Hz and 2.5 Hz) at 6.92 \(\delta\) corresponded to C\(_6\)-proton. Doublet (J = 7.1 Hz) at 7.19 \(\delta\) was accounted for C\(_7\)-proton while another doublet (J = 2.5 Hz) at 7.69 \(\delta\) was related to C\(_4\)-proton.

IR spectrum of 374 (Fig. 131) displayed strong stretching bands at 1733 cm\(^{-1}\) and 1687 cm\(^{-1}\) due to triazole ester carbonyls and C\(_3\)-ester carbonyl respectively. \(^1\)H NMR spectrum of 374 (Fig. 132) exhibited triplet (J = 7.1 Hz) at 1.46 \(\delta\) due to C\(_2\)-ester methyl protons. Singlet at 2.52 \(\delta\) corresponded to C\(_2\)-methyl protons. Singlets at 3.60 \(\delta\), 3.87 \(\delta\) and 3.94 \(\delta\) belonged to two triazole ester methyls and C\(_5\)-methoxy protons. Quartet (J = 7.1 Hz) at 4.35 \(\delta\)
was assigned to C₃-ester methylene. Triplet (J = 7.1 Hz) at 4.57 δ was accounted for indole N-CH₂ while another triplet (J = 7.1 Hz) at 5.0 δ was assigned to triazolyl N-CH₂. Doublet of doublet (J = 8.5 Hz and 2.5 Hz) at 6.86 δ corresponded to C₆-proton. Doublet (J = 8.5 Hz) at 6.99 δ belonged to C₇-proton and C₄-proton resonated as doublet (J = 2.5 Hz) at 7.63 δ.

The proton decoupled ¹³C NMR spectrum of 374 (Fig. 133) displayed a peak at 11.8 δ, 14.9 δ due to C₃-ester CH₃ and C₂-CH₃ carbons respectively. The triazole NCH₂ carbon displayed a peak at 43.5 δ while indole NCH₂ carbon resonated at 48.9 δ. Two ester methyl carbons of triazole resonated at 53.1 δ and 53.6 δ. The OCH₃ carbon showed a peak at 56.0 δ and C₃-ester CH₂ carbon displayed at peak at 59.9 δ. The C₇-carbon of indole ring resonated at 104.5 δ while peaks of C₆- and C₄- carbons were observed at 105.4 δ and 109.3 δ respectively. The peak at 112.6 δ was attributed to C₃-carbon while peak at 127.9 δ was assigned to junction [b] carbon. Junction [a] carbon displayed a peak at 130.9 δ while two triazole carbons resonated at 140.3 δ. The C₂-carbon of indole exhibited a peak at 144.8 δ while C₅-carbon resonated at 156.3 δ. The signals at 158.5 δ, 160.4 δ and 166.1 δ were related to two triazole ester carbonyls and C₃ –ester carbonyl respectively.

The FAB mass spectrum of 374 (Fig. 134) displayed a molecular ion peak M⁺ at m/z (%) 444(70). The fragment F₁ exhibited base peak at m/z (%) 399 (100) obtained by the loss of OC₂H₅ from the molecular ion. The peak at m/z (%) 246 (6) was attributed to the fragment F₂ resulted from the loss of C₇H₈N₃O₄ from the molecular ion. The fragment F₃ showed a peak at m/z (%) 187(5) due to the loss of OC₂H₅ and C₉H₁₀N₃O₄ from the molecular ion [Scheme – 33].
Scheme – 33

F₂
m/z (%) 246(6)

C₅H₄N₂O₄

F₁
m/z (%) 399(100)

M⁺
m/z (%) 444(70)

OC₃H₅, C₅H₄N₂O₄

F₃
m/z (%) 187(5)
IR spectrum of 375 (Fig. 135) showed a strong stretching band at 3104 cm\(^{-1}\) due to triazole CH and strong stretching bands at 1733 cm\(^{-1}\) and 1684 cm\(^{-1}\) were assigned to triazole ester and C\(_3\)-ester carbonyls respectively. \(^1\)H NMR spectrum of this sample 375 (Fig. 136) exhibited two overlapping triplets (\(J = 7.1\) Hz) at 1.37 \(\delta\) and 1.45 \(\delta\) due to triazole ester methyl and C\(_3\)-ester methyl protons respectively. Singlet at 2.41 \(\delta\) belonged to C\(_2\)-methyl protons while another singlet at 3.89 \(\delta\) was accounted for C\(_5\)-methoxy protons. Multiplet ranging from 4.39 to 4.40 \(\delta\) was assigned for C\(_3\)-ester methylene and triazole ester methylene protons. Two distorted triplets at 4.66 \(\delta\) and 4.78 \(\delta\) were accounted for indole N-CH\(_2\) and triazole N-CH\(_2\) protons respectively. Multiplet ranging from 6.86 \(\delta\) to 7.44 \(\delta\) belonged to three indole ring protons. Singlet at 7.69 \(\delta\) was attributed to triazole proton.

The FAB mass spectrum of 375 (Fig. 137) showed molecular ion peak \(M^+\) at \(m/z\) (%) 400. The fragment \(F_1\) showed a base peak at \((m/z) 355\) 100) after the loss of OC\(_2\)H\(_5\) from the molecular ion. The peak at \(m/z\) (%) 327(4) was attributed to fragment \(F_2\) resulted by the loss of COOC\(_2\)H\(_5\) from the molecular ion. The fragment \(F_3\) displayed a peak at \(m/z\) (%) 246 (12) by the loss of C\(_6\)H\(_8\)N\(_3\)O\(_2\) from the molecular ion. The fragment \(F_4\) obtained after the loss of OC\(_2\)H\(_5\) and C\(_7\)H\(_{10}\)N\(_3\)O\(_2\) from the molecular ion exhibited a peak at \(m/z\) (%) 187(6). The base peak at \(m/z\) (%) 154 (100) was assigned to fragment \(F_5\) which resulted by the loss of C\(_{14}\)H\(_{16}\)NO\(_3\) from the molecular ion [Scheme – 34].
IR spectrum of 377 (Fig. 138) exhibited strong stretching bands at 1734 cm$^{-1}$ and 1682 cm$^{-1}$ due to triazole ester carbonyl and C$_3$-ester carbonyl functions respectively. $^1$H NMR spectrum of 377 (Fig. 139) displayed triplets ($J = 7.1$ Hz) at 1.08 $\delta$ and 1.43 $\delta$ due to triazole ester methyl and C$_3$-ester methyl protons. Two singlets at 2.64 $\delta$ and 3.84 $\delta$ were assigned to C$_2$-methyl and C$_5$-methoxy protons respectively. Quartet ($J = 7.1$ Hz) at 3.99 $\delta$ belonged to triazole ester methylene and another quartet ($J = 7.1$Hz) at 4.38 $\delta$ was assigned to C$_3$-ester methylene protons. Triplet ($J = 7.1$ Hz) at 4.61 $\delta$ was due to N-CH$_2$ and another triplet ($J=7.1$ Hz) at 5.13 $\delta$ was accounted for triazole NCH$_2$. Doublet of doublet ($J = 8.5$ Hz and 2.5 Hz) at 6.81 $\delta$ corresponded to C$_6$-proton and doublet ($J = 8.5$ Hz) at 6.98 $\delta$ was related to C$_7$-proton. Multiplet ranging from 7.34 to 7.53 $\delta$ was assigned to phenyl protons while doublet ($J = 2.5$ Hz) at 7.63 $\delta$ was ascribed to C$_4$-proton.

