1,3-Dipolar cycloaddition reactions: Synthesis and antimicrobial activity of novel 1-triazolylethylindole and 1-triazolylethylbenz[g]indole derivatives

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Indole azide 4 and benz[g]indole azide 12 are reacted separately with dimethyl acetylenedicarboxylate to secure the desired 1-[4,5-dimethoxycarbonyl-1,2,3-triazol-1-yl]ethyl-3-ethoxycarbonyl-5-methoxy-2-methylindole 5 and 1-[4,5-dimethoxycarbonyl-1,2,3-triazol-1-yl]ethyl-3-ethoxycarbonyl-5-methoxy-2-methylbenz[g]indole 13, respectively. The reaction of indole azide 4 and benz[g]indole azide 12 with ethyl propiolate has been found to be regiospecific and produce only the 1-[4-ethoxycarbonyl-1,2,3-triazol-1-yl]ethyl-3-ethoxycarbonyl-5-methoxy-2-methylindole 6 and 1-[4-ethoxycarbonyl-1,2,3-triazol-1-yl]ethyl-3-ethoxycarbonyl-5-methoxy-2-methylbenz[g]indole 14, respectively. Indole azide 4 is also reacted with ethyl phenylpropionate to secure two isomeric products 1-[4-ethoxycarbonyl-5-phenyl-1,2,3-triazol-1-yl]ethyl-3-ethoxycarbonyl-5-methoxy-2-methylindole 8 and 1-[4-phenyl-5-ethoxycarbonyl-1,2,3-triazol-1-yl]ethyl-3-ethoxycarbonyl-5-methoxy-2-methylbenz[g]indole 9. All these newly synthesised compounds are screened for their antimicrobial activities.

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Azides are considered to be very important class of compounds due to their both industrial as well as biological applications. Azide derivatives have been used in rubber vulcanization, polymer cross linking, dyes, tire cored adhesives, foaming of plastics, pharmaceuticals, pesticides and herbicides. Many azides show magnetic properties. The chemistry of azides thus attracted the attention of many chemists since many of these compounds play important role in organic chemistry. One of the more useful synthetic applications of azides is preparation of 1,2,3-triazoles via 1,3-dipolar cycloaddition reactions of azides with substituted acetylenic compounds. 1,2,3-Triazole moiety is a substructure of a number of biologically active compounds. A number of their derivatives found diverse uses in synthetic, analytical, medicinal, pharmaceutical, agrochemical and photographic chemistry and in other applications as corrosion inhibitors, dye stuffs, fluorescent whiteners, asymmetric dihydroxylation catalysts and photosensitizers. 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-triazolindoles. Hence, it was thought of considerable interest to undertake the synthesis of novel triazolindoles via 1,3-dipolar cycloaddition reaction wherein, the bioactive 1,2,3-triazole is linked to position-1 of pharmacologically active indole and benz[g]indole systems.

In the present investigation, 1-hydroxyethyl-5-hydroxyindole 1 and 1-hydroxyethyl-5-hydroxybenz[g]indole 10 were separately reacted with methyl iodide in refluxing dry acetone to get the required 1-[2-hydroxyethyl]-3-ethoxycarbonyl-5-methoxy-2-methylindole 2 and 1-[2-hydroxyethyl]-3-ethoxycarbonyl-5-methoxy-2-methylbenz[g]indole 10. The 5-methoxyindole 2 and 5-methoxybenz[g]indole 11 were further separately reacted with methane sulphonyl chloride in dry pyridine to produce the desired 1-[2-mesylethyl]-3-ethoxycarbonyl-5-methoxy-2-methylindole 3 and 1-[2-mesylethyl]-3-ethoxycarbonyl-5-methoxy-2-methylbenz[g]indole 12. The mesylates 3 and 12 were separately reacted with NaN₃ in refluxing dimethyl formamide to secure new 1-[2-azidoethyl]-3-ethoxycarbonyl-5-methoxy-2-methylindole 4 and 1-[2-azidoethyl]-3-ethoxycarbonyl-5-methoxy-2-methylbenz[g]indole 13, respectively (Scheme 1). These azides 4 and 13 were further separately reacted first time with dimethyl acetylenedicarboxylate in refluxing dry acetone to obtain new 1-[4,5-dimethoxycarbonyl-1,2,3-triazol-1-yl]ethyl-3-ethoxycarbonyl-5-methoxy-
2-methylindole 5 and 1-[4,5-dimethoxycarbonyl-1,2,3-triazol-1-yl]ethyl-3-ethoxycarbonyl-5-methoxy-2-methylbenz[g]indole 14, respectively. Also, these azides 4 and 13 were separately reacted with ethyl propiolate in refluxing dry acetone to get the new 1-[4-ethoxycarbonyl-1,2,3-triazol-1-yl]ethyl-3-ethoxycarbonyl-5-methoxy-2-methylindole 6 and 1-[4-ethoxycarbonyl-1,2,3-triazol-1-yl]ethyl-3-ethoxycarbonyl-5-