The proton decoupled $^{13}$C NMR spectrum of 377 (Fig. 140) displayed peaks at 12.0 $\delta$ and 13.9 $\delta$ due to C$_3$-ester CH$_3$ and C$_2$-CH$_3$ carbons respectively. The peaks at 43.8 $\delta$ and 49.2 $\delta$ were attributed to triazole NCH$_2$ and indole NCH$_2$ carbons respectively. The C$_5$-OCH$_3$ and C$_3$-ester CH$_2$ carbons displayed peaks at 59.8 $\delta$ and 62.3 $\delta$ respectively. The signal due to C$_7$-carbon was observed at 104.5 $\delta$ while C$_8$-carbon showed a peak at 105.2 $\delta$. The C$_4$- and C$_3$-carbons exhibited peaks at 109.5 $\delta$ and 112.4 $\delta$ respectively. The peak at 125.5 $\delta$ was attributed to C$_5$ carbon of triazole while junction [b] carbon displayed a peak at 127.9 $\delta$. The peak at 128.2 $\delta$ was due to C$_4^1$-carbon of phenyl while C$_3^1$ and C$_5^1$ phenyl carbons resonated at 129.4 $\delta$. The C$_2^1$ and C$_6^1$ phenyl carbons exhibited a peak at 129.9 $\delta$. Junction [a] carbon resonated at 130.3 $\delta$ and C$_1^1$-carbon of phenyl displayed a peak at 131.3 $\delta$. The signal due to C$_2$-carbon appeared at 145.1 $\delta$ and C$_4$-triazole carbon displayed at peak at 150.6 $\delta$. The C$_5$-carbon resonated at 156.2 $\delta$ while peaks at 158.9 $\delta$ and 166.2 $\delta$ were attributed to triazole ester and C$_3$-ester carbonyl carbons respectively.

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IR spectrum of the sample 378 (Fig. 141) displayed strong stretching bands at 1703 cm$^{-1}$ and 1684 cm$^{-1}$ due to triazole ester carbonyl and C$_3$-ester carbonyl groups respectively. $^1$H NMR spectrum of 378 (Fig. 142) exhibited triplets (J = 7.1 Hz) at 1.23 $\delta$ and 1.44 $\delta$ due to triazole ester methyl and C$_3$-ester methyl protons respectively. Singlets at 2.32 $\delta$ and 3.86 $\delta$ were accounted for C$_2$-methyl and C$_5$-methoxy protons respectively. Quartets (J = 7.1 Hz) at 4.25 $\delta$ and 4.38 $\delta$ were assigned to triazole ester methylene and C$_3$-ester methylene protons respectively. Multiplet ranging from 4.5 to 4.6 $\delta$ corresponded to N-CH$_2$-CH$_2$-N protons. Multiplet ranging from 6.67 to 7.40 $\delta$ were attributed to seven aromatic protons. Doublet (J = 2.5 Hz) at 7.61 $\delta$ was related to C$_4$-proton.

The proton decoupled $^{13}$C NMR spectrum of 378 (Fig. 143) displayed peaks at 11.6 $\delta$ and 14.3 $\delta$ due to C$_3$ ester CH$_3$ and triazole ester CH$_3$ carbons respectively. The peak at 14.9 $\delta$ was attributed to C$_2$-CH$_3$ carbon while triazole NCH$_2$ carbon resonated at 43.5 $\delta$. The indole NCH$_2$ carbon resonated at 47.1 $\delta$ and C$_5$-OCH$_3$ carbon displayed a peak at 56.1 $\delta$. Peaks at 59.9 $\delta$ and 61.5 $\delta$ were accounted for C$_3$-ester CH$_2$ and triazole ester CH$_2$ carbons respectively. The C$_7$-carbon of indole displayed at peak at 104.4 $\delta$ while C$_6$-carbon showed a peak at 105.4 $\delta$. The C$_4$-carbon displayed a peak at 109.2 $\delta$ and C$_7$-carbon exhibited a peak at 112.5 $\delta$. The peak at 125.0 $\delta$ was accounted for C$_4$-carbon of triazole while junction [b] carbon showed a peak at 127.9 $\delta$. The peak at 128.8 $\delta$ was due to C$_{4'}$-carbon of phenyl while C$_3'$ and C$_5'$-carbons of phenyl showed a peak at 129.5 $\delta$. The junction [a] carbon showed a peak at 130.8 $\delta$. The C$_1'$-carbon of phenyl displayed a peak at 137.2 $\delta$ while C$_4$-carbon of triazole exhibited a peak at 142.6 $\delta$. The peak due to C$_2$-carbon was observed at 144.5 $\delta$ and signal due to C$_3$-carbon appeared at 156.2 $\delta$. Two peaks at 160.9 $\delta$ and 166.1 $\delta$ were accounted for triazole ester and C$_3$-ester carbonyl carbons respectively.
The trizolylindole triester 374 was reacted with hydrazine hydrate (99%) in refluxing ethanol to get 1-[bis-4,5-hydrazinocarbonyl-1,2,3-triazol-1-yl]ethyl-3-ethoxycarbonyl-5-methoxy-2-methylindole 381.

IR spectrum of 381 (Fig. 144) exhibited strong stretching bands at 3345 cm\(^{-1}\), 3314 cm\(^{-1}\), 3302 cm\(^{-1}\) and 3252 cm\(^{-1}\) due to NH/NH\(_2\). Strong stretching bands at 1678 cm\(^{-1}\) and 1641 cm\(^{-1}\) were due to C\(_3\)-ester and amide carbonyls. \(^1\)H NMR spectrum of 381 (Fig. 145) displayed a triplet (\(J = 7.1\) Hz) at 1.35 \(\delta\) due to C\(_3\)-ester methyl protons. Singlets at 2.50 \(\delta\) and 3.76 \(\delta\) were attributed to C\(_2\)-methyl and C\(_5\)-methoxy protons respectively. Quartet (\(J = 7.1\) Hz) at 4.24 \(\delta\) was assigned to C\(_3\)-ester methylene. Two triplets (\(J = 7.1\) Hz) at 4.71 \(\delta\) and 5.10 \(\delta\) were accounted for indole N-CH\(_2\) and triazolyl CH\(_2\) protons respectively. Doublet of doublet (\(J = 8.5\) Hz and 2.5 Hz) at 6.76 \(\delta\) was related to C\(_6\)-proton. Doublet (\(J = 8.5\) Hz) at 7.28 was attributed to C\(_7\)-proton while another doublet (\(J = 2.5\) Hz) at 7.45 \(\delta\) was accounted for C\(_4\)-proton. Broad singlet at 12.03 \(\delta\) belonged to amide NH which vanished on D\(_2\)O exchange.

The FAB mass spectrum of 381 (fig. 146) displayed a molecular ion peak at m/z (%) 444 (30). The fragment F\(_1\) exhibited a peak at m/z (%) 412 (6) obtained by the loss of 2NH\(_2\) from the molecular ion. The fragment F\(_2\) displayed a peak at m/z (%) 399 (72) due to the loss of OC\(_2\)H\(_5\) from the molecular ion. The peak at m/z (%) 367 (10) was attributed to fragment F\(_3\) resulted by the loss of NHNH\(_2\) and C\(_2\)H\(_5\)OH from the molecular ion. The fragment F\(_4\) displayed a peak at m/z (%) 246 (20) due to the loss of C\(_3\)H\(_8\)N\(_4\)O\(_2\). The peak at m/z(%) 200(6) was accounted for fragment F\(_5\) resulted by the loss of C\(_3\)H\(_8\)N\(_4\)O\(_2\) and C\(_2\)H\(_5\)OH from the molecular ion. The peak at m/z (%) 188 (12) was attributed to fragment F\(_6\) obtained by the loss of C\(_2\)H\(_4\), CO\(_2\) and C\(_4\)H\(_6\)N\(_7\)O\(_2\) from the molecular ion. The fragment F\(_7\) displayed base peak at m/z (%) 138 (100) due to the loss of C\(_6\)H\(_{20}\)N\(_7\)O\(_5\) from the molecular ion [Scheme – 35].
IR spectrum of 382 (Fig. 147) displayed a stretching band at 3431 cm\(^{-1}\) due to NH and strong stretching bands at 1696 cm\(^{-1}\) and 1684 cm\(^{-1}\) due to C\(_3\)-ester and amide carbonyls. \(^1\)H NMR spectrum of 382 (Fig. 148) exhibited triplet (\(J = 7.1\) Hz) at 1.34 \(\delta\) due to C\(_3\)-ester methyl protons. Singlet at 2.00 \(\delta\) was due to four pyrrole methyls. Singlet at 2.53 \(\delta\) corresponded to C\(_2\)-methyl protons and another singlet at 3.73 \(\delta\) belonged to C\(_5\)-methoxy protons. Quartet (\(J = 7.1\) Hz) at 4.27 \(\delta\) was assigned to C\(_3\)-ester methylene protons. Two triplets (\(J = 7.1\) Hz) at 4.75 \(\delta\) and 5.04 \(\delta\) were related to indole N-CH\(_2\) and triazolyl N-CH\(_2\) protons. Two singlets at 5.67 \(\delta\) and 5.69 \(\delta\) corresponded to pyrrole C\(_3\)- and C\(_4\)- protons. Doublet of doublet (\(J = 8.5\) Hz and 2.5 Hz) at 6.70 \(\delta\) belonged to C\(_6\)-proton and doublet (\(J = 8.5\) Hz) at 7.08 \(\delta\) was assigned to C\(_7\)-proton while another doublet (\(J = 2.5\) Hz) at 7.43 \(\delta\) was attributed to C\(_4\)-proton. Two singlets at 11.91 \(\delta\) and 12.20 \(\delta\) were assigned to two amide NH protons which vanished on D\(_2\)O exchange.

IR spectrum of 383 (Fig. 149) displayed strong stretching bands at 3546 and 3404 cm\(^{-1}\) due to two oxadiazole NH functions. Two strong stretching bands at 1683 cm\(^{-1}\) and 1055 cm\(^{-1}\) were attributed to C\(_3\)-ester carbonyl and C=S respectively. \(^1\)H NMR spectrum of 383 (Fig. 150) exhibited a triplet (\(J = 7.1\) Hz) at 1.36 \(\delta\) due to C\(_3\)-ester methyl protons. Singlet at 2.56 \(\delta\) was attributed to C\(_2\)-methyl protons while another singlet at 3.78 \(\delta\) was assigned to C\(_5\)-methoxy protons. Quartet (\(J = 7.1\) Hz) at 4.29 \(\delta\) corresponded to C\(_3\)-ester methylene protons. Two triplets (\(J = 7.1\) Hz) at 4.78 \(\delta\) and 4.81 \(\delta\) were accounted for indole NCH\(_2\) and triazole NCH\(_2\) functions respectively. Doublet of doublet (\(J = 8.5\) Hz and 2.5 Hz) at 6.78 \(\delta\) was ascribed to C\(_6\)-proton while doublet (\(J = 8.5\) Hz) at 7.30 \(\delta\) was assigned to C\(_7\)-proton. Doublet (\(J = 2.5\) Hz) at 7.48 \(\delta\) belonged to C\(_4\)-proton. Two singlets at 8.48 \(\delta\) and 13.08 \(\delta\) were attributed to oxadiazole SH/NH protons which vanished on D\(_2\)O exchange.

In another investigation 5-hydroxybenz(g)indole 296 was reacted with methyl iodide in refluxing dry acetone in presence of anhydrous potassium.
carbonate to get the required 1-[2-hydroxyethyl]-3-ethoxycarbonyl-5-methoxy-2-methylbenz(g)indole \textbf{384}. This 5-methoxybenz(g)indole \textbf{384} was further reacted with methane sulphonyl chloride in dry pyridine to get the required 1-[2-mesylethyl]-3-ethoxycarbonyl-5-methoxy-2-methylbenz(g)indole \textbf{385}. Further, this benz(g)indole mesylate \textbf{385} was reacted with sodium azide in refluxing dimethylformamide to secure 1-[2-azidoethyl]-3-ethoxycarbonyl-5-methoxy-2-methylbenz(g)indole \textbf{386}.

Benz(g)indolylazide \textbf{386} was further subjected to 1,3-dipolar cycloaddition by reacting separately with dimethylacetylene dicarboxylate and ethyl propiolate in refluxing acetone to secure 1-[4,5-dimethoxycarbonyl-1,2,3-triazol-1-yl]ethyl-3-ethoxycarbonyl-5-methoxy-2-methylbenz(g)indole \textbf{387} and 1-[4-ethoxycarbonyl-1,2,3-triazol-1-yl]ethyl-3-ethoxycarbonyl-5-methoxy-2-methylbenz(g)indole \textbf{388}. The reaction of the benz(g)indole azide with ethyl propiolate was found to be regiospecific leading to the exclusive formation of only one isomer \textbf{388} and not the other expected isomer \textbf{389} [Scheme-36].

The triazolylbenz(g)indole triester \textbf{387} was further reacted with hydrazine hydrate (99\%) in refluxing ethanol with a desire to obtain the pyridazine derivative \textbf{390}. But this reaction produced only the dicarbohydrazide \textbf{392}. The C3-ester group did not react with hydrazine hydrate which is in conformity with our earlier reports\textsuperscript{133} [Scheme – 37].

The dicarbohydrazide \textbf{392} was reacted separately with acetonyl acetone and CS\textsubscript{2}/KOH to get the desired 1-[4,5-bis(2,5-dimethylpyrrol-1-yl)aminocarbonyl-1,2,3-triazol-1-yl]ethyl-3-ethoxycarbonyl-5-methoxy-2-methylbenz(g)indole \textbf{393} and 1-[4,5-bis(5-mercapto-1,3,4-oxadiazol-2-yl)-1,2,3-triazol-1-yl]ethyl-3-ethoxycarbonyl-5-methoxy-2-methylbenz(g)indole \textbf{394} respectively [Scheme – 37].
Scheme 36

\[ \text{Scheme 36} \]

\[ \begin{align*}
\text{HO} & \quad \text{CH}_3 \quad \text{COOCH}_3 \\
\text{H}_2\text{C} & \quad \text{CH}_2\text{OH} \\
\text{296} \quad \text{CH}_3 & \quad \text{K}_2\text{CO}_3 \\
\text{CH}_2\text{I} & \quad \text{dry acetone} \quad \Delta \\
\text{H}_3\text{CO} & \quad \text{CH}_3 \quad \text{COOCH}_3 \\
\text{H}_2\text{C} & \quad \text{CH}_2\text{OH} \\
\text{384} \quad \text{H}_3\text{SO}_2\text{Cl} & \quad \text{dry pyridine} \\
& \quad \text{stir at RT} \\
\text{H}_3\text{CO} & \quad \text{CH}_3 \quad \text{COOCH}_3 \\
\text{H}_2\text{C} & \quad \text{CH}_2\text{N}_3 \\
\text{385} \quad \text{NaN}_3 & \quad \text{DMF} \quad \Delta \\
\text{H}_3\text{COOC} & \quad \text{C} \equiv \text{C} \\
& \quad \text{COOCH}_3 \\
& \quad \text{Acetone} \quad \Delta \\
\text{386} \quad \text{HC} \equiv \text{C} & \quad \text{COOC}_2\text{H}_5 \quad \text{acetone, } \Delta \\
\text{H}_3\text{COOC} & \quad \text{C} \equiv \text{C} \\
& \quad \text{COOCH}_3 \\
& \quad \text{387} \\
\text{H}_3\text{CO} & \quad \text{CH}_3 \quad \text{N}_2\text{N} \\
\text{H}_2\text{C} & \quad \text{CH}_2\text{N}_2\text{N} \\
\text{388} \quad \text{H}_3\text{COOC} & \quad \text{C} \equiv \text{C} \\
& \quad \text{COOCH}_3 \\
& \quad \text{389} \\
\end{align*} \]
IR spectrum of 384 (Fig. 151) exhibited strong stretching band at 3449 cm\(^{-1}\) due to alcoholic OH and strong stretching band at 1662 cm\(^{-1}\) was due to C\(_3\)-ester carbonyl. \(^1\)H NMR spectrum of this sample 384 (Fig. 152) displayed a triplet (\(J = 7.1\) Hz) at 1.40 \(\delta\) due to C\(_3\)-ester methyl protons. Singlets at 2.80 \(\delta\) and 4.03 \(\delta\) were accounted for C\(_2\)-methyl and C\(_5\)-methoxy protons respectively. Triplet (\(J = 7.1\) Hz) at 4.11 \(\delta\) belonged to CH\(_2\)-O- protons while quartet (\(J = 7.1\) Hz) at 4.34 \(\delta\) was attributed to C\(_3\)-ester methylene protons. Triplet (\(J = 7.1\) Hz) at 4.70 \(\delta\) was ascribed to indole NCH\(_2\) protons. Multiplet ranging from 7.40 to 7.56 \(\delta\) corresponded to C\(_7\)- and C\(_8\)- protons. Singlet at 7.73 \(\delta\) was attributed to C\(_4\)-proton. Doublet (\(J = 8.5\) Hz) at 8.16 \(\delta\) was related to C\(_6\)-proton while another doublet (\(J = 8.5\) Hz) at 8.42 \(\delta\) was assigned to C\(_9\)-proton.