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\begin{align*}
\text{Scheme I}
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methoxy-2-methylbenz[g]indole 15, respectively (Scheme I). The reaction of the azides 4 and 13 with ethyl propiolate was found to be regiospecific resulting in the formation of only one isomer 6 and 15, respectively which has been confirmed by TLC and spectral data and this also is in conformity with the earlier report14. Indole azide 4 was also reacted with ethyl phenylpropionate in refluxing dry acetone to yield a mixture of two isomeric products, 1-[4-ethoxycarbonyl-5-phenyl-1,2,3-triazol-1-yl]ethyl-3-ethoxycarbonyl-5-methoxy-2-methylindole 8 and 1-[4-phenyl-5-ethoxycarbonyl-1,2,3-triazol-1-yl]ethyl-3-ethoxycarbonyl-5-methoxy-2-methylindole 9. Compounds 8 and 9 were separated by column chromatography. In the IR spectrum of triazolyl ester carbonyl stretching band of compound 8 was observed at 1734 cm\(^{-1}\), while in compound 9 was found at lower frequency of 1703 cm\(^{-1}\) confirming the presence of ester group in compound 8 adjacent to pyridine type nitrogen while in that of compound 9 adjacent to pyrrole type nitrogen. Further, the \(^1\)H NMR of compound 8 displayed a downfield triplet at \(\delta\) 5.31 due to the protons of methylene attached to triazole carrying phenyl group at position-5 which has exerted deshielding effect on the said methylene protons, while similar methylene protons of compound 9 carrying ester group at position-5 showed peak in the upfield region of \(\delta\) 4.5-4.6. Thus, the structures of isomers 8 and 9 have been confirmed. Triazole 8 was expected to be the major product on the basis of steric consideration. 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 (ref. 15,16). The structures of these newly synthesised compounds were confirmed by their spectral and analytical data.

**Antimicrobial activity**

All the newly synthesised compounds were screened for their antimicrobial activity against Gram-positive bacterium *Micrococcus* and Gram-negative bacterium *Escherichia coli* using Norfloxacin as a standard and for antifungal activity against *Penicillium* and *Aspergillus niger* using Griseofulvin as standard. Cup plate method17,18 was employed using nutrient agar as culture medium. Test solution was prepared by dissolving 1 mg (1000 μg) of compound in 1 mL of DMF and 0.1 mL (100 μg) of this solution was used for testing. The zones of inhibition were measured in mm (12-16 mm, 17-21 mm, 22-30 mm for weak, moderate and highly active zones, respectively). Norfloxacin showed a zone inhibition of 25 mm for *Micrococcus* and 28 mm for *E. coli*. Griseofulvin exhibited a zone of inhibition of 30 mm for both *Penicillium* and *Aspergillus niger*. The screening results revealed that the compound 13 was moderately active towards *Micrococcus* and compounds 4 and 6 were inactive towards both *Micrococcus* and *E. coli*. Rest of the compounds exhibited weak activity towards both *Micrococcus* and *E. coli*. Compounds 5, 12 and 15 have exhibited moderate activity towards both *Penicillium* and *A. niger*, while rest of the compounds displayed weak activity towards both fungi (Table I).