IR spectrum of 385 (Fig. 153) showed strong stretching band at 1663 cm\(^{-1}\) due to C\(_3\)-ester carbonyl. Asymmetric and symmetric stretching bands of mesyl sulphonyl group were observed at 1357 cm\(^{-1}\) and 1171 cm\(^{-1}\). \(^1\)H NMR spectrum of this sample 385 (Fig. 154) displayed triplet (\(J = 7.1\) Hz) at 1.50 \(\delta\) due to C\(_3\)-ester methyl protons. Singlets at 2.72 \(\delta\), 2.88 \(\delta\) and 4.08 \(\delta\) were assigned to C\(_2\)-methyl, mesylmethyl and C\(_5\)-methoxy protons respectively. Quartet (\(J = 7.1\) Hz) at 4.46 \(\delta\) belonged to C\(_3\)-ester methylene protons. Triplets (\(J = 7.1\) Hz) at 4.66 \(\delta\) and 4.94 \(\delta\) were attributed to N-CH\(_2\) and CH\(_2\)-O-SO\(_2\)- protons respectively. Multiplet ranging from 7.47 \(\delta\) to 7.64 \(\delta\) corresponded to C\(_7\)- and C\(_8\)- protons. Singlet at 7.81 \(\delta\) was related to C\(_4\)-proton. Two doublets (\(J = 8.5\) Hz) at 8.13 \(\delta\) and 8.47 \(\delta\) were due to C\(_6\)- and C\(_9\)- protons respectively.

IR spectrum of 386 (Fig. 155) displayed stretching band at 2103 cm\(^{-1}\) due to N\(_3\) and another strong stretching band at 1689 cm\(^{-1}\) was due to C\(_3\)-ester carbonyl. \(^1\)H NMR spectrum of 386 (Fig. 156) displayed triplet (\(J = 7.1\) Hz) at 1.51 \(\delta\) due to C\(_3\)-ester methyl protons. Singlet at 2.89 \(\delta\) belonged to C\(_2\)-methyl protons and triplet (\(J = 7.1\) Hz) at 3.85 \(\delta\) was assigned to CH\(_2\)-N\(_3\) protons. Singlet at 4.09 \(\delta\) was ascribed to C\(_5\)-methoxy protons while quartet (\(J = 7.1\) Hz) at 4.46 \(\delta\) corresponded to C\(_3\)-ester methylene protons. Triplet at 4.74 \(\delta\)
belonged to NCH₂ protons. Multiplet ranging from 7.46 to 7.64 δ was ascribed to C₇ and C₈-protons. Singlet at 7.83 δ was due to C₄-proton. Doublets (J = 8.5 Hz) at 8.14 δ and 8.48 δ were accounted for C₆- and C₉-protons respectively.

IR spectrum of 387 (Fig. 157) displayed strong stretching bands at 1739 cm⁻¹ and 1681 cm⁻¹ due to triazole ester carbonyl and C₃-ester carbonyl functions respectively. ¹H NMR spectrum of 387 (Fig. 158) exhibited triplet (J = 7.1 Hz) at 1.46 δ due to C₂-ester methyl protons. Singlet at 2.54 δ belonged to C₂-methyl protons. Singlets at 3.55 δ, 3.97 δ and 4.08 δ corresponded to C₅-methoxy and triazolyl ester methyl protons. Quartet (J = 7.1 Hz) at 4.42 δ was due to C₃-ester methylene protons. Multiplet ranging from 5.07 to 5.15 δ was attributed to indole N-CH₂ and triazolyl N-CH₂ protons. Multiplet ranging from 7.48 to 7.68 δ was assigned to C₇- and C₈-protons. Singlet at 7.79 δ was accounted for C₄-proton. Two doublets (J = 8.5 Hz) at 8.28 δ and 8.46 δ were due to C₆- and C₉-protons respectively.

Proton decoupled ¹³C NMR spectrum of 387 (Fig. 159) exhibited peaks at 11.7 δ, 14.9 δ due to C₃-ester CH₃ and C₂-CH₃ carbons. The peaks at 45.5 δ and 49.1 δ were attributed to triazole NCH₂ and indole NCH₂ carbons respectively. Two triazole ester CH₃ carbons showed peaks at 53.1 δ and 53.67 δ. The signal due to C₅-OCH₃ carbon appeared at 55.9 δ and C₃-ester CH₂ carbon signal appeared at 59.9 δ. The peaks at 98.8 δ and 106.7 δ were accounted for C₇- and C₉-carbons respectively. The C₆- and C₄-carbons displayed peaks at 119.5 δ and 122.6 δ respectively. The C₇-carbon showed a peak at 123.7 δ while C₈-carbon displayed a peak at 123.9 δ. Two junction carbons of naphthalene exhibited peaks at 124.2 δ and 124.5 δ. Junction [b] carbon of indole displayed a peak at 125.3 δ while C₂-carbon peak was observed at 127.4 δ. Peaks at 130.8 δ and 140.3 δ were assigned to triazole carbons. Junction [a] carbon displayed a peak at 142.8 δ. The peak at 151.9 δ was due to C₅-carbon.
Peaks at 158.4 δ, 160.5 δ and 166.1 δ were attributed to two triazole ester carbonyl and C₃-ester carbonyl carbons respectively.

IR spectrum of 388 (Fig. 160) exhibited sharp stretching band at 3105 cm⁻¹ related to triazole CH while strong stretching bands at 1727 cm⁻¹ and 1686 cm⁻¹ were assigned to triazole ester carbonyl and C₃-ester carbonyl groups respectively. ¹H NMR spectrum of 388 (Fig. 161) displayed two triplets (J = 7.1 Hz) at 1.27 δ and 1.40 δ due to triazole ester methyl and C₃-ester methyl protons respectively. Singlet at 2.50 δ belonged to C₂-methyl protons while another singlet at 4.01 δ corresponded to C₅-methoxy protons. Overlapping quartet (J = 7.1 Hz) at 4.27 δ was related to triazole ester methylene and C₃-ester methylene protons. Distorted triplets at 4.97 δ and 5.13 δ were accounted for NCH₂-CH₂-N protons. Multiplet ranging from 7.45 to 7.66 δ was attributed to C₈- and C₇-protons. Singlet at 7.72 δ was related to C₄-proton while two doublets (J = 8.5 Hz) at 8.33 δ and 8.43 δ belonged to C₆- and C₉- protons respectively. Singlet at 8.46 δ corresponded to triazole proton.

The triazolylbenz(g)indole triester 387 was reacted with hydrazine hydrate (99%) in refluxing ethanol to produce exclusively 1-[bis-4,5-hydrazinocarbonyl-1,2,3-triazol-1-yl]ethyl-3-ethoxycarbonyl-5-methoxy-2-methylbenz(g)indole 392. IR spectrum of 392 (Fig. 162) displayed strong stretching bands at 3448 cm⁻¹, 3267 cm⁻¹, 3213 cm⁻¹ and 3142 cm⁻¹ related to NH/NH₂ functions. Strong stretching bands at 1662 cm⁻¹ and 1642 cm⁻¹ were attributed to C₃-ester and triazole amide carbonyls. ¹H NMR spectrum of this sample 392 (Fig. 163) showed triplet (J = 7.1 Hz) at 1.46 δ due to C₃-ester methyl protons. Singlet at 2.71 δ was accounted for C₂-methyl protons. Singlet at 4.06 δ was assigned to C₅-methoxy protons. Quartet (J = 7.1 Hz) at 4.42 δ was related to C₃-ester methylene protons. Broad singlet at 4.91 δ was ascribed to NH₂ protons which vanished on D₂O exchange. Two triplets at 5.12 δ and 5.35 δ were assigned to NCH₂-CH₂-N protons. Multiplet ranging from 7.45 to 7.67 δ was attributed to C₇- and C₈- protons. Singlet at 7.75 δ was related to C₄-
proton while two doublets ($J = 8.5$ Hz) at 8.41 $\delta$ and 8.44 $\delta$ were attributed to C$_6$- and C$_9$- protons respectively.

The FAB mass spectrum of this sample 392 (Fig. 164) showed molecular ion peak at m/z (%) 494 (40). The fragment F$_1$ exhibited a peak at m/z (%) 480 (10) due to the loss of CH$_2$ from the molecular ion. The peak at m/z (%) 460 (10) was attributed to the fragment F$_2$ resulted by the loss of 2NH$_3$ from the molecular ion. The fragment F$_3$ displayed a peak at m/z (%) 449 (25) due to the loss of OC$_2$H$_5$ from the molecular ion. The peak at m/z (%) 435 (6) was assigned to fragment F$_4$ obtained by the loss of CONH$_2$ from the molecular ion. The fragment F$_5$ exhibited a peak at m/z (%) 391 (18) due to the loss of C$_2$H$_4$, CO$_2$ and NH$_2$ from the molecular ion. The peak at m/z (%) 345 (20) was assigned to fragment F$_6$ secured by the loss of 2CONHNH$_2$ and OCH$_3$ from the molecular ion. The fragment F$_7$ displayed a base peak at m/z (%) 154 (100) due to the loss of C$_{19}$H$_{22}$N$_3$O$_3$ from the molecular ion [Scheme – 38].
IR spectrum of 393 (Fig. 165) exhibited strong stretching bands at 3268 cm\(^{-1}\) related to amide NH group and strong stretching band at 1697 cm\(^{-1}\) due to C\(_3\)-ester and amide carbonyls. \(^1\)H NMR spectrum of 393 (Fig. 166) showed triplet (J = 7.1 Hz) at 1.47 \(\delta\) due to C\(_3\)-ester methyl protons. Two singlets at 2.07 \(\delta\) and 2.13 \(\delta\) corresponded to pyrrole methyl protons. The C\(_2\)-methyl protons resonated at 2.68 \(\delta\) as a singlet and singlet at 3.94 \(\delta\) was ascribed to C\(_5\)-methoxy protons. Quartet (J = 7.1 Hz) at 4.38 \(\delta\) was attributed to C\(_3\)-ester methylene protons. Two triplets at 5.18 \(\delta\) and 5.42 \(\delta\) were due to N-CH\(_2\) and triazole N-CH\(_2\) protons. Two singlets at 5.75 \(\delta\) and 5.79 \(\delta\) corresponded to pyrrole C\(_3\)'- and C\(_4\)'- protons. Multiplet ranging from 7.44 \(\delta\) to 7.63 \(\delta\) was assigned to C\(_7\)- and C\(_8\)-protons. Singlet at 7.76 \(\delta\) was due to C\(_4\)-proton. Multiplet ranging from 8.39 \(\delta\) to 8.48 \(\delta\) was accounted for C\(_6\)- and C\(_9\)-protons. Two singlets at 12.18 \(\delta\) and 13.02 \(\delta\) were assigned amide to NH protons which vanished on D\(_2\)O exchange.

The proton decoupled \(^{13}\)C NMR spectrum of sample 393 (Fig. 167) displayed a peak at 10.9 \(\delta\) due to four pyrrole methyl carbons while peak at 11.1 \(\delta\) was attributed to C\(_3\)-ester CH\(_3\) carbon. The peak at 14.2 \(\delta\) was assigned to C\(_2\)-methyl carbon. The triazole NCH\(_2\) and indole NCH\(_2\) carbons displayed peaks at 44.8 \(\delta\) and 49.6 \(\delta\) respectively. Peaks at 55.3 \(\delta\) and 59.1 \(\delta\) were accounted for C\(_5\)-OCH\(_3\) and C\(_3\)-ester CH\(_2\) carbons. Peak at 98.2 \(\delta\) was due to C\(_1\)-carbon while peak at 103.2 \(\delta\) was ascribed to C\(_9\)-carbon. Peaks at 103.6 \(\delta\) and 105.0 \(\delta\) were accounted for C\(_3\)- and C\(_4\)-carbon of pyrrole. The C\(_6\)-carbon resonated at 120.0 \(\delta\) while C\(_4\)-carbon displayed a peak at 121.9 \(\delta\). The signal due to C\(_7\)-carbon appeared at 122.9 \(\delta\) while peak of C\(_8\)-carbon was observed at 123.1 \(\delta\). Peaks at 123.2 \(\delta\) and 123.4 \(\delta\) were attributed to junction carbons of naphthalene. The junction [b] carbon displayed a peak at 124.1 \(\delta\) while C\(_2\)-carbon showed a peak at 126.8 \(\delta\). Peak at 126.9 \(\delta\) was assigned to C\(_2\)- and C\(_5\)-carbons of pyrrole. Peaks at 131.6 \(\delta\) and 137.9 \(\delta\) were accounted for C\(_4\)- and C\(_3\)-carbons of triazole. Junction[a] carbon displayed a peak at 143.0 \(\delta\).
while signal of C₅-carbon appeared at 150.5 δ. Peak at 156.8 δ was accounted for one amide carbonyl carbon. Signal due to amide carbonyl and C₃-ester carbonyl carbons appeared at 159.5 δ and 164.9 δ respectively.

The FAB mass spectrum of 393 (Fig. 168) exhibited molecular ion peak at m/z(%) 650(90). The fragment F₁ displayed a peak at m/z(%) 605(72) due to the loss of OC₂H₅ from the molecular ion. The peak at m/z(%) 557(40) was attributed to the fragment F₂ secured by the loss of C₆H₇N from the molecular ion. The fragment F₃ displayed a peak at m/z(%) 209(4) due to the loss of C₃H₅O₂ and C₁₈H₂₂N₇O₂ from the molecular ion [Scheme-39].
Scheme - 39

F₂
m/z (%) 557 (40)

C₆H₇N

F₁
m/z (%) 605 (72)

F₃
m/z (%) 209 (4)

C₆H₄O₂,
C₁₈H₂₂N₂O₂
The IR spectrum of the sample 394 (Fig. 169) displayed strong stretching band at 3175 cm\(^{-1}\) due to oxadiazole NH functions and strong stretching band at 1672 cm\(^{-1}\) was attributed to C\(_3\) ester carbonyl.

The FAB mass spectrum of 394 (Fig. 170) exhibited molecular ion peak at m/z(%) 578(70). The fragment F\(_1\) displayed a peak at m/z(%) 533(45) due to the loss of OC\(_2\)H\(_5\) from the molecular ion. The peak at m/z (%) 477(4) was accounted for fragment F\(_2\) obtained from the molecular ion after the loss of C\(_2\)HN\(_2\)OS. The fragment F\(_3\) exhibited a peak at m/z(%) 209(4) due to the loss of OC\(_2\)H\(_5\) and C\(_6\)H\(_6\)N\(_7\)O\(_2\)S\(_2\) from the molecular ion. The peak at m/z(%) 102(22) was attributed to the fragment F\(_4\) secured by the loss of C\(_{23}\)H\(_{20}\)N\(_6\)O\(_4\)S from the molecular ion [Scheme-40].
In another investigation, 5-methoxy-2-methylindole 306a was reacted with bromine in acetic acid to produce 1-ethoxycarbonylmethyl-3-ethoxycarbonyl-5-methoxy-6-bromo-2-methylindole 395a. This 6-bromo-2-methylindole 395a was reacted with N-bromosuccinimide in refluxing carbon tetrachloride in presence of dibenzoyl peroxide to secure the desired 1-ethoxycarbonylmethyl-3-ethoxycarbonyl-5-methoxy-6-bromo-2-bromomethylindole 395a. When this bromomethylindole 396a was reacted with sodium azide in acetone at room temperature produced the required 1-ethoxycarbonylmethyl-3-ethoxycarbonyl-5-methoxy-6-bromo-2-azidomethylindole 397a. This 2-azidomethylindole 397a was subjected to 1,3-dipolar cycloaddition reaction with dimethylacetylene dicarboxylate in refluxing acetone to get the desired 1-ethoxycarbonylmethyl-3-ethoxycarbonyl-5-methoxy-6-bromo-2-[4,5-dimethoxycarbonyl-1,2,3-triazol-1-yl]methylindole 398a [Scheme-41].
Scheme-41