**Experimental Section**

Melting points were determined in open capillary tubes and are uncorrected. IR spectra (cm\(^{-1}\)) were recorded on a Perkin-Elmer 881 and Thermo Nicolet spectrometers; \(^1\)H NMR and \(^13\)C NMR spectra in CDCl\(_3\) or DMSO-d\(_6\) on AMX 400 MHz and Brucker’s 300 MHz NMR spectrometers (chemical shifts in δ, ppm); and FAB mass spectra on a JEOL SX 102/DA-6000 spectrometer/Data system using argon/Xenon (6 KV, 10mA) as the FAB gas. Elemental analysis was carried out on Heraeus CHN rapid analyser.

**Table I** — Antibacterial and antifungal activities of the compounds 2-6, 8,9 and 11-15

<table>
<thead>
<tr>
<th>Compd</th>
<th>Micrococcus</th>
<th>E.coli</th>
<th>Penicillium</th>
<th>A.niger</th>
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<tbody>
<tr>
<td>2</td>
<td>+</td>
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<td>+</td>
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<td>3</td>
<td>+</td>
<td>+</td>
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<td>+</td>
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<td>4</td>
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<td>+</td>
<td>+</td>
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<tr>
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<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
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<tr>
<td>8</td>
<td>+</td>
<td>+</td>
<td>+</td>
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<tr>
<td>9</td>
<td>+</td>
<td>+</td>
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<td>+</td>
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<tr>
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<td>15</td>
<td>+</td>
<td>+</td>
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(-) = inactive, (+) = weakly active(12-16 mm), (+++) = highly active (22-30 mm).
and KI (0.1 g). The mixture was heated at reflux for 40 hr and filtered hot. The solvent was removed under reduced pressure and residue was recrystallised from ethanol, yield 2.5 g (70%), m.p. 101-02°C (lit. m.p. 103°C) (brown granules); IR (KBr): 3399 (alcoholic OH group), 1653 (C3-ester CO); 1H NMR (CDCl3/TMS): δ 1.45 (t, J = 7.1 Hz, 3H, C3-ester CH3), 2.78 (s, 3H, C2-CH3), 3.89-3.99 (m, 5H, C5-OCH3 and CH2-O), 4.26-4.38 (m, 5H, C3-ester CH2, NCH2 and OH). 6.87 (dd, J = 8.5 Hz and 2.5 Hz, 1H, C6-H), 7.27 (d, J = 8.5 Hz, 1H, C7-H), 7.66 (d, J = 2.5 Hz, 1H, C4-H). Anal. Found: C, 64.82; H, 6.78; N, 5.14. Calcd for C15H19NO4: C, 64.97; H, 6.90; N, 5.05%.

1-[2-Mesylethyl]-3-ethoxycarbonyl-5-methoxy-2-methylindole 3. To the indole mesylate (1.23 g, 0.0108 mole) in pyridine (50 mL) was added 5-methoxyindole sulphonyl chloride (1.23 g, 0.0108 mole) in pyridine (50 mL) was added 5-methoxyindole 3 (15 g, 0.0054 mole) in small portions. This solution was stirred at room temperature for 12 hr and poured into crushed ice (50 g). The separated solid was filtered, washed with water and recrystallised from ethanol, yield 1.2 g (76%), m.p. 166-67°C (brown granules); IR (KBr): 1733 (triazole ester CO), 1031, 1004 (C-O and C=O); 1H NMR (CDCl3): δ 11.8 (C3-ester CH3 C), 14.9 (C2-CH3 C), 43.5 (triazole NCH2 C), 48.9 (indole NCH2 C), 53.1 (triazole ester CH3 C), 53.6 (triazole ester CH2 C), 56.0 (OCH3 C), 59.9 (C3-ester CH2 C), 104.5 (C7), 105.4 (C6), 109.3 (C4), 112.6 (C3), 127.9 (junction [b] C), 127.9 (junction [a] C), 140.3 (triazole C' and C'), 144.8 (C2), 156.3 (C5), 158.5 (triazole ester carbonyl C), 160.4 (triazole ester carbonyl C), 166.1 (C3-ester carbonyl C); FABMS (m/z, relative intensity): 444 (M+ 70), 399(100), 391(25), 307(30), 246(6), 187(5), 154(70), 136(50). Anal. Found: C, 56.84; H, 5.56; N, 12.43. Calcd for C15H19NO4: C, 56.75; H, 5.47; N, 12.61%.