306 a-b

\[ \text{Br}_2/\text{AcOH} \]

395 a- b

\[ \Delta \]

397 a-b

\[ \text{NaN}_3/\text{Acetone} \]

396 a-b

\[ \text{DMAD} \]

acetone

398 a-b

\[ R \]

\[ a - \text{CH}_2\text{COOC}_2\text{H}_5 \]

\[ b - \text{C}_4\text{H}_4^- \]
5-Methoxyindole 306a was reacted with bromine in acetic acid to secure 1-ethoxycarbonylmethyl-3-ethoxycarbonyl-5-methoxy-6-bromo-2-methyl-indole 395a. IR spectrum of this sample 395a (Fig. 171) displayed strong stretching bands at 1722 cm\(^{-1}\) and 1683 cm\(^{-1}\) due to 1-ester and C3-ester carbonyls respectively. \(^1\)H NMR spectrum 395a (Fig. 172) showed two triplets (J=7.1 Hz) at 1.29 \(\delta\) and 1.46 \(\delta\) due to 1-ester methyl and C3-ester methyl protons respectively. Two singlets at 2.71 \(\delta\) and 3.97 \(\delta\) were attributed to C2-methyl and C3-methoxy protons. Two quartets (J=7.1 Hz) at 4.28 \(\delta\) and 4.40 \(\delta\) were ascribed to 1-ester methylene and C3-ester methylene protons. Singlet at 4.77 \(\delta\) was due to NCH2 protons. Two singlets at 7.40 \(\delta\) and 7.73 \(\delta\) belonged to C7 and C4-protons.

6-Bromo-2-methyl indole derivative 395a was further reacted with N-bromosuccinimide in refluxing carbon tetrachloride in presence of dibenzoyl peroxide to secure 1-ethoxycarbonylmethyl-3-ethoxycarbonyl-5-methoxy-6-bromo-2-bromomethylindole 396a. IR spectrum of 396a (Fig. 173) displayed strong stretching bands at 1742 cm\(^{-1}\) and 1705 cm\(^{-1}\) due to the 1-ester and C3-ester carbonyls respectively. \(^1\)H NMR spectrum of 396a (Fig. 174) displayed triplets (J=7.1 Hz) at 1.28 \(\delta\) and 1.49 \(\delta\) due to 1-ester methyl and C3-ester methyl protons respectively. Singlet at 3.97 \(\delta\) was accounted for C5-methoxy protons. Two quartets (J=7.1 Hz) at 4.28 \(\delta\) and 4.45 \(\delta\) were attributed to 1-ester methylene and C3-ester methylene protons respectively. Two singlets at 4.49 \(\delta\) and 4.97 \(\delta\) were assigned to NCH2 and CH2-Br protons. Two singlets at 7.47 \(\delta\) and 7.73 \(\delta\) corresponded to C7 and C4-protons respectively.

2-Bromomethylyndole 396a was further reacted with sodium azide in acetone to secure the desired 1-ethoxycarbonylmethyl-3-ethoxycarbonyl-5-methoxy-6-bromo-2-azidomethylindole 397a. IR spectrum of 397a (Fig. 175) displayed strong stretching band at 2112 cm\(^{-1}\) related to N3. Strong stretching bands at 1741 cm\(^{-1}\) and 1703 cm\(^{-1}\) were attributed to the 1-ester and C3-ester...
carbonyls respectively. $^1H$ NMR spectrum 397a (Fig. 176) exhibited two triplets ($J = 7.1$ Hz) at 1.28 $\delta$ and 1.48 $\delta$ due to 1-ester methyl and C3-ester methyl protons respectively. Singlet at 3.98 $\delta$ belonged to C5-methoxy protons. Two quartets $(J=7.1$ Hz) at 4.26 $\delta$ and 4.44 $\delta$ were attributed to 1-ester methylene and C3-ester methylene protons. Two singlets at 4.87 $\delta$ and 4.91 $\delta$ were accounted for CH2-N3 and N-CH2 protons respectively. Two singlets at 7.47 $\delta$ and 7.53 $\delta$ were due to C6- and C4-protons.

2-Azidomethylindole 397a was further reacted with dimethylacetylene dicarboxylate in refluxing acetone to yield 1-ethoxycarbonylmethyl-3-ethoxycarbonyl-5-methoxy-6-bromo-2-(4,5-dimethoxycarbonyl-1,2,3-triazol-1-yl)methylindole 398a. IR spectrum of 398a (Fig. 177) displayed strong stretching bands at 1739 cm$^{-1}$ and 1697 cm$^{-1}$ due to 1-ester, triazole ester and C3-ester carbonyls respectively. $^1H$ NMR spectrum of 398a (Fig. 178) displayed two triplets $(J = 7.1$ Hz) at 1.30 $\delta$ and 1.44 $\delta$ due to 1-ester methyl and C3-ester methyl protons respectively. Singlets at 3.95 $\delta$ and 4.00 $\delta$ corresponded to C5-methoxy and triazole ester methyl protons. Two quartets $(J=7.1$ Hz) at 4.23 $\delta$ and 4.40 $\delta$ belonged to 1-ester methylene and C3-ester methylene protons respectively. Two singlets at 5.14 $\delta$ and 6.30 $\delta$ were accounted for N-CH2 and triazolyl N-CH2 respectively. Two singlets at 7.51 $\delta$ and 7.66 $\delta$ were attributed to C7- and C4-protons respectively.
Fig. 125: IR Spectrum

Fig. 126: $^1$H NMR Spectrum
CDCl$_3$
Fig. 127: IR Spectrum

Fig. 128: $^1$H NMR Spectrum

CDCl$_3$
Fig. 129: IR Spectrum

Fig. 130: $^1$H NMR Spectrum

CDCl$_3$
Fig. 131: IR Spectrum

Fig. 132: $^1$H NMR Spectrum
CDCl$_3$
Fig. 133: $^{13}$C NMR Spectrum

CDCl$_3$
Fig. 134: FAB Mass Spectrum
Fig. 135: IR Spectrum

Fig. 136: ^1H NMR Spectrum

CDCl₃
Fig. 137: FAB Mass Spectrum

MASS SPECTRUM

Sample: IPP DR MG BHAVI DHARWAD #5456
RT 0'12" FAB(POS.) GC 1.4c BP: m/z 154.0000 Int. 24.0581 LV 0.00
Scan# (2 to 3)
Fig. 138: IR Spectrum

Fig. 139: $^1$H NMR Spectrum
CDCl$_3$
Fig. 143: $^{13}$C NMR Spectrum

CDCl$_3$

$^{13}$C NMR Spectrum

CDCl$_3$

$^{13}$C NMR Spectrum

CDCl$_3$

$^{13}$C NMR Spectrum

CDCl$_3$

$^{13}$C NMR Spectrum

CDCl$_3$

$^{13}$C NMR Spectrum

CDCl$_3$

$^{13}$C NMR Spectrum

CDCl$_3$

$^{13}$C NMR Spectrum

CDCl$_3$

$^{13}$C NMR Spectrum

CDCl$_3$
Fig. 144: IR Spectrum

Fig. 145: $^1$H NMR Spectrum
DMSO-d$_6$

On D$_2$O exchange
Fig. 146: FAB Mass Spectrum

MASS SPECTRUM Data File: 3EIN10AB
Sample: ICAR MR MG BHUVI, DHARWAD #5642
RT 0'00" FAB(POS.) GC 1.4c BP: m/z 138.0000 Int. 65.7852 LV 0.00
Scan# (1 to 2)
**Fig. 147: IR Spectrum**

**Fig. 148: $^1$H NMR Spectrum**

On D$_2$O exchange

```
ppm   12  10  8   6   4   2
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Fig. 149: IR Spectrum

Fig. 150: $^1$H NMR Spectrum

DMSO-$d_6$

On D$_2$O exchange

On D$_2$O exchange
Fig. 155: IR Spectrum

Fig. 156: $^1$H NMR Spectrum

$\text{CDCl}_3$
Fig. 157: IR Spectrum

Fig. 158: $^1$H NMR Spectrum
CDCl$_3$

**Fig. 158: $^1$H NMR Spectrum**

**CDCl$_3$**
Fig. 159: $^{13}$C NMR Spectrum

CDCl$_3$
Fig. 162: IR Spectrum

![IR Spectrum Image]

H₂NHNOC → CONNH₂

Fig. 163: ¹H NMR Spectrum

CDCl₃ + DMSO-d₆

![NMR Spectrum Image]

On D₂O exchange

H₂NHNOC → CONNH₂
Fig. 165: IR Spectrum

Fig. 166: $^1$H NMR Spectrum
DMSO-$d_6$

On D$_2$O exchange
Fig. 168: FAB Mass Spectrum

MASS SPECTRUM

Sample: BP MR MG BHOOI, DHARWAD #SE42
RT 0'24" FAB(POS.) GC 1.4e BP: m/z 154.0000 Int. 42.8504 UV 0.00
Scan# (3 to 4)
Fig. 169: IR Spectrum

Fig. 170: FAB Mass Spectrum
Fig. 171: IR Spectrum

Fig. 172: $^1$H NMR Spectrum
CDCl$_3$
Fig. 173: IR Spectrum

Fig. 174: $^1$H NMR Spectrum

CDCl$_3$
Fig. 175: IR Spectrum

Fig. 176: $^1$H NMR Spectrum
CDCl$_3$
Experimental
1-[2-Hydroxyethyl]-3-ethoxycarbonyl-5-methoxy-2-methylindole : 371

To the solution of 5-hydroxyindole 283 (3g, 0.011 mol) in dry acetone (25 mL) were added methyl iodide (3.18 g, 0.022 mol) and anhydrous potassium carbonate (2g) and potassium iodide (0.1g). The mixture was heated at reflux for 40 hours and filtered hot. The solvent was removed under reduced pressure and residue was recrystallised from ethanol as brown granules, m.p. 101-2°C (lit. 103°C), yield : 2.5g, 79%.

Anal. Calcd for C_{15}H_{19}N_{0.4}: C, 64.97; H, 6.90; N, 5.05. Found : C, 64.82; H, 6.78; N, 5.14.

1-[2-Mesylethyl]-3-ethoxycarbonyl-5-methoxy-2-methylindole : 372

To the ice cold solution of methanesulphonyl chloride (1.23g, 0.0108 mol) in pyridine (50 mL) was added 5-methoxylindole 371 (1.5 g, 0.0054 mol) in small portions. This solution was stirred at room temperature for 12 hours, poured into ice (50 g). The separated solid was filtered, washed with water and recrystallised from ethanol as brown granules, m.p. 166-7°C, yield : 1.2g, 76%.

Anal. Calcd for C_{16}H_{2i}N_{0.6}S: C, 54.07; H, 5.90; N, 3.94. Found : C, 54.14; H, 5.82; N, 3.88.

1-[2-Azidoethyl]-3-ethoxycarbonyl-5-methoxy-2-methylindole : 373

To the solution of mesylate 372 (1.8g, 0.005 mol) in dimethylformamide was added sodium azide (0.33g, 0.005 mol) in water. The mixture was refluxed for 6 hours and poured into ice water. The solid separated was filtered, dried and recrystallised from ethanol as brown granules, m.p. 182-3°C, yield : 1.3g, 89%.

Anal Calcd for C_{13}H_{18}N_{4}O_{3}: C, 62.49; C, 6.29; N, 14.57. Found : C, 62.56; H, 6.36; N, 14.32.
1-[4,5-dimethoxycarbonyl-1,2,3-triazol-1-yl]ethyl-3-ethoxycarbonyl-5-methoxy-2-methylindole : 374

To the solution of azidoindole 373 (0.3g, 0.001mol) in dry acetone (25 mL) was added dimethylacetylene dicarboxylate (0.15g, 0.001 mol) and the mixture was heated at reflux for 6 hours. The solvent was removed under reduced pressure and residue was recrystallised from ethanol as colourless prisms, m.p. 211-2° C yield : 0.32g, 69.5%.

Anal. Calcd for C_{21}H_{24}N_{4}O_{7} : C, 56.75; H, 5.44; N, 12.61. Found C, 56.84; H, 5.56; N, 12.43.

1-[4-ethoxycarbonyl-5-phenyl-1,2,3-triazol-1-yl]ethyl-3-ethoxycarbonyl-5-methoxy-2-methylindole : 375

To the solution of azidoindole 373 (0.3g, 0.001mol) in dry acetone (25 mL) was added ethyl propiolate (0.098g, 0.001 mol) and the mixture was heated at reflux for 8 hours. The solvent was removed under reduced pressure and the residue was recrystallised from ethanol as pale yellow granules, m.p. 220-1° C yield : 0.3g, 72%.


1-[4-ethoxycarbonyl-5-phenyl-1,2,3-triazol-1-yl]ethyl-3-ethoxycarbonyl-5-methoxy-2-methylindole : 377 and 1-[4-phenyl-5-ethoxycarbonyl-1,2,3-triazol-1-yl]ethyl-3-ethoxycarbonyl-5-methoxy-2-methylindole : 378

To the solution of azidoindole 373 (0.4g, 0.0014mol) in dry acetone (25 mL) was added ethyl phenyl propiolate (0.24g, 0.0014 mol). The mixture was refluxed for 12 hours. Evaporation of solvent afforded an oil which was chromatographed on silica gel column. Evaporation of the eluates (eluting system (Benzene/ethylacetate 9:1) afforded a solid residue 377 as brown granules, m.p. 189° C yield : 0.31g, 46.9%.
Evaporation of the another eluate (eluting system Benzene/ethylacetate 7:3) afforded a solid residue 378 as brown granules, m.p. 174-5°C yield : 0.22g, 33%.

1-[Bis-4,5-hydrazinocarbonyl-1,2,3-triazol-1-yl]ethyl-3-ethoxycarbonyl-5-methoxy-2-methylindole : 381

A mixture of triazolylindole triester 374 (0.650g, 0.0015 mol) in ethanol (50 mL), hydrazine hydrate (99%) (0.15g, 0.003 mol) and pyridine (2 drops) were heated on boiling water bath for 3 hours and concentrated to half volume and left overnight. The solid separated was filtered, washed with little ethanol and recrystallised from ethanol as white flowery crystals, m.p. 246°C, yield : 0.4g, 61.5%.

1-[4,5-Bis(2,5-dimethylpyrrol-1-yl)aminocarbonyl-1,2,3-triazol-1-yl]ethyl-3-ethoxycarbonyl-5-methoxy-2-methylindole : 382

To the suspension of triazolylindole dicarbohydrazide 381 (0.45g, 0.001 mol) in ethanol (75 mL) was added acetonyl acetone (0.46g, 0.004 mol) and glacial acetic acid (1 mL) and the reaction mixture was concentrated to half of its original volume and poured into crushed ice (50 g). The separated solid was filtered, washed with water, dried and recrystallised from ethanol as pinkish brown granules, m.p. 169°C, yield : 0.5g, 83.3%.

Anal. Calcd for $C_{26}H_{28}N_4O_5$: C, 65.53; H, 5.92; N, 11.76 Found : C, 65.84, H, 5.83; N, 11.91.

Anal. Calcd for $C_{26}H_{28}N_4O_5$: C, 65.53; H, 5.92; N, 11.76. Found : C, 65.46; H, 5.76; N, 11.48.
1-[4,5-Bis(5-mercapto-1,3,4-oxadiazol-2-yl)-1,2,3-triazol-1-yl]ethyl-3-ethoxycarbonyl-5-methoxy-2-methylindole : 383

A mixture of triazolylindole dicarbohydrazide 381 (0.65g, 0.0015 mol) in ethanol (20 mL), potassium hydroxide (0.32g, 0.006 mol) dissolved in water (3 mL) and carbon disulphide (0.68g, 0.009 mol) was heated under reflux until the evolution of H₂S ceased (about 25 hours). The reaction mixture was cooled to room temperature and poured into ice cold water (100 mL). It was then neutralised with dilute hydrochloric acid. The precipitated solid was filtered, washed with water and dried product was recrystallised from ethanol as white granules, m.p. 203-4°C, yield : 0.5g, 64.3%. Anal. Calcd for C₂₁H₂₀N₈O₅S₂ : C, 47.72; H, 3.81; N, 21.19. Found : C, 47.91; H, 3.63; N, 21.34.

1-[2-Hydroxyethyl]-3-ethoxycarbonyl-5-methoxy-2-methylbenz(g)indole : 384

This compound 384 was prepared from 296 (3g, 0.001 mol) according to the procedure depicted for 371 and recrystallised for ethanol as colourless needles, m.p. 146°C, yield : 2.5g, 79.8%. Anal. Calcd for C₁₉H₂₁N₄O₄ : C, 69.71; H, 6.47; N, 4.28. Found : C, 69.92; H, 6.31; N, 4.43.

1-[2-Mesylethyl]-3-ethoxycarbonyl-5-methoxy-2-methylbenz(g)indole : 385

This compound 385 was prepared from 384 (2g, 0.006 mol) according to the procedure given for 372 and recrystallised from ethanol as brown granules, needles, m.p. 165-6°C, yield : 1.8g, 72.9%.

1-[2-Azidoethyl]-3-ethoxycarbonyl-5-methoxy-2-methybenz(g)indole : 386

This compound 386 was prepared as per the procedure given for compound 373 from 385 (1.5g, 0.33 mol) and recrystallised from ethanol as brown needles, m.p. 193-4°C, yield : 1.1g, 84.6%.

Anal. Calcd for C_{19}H_{20}N_{4}O_{3} : C, 64.76; H, 5.72; N, 15.89. Found : C, 64.32; H, 5.86; N, 15.43.

1-[4,5-Dimethoxycarbonyl-1,2,3-triazol-1-yl]ethyl-3-ethoxycarbonyl-5-methoxy-2-methylbenz(g)indole : 387

This compound 387 was prepared from 386 (0.35g, 0.001 mol) according to the procedure given for 374 and recrystallised from ethanol as dark brown prisms, m.p. 129°C, yield : 0.38g, 77.6%.

Anal. Calcd for C_{25}H_{26}N_{5}O_{7} : C, 60.72; H, 5.29; N, 11.33. Found C, 60.86; H, 5.38; N, 11.15.

1-[4-Ethoxycarbonyl-1,2,3-triazol-1-yl]ethyl-3-ethoxycarbonyl-5-methoxybenz(g)indole : 388

This compound 388 was prepared from (0.35g, 0.001 mol) 386 as per the procedure given for compound 375 and recrystallised from ethanol as colourless granules, m.p. 210°C, yield : 0.32g, 72.7%.

Anal. Calcd for C_{24}H_{26}N_{4}O_{5} : C, 63.98; H, 5.81; N, 12.44. Found C, 62.64; H, 5.92; N, 12.12.

1-[Bis-4, 5-hydrazinocarbonyl-1, 2, 3-triazol-1-yl]ethyl-3-ethoxycarbonyl-5-methoxy-2-methylbenz(g)indole : 392

This compound 392 was prepared from 388(0.5g, 0.001 mol) according to the procedure given for the compound 381 and recrystallised from ethanol as colourless flakes, m.p. 234-5°C, yield : 0.35g, 70%.

Anal. Calcd for C_{23}H_{26}N_{8}O_{5} : C, 55.86; H, 5.29; N, 22.66. Found : C, 55.59; H, 5.34; N, 22.52.
1-[4,5-Bis(2,5-dimethylpyrrol-1-yl)aminocarbonyl-1, 2, 3-triazol-1-yl]ethyl-3-ethoxycarbonyl-5-methoxy-2-methylbenz(g)indole : 393

This compound 393 was prepared according to the procedure given for the compound 382 from 392 (0.5g, 0.001 mol) and recrystallised from ethanol-dioxane as pale pinkish garnules, m.p. 192-3°C, yield : 0.48g, 72.9%. 

Anal. Calcd for C_{35}H_{38}N_{8}O_{5} : C, 64.60; H, 5.89; N, 17.22. Found : C, 64.72; H, 5.96; N, 17.13.

1-[4,5-Bis(5-mercapto-1,3,4-oxadiazol-2-yl)-1,2,3-triazol-1-yl]ethyl-3-ethoxycarbonyl-5-methoxy-2-methylindole : 394

This compound 394 was prepared from 392 (0.5g, 0.001 mol) according to the procedure depicted for compound 383 and recrystallised from ethanol-dioxane as dark brown flakes, m.p. 213-4°C, yield : 0.45g, 65.5%. 

Anal. calcd for C_{25}H_{22}N_{8}O_{5}S_{2} : C, 51.89; H, 3.83; N, 19.37. Found : C, 51.72; H, 3.98; N, 19.16.

1-Ethoxycarbonyl-3-ethoxycarbonyl-5-methoxy-6-bromo-2-methylindole :395a

To an efficiently stirred solution of 5-methoxyindole 306a (3.2g, 0.01mol) in glacial acetic acid (80 mL) was added dropwise bromine (3.16g, 0.02 mol) during 20 minutes. The reaction mixture was stirred further at room temperature for 2 hours and then poured into ice(100 g). The separated solid was filtered, washed with water, dried and recrystallised from ethanol as brown granules, m.p. 210°C yield : 3g, 75.4%. 

Anal. Calcd for C_{17}H_{20}NO_{5}Br : C, 51.27; H, 5.06; N, 3.52. Found : C, 51.39; H, 5.23; N, 3.84.

1-Ethoxycarbonyl-3-ethoxycarbonyl-5-methoxy-6-bromo-2-bromomethylindole : 396a

The mixture of indole derivative 395a (4g, 0.01 mol), powdered N-bromosuccinimide (1.79g, 0.01 mol) and dibenzoyl peroxide (0.5g) in CCl_{4} (100 mL) was heated at reflux for 3-5 hours. The succinimide formed
was filtered off and the solvent was removed under reduced pressure. The residue was recrystallised from ethanol as pale yellow granules, m.p. 198°C, yield: 3g, 62.6%.

Anal. Calcd for C\textsubscript{17}H\textsubscript{19}NO\textsubscript{3}Br\textsubscript{2}: C, 42.79; H, 4.01; N, 2.94. Found: C, 42.49; H, 4.23; N, 2.26.

**1-Ethoxycarbonyl-3-ethoxycarbonyl-5-methoxy-6-bromo-2-azidomethylindole \( : 397a \)**

To a stirred solution of 2-bromomethylindole derivative \( 396a \) (2.5g, 0.005 mol) in acetone (50 mL) was added sodium azide (0.32g, 0.005 mol) in water (5 ml). The reaction mixture was further stirred overnight and poured over crushed ice (75 g). The separated solid was filtered and recrystallised from ethanol as brown granules, m.p. 166-7°C yield: 2.3g, 86.9%.

Anal. Calcd for C\textsubscript{17}H\textsubscript{19}N\textsubscript{4}O\textsubscript{2}Br: C, 46.48; H, 4.36; N, 12.75. Found: 46.29; H, 4.63; N, 12.47.

**1-Ethoxycarbonyl-3-ethoxycarbonyl-5-methoxy-6-bromo-2-(4,5-dimethoxycarbonyl-1,2,3-triazol-1-yl)methylindole : 398a**

This compound 398a was prepared according to the procedure given for the compound 374 from 397a (0.4g, 0.0009 mol) and recrystallised from ethanol as dark brown needless, m.p. 183-4°C, yield: 0.36g, 78.2%.

Anal. Calcd for C\textsubscript{17}H\textsubscript{23}N\textsubscript{4}O\textsubscript{3}Br: C, 40.09; H, 4.95; N, 11.00. Found: C, 40.26; H, 4.44; N, 11.32.