1-[2-Azidoethyl]-3-ethoxycarbonyl-5-methoxy-2-methylindole 4. To the indole mesylate 3 (1.8 g, 0.005 mole) in dimethyl formamide (50 mL) was added NaN3 (0.33 g, 0.005 mole) in water (5 mL). The mixture was refluxed for 6 hr and poured into crushed ice (50 g). The separated solid was filtered, dried and recrystallised from ethanol, yield 1.3 g (70%), m.p. 182-83°C (brown granules); IR (KBr): 1733 (C3-ester CO), 1448, 1434, 1059 (asymmetric and symmetric SO2); 1H NMR (CDCl3/TMS): δ 1.49 (t, J = 7.1 Hz, 3H, C3-ester CH3), 2.70 (s, 3H, C2-CH3), 2.80 (s, 3H, SO2CH3), 3.90 (s, 3H, C5-OCH3), 4.38-4.49 (m, 6H, C3-ester CH2 and NCH2-CH2), 6.92 (dd, J = 8.5 Hz and 2.5 Hz, 1H, C6-H), 7.27 (d, J = 8.5 Hz, 1H, C7-H), 7.66 (d, J = 2.5 Hz, 1H, C4-H). Anal. Found: C, 64.97; H, 6.90; N, 5.05%.

1-[4,5-Dimethoxycarbonyl-1,2,3-triazol-1-yl]ethyl-3-ethoxycarbonyl-5-methoxy-2-methylindole 5. To the solution of indole azide 4 (0.3 g, 0.001 mole) in dry acetone (25 mL) was added dimethyl acetylene dicarboxylate (0.15 g, 0.0001 mole) and the mixture was heated at reflux for 1 hr. The solvent was removed under reduced pressure and the residue was recrystallised from ethanol, yield 0.32 g (70%), m.p. 211-12°C (colourless prism). IR (KBr): 1733 (triazole ester CO), 1687 cm-1 (C3-ester CO); 1H NMR (CDCl3/TMS): δ 1.46 (t, J = 7.1 Hz, 3H, C3-ester CH3), 2.52 (s, 3H, C2-CH3), 3.60 (s, 3H, triazole ester CH3), 3.87 (s, 3H, triazole ester CH2), 3.94 (s, 3H, C2-OCH3), 4.35 (q, J = 7.1 Hz, 2H, C3-ester CH2), 4.57 (t, J = 7.1 Hz, 2H, indole NCH2), 5.0 (t, J = 7.1 Hz, 2H, triazole NCH2), 6.86 (dd, J = 8.5 Hz and 2.5 Hz, 1H, C6-H), 6.99 (d, J = 8.5 Hz, 1H, C7-H), 7.63 (d, J = 2.5 Hz, 1H, C4-H); 13C NMR (CDCl3): δ 11.8 (C3-ester CH3 C), 14.9 (C2-CH3 C), 43.5 (triazole NCH2 C), 48.9 (indole NCH2 C), 53.1 (triazole ester CH3 C), 53.6 (triazole ester CH2 C), 56.0 (OCH3 C), 59.9 (C3-ester CH2 C), 104.5 (C7), 105.4 (C6), 109.3 (C4), 112.6 (C3), 127.9 (junction [b] C), 130.9 (junction [a] C), 140.3 (triazole C' and C'), 144.8 (C2), 156.3 (C5), 158.5 (triazole ester carbonyl C), 160.4 (triazole ester carbonyl C), 166.1 (C3-ester carbonyl C); FABMS (m/z, relative intensity): 444 (M+ 70), 399(100), 391(25), 307(30), 246(6), 187(5), 154(70), 136(50). Anal. Found: C, 56.84; H, 5.56; N, 12.43. Calcd for C15H19NO4: C, 56.75; H, 5.47; N, 12.61%.

1-[4-Ethoxycarbonyl-1,2,3-triazol-1-yl]ethyl-3-ethoxycarbonyl-5-methoxy-2-methylindole 6. To the solution of indole azide 4 (0.3 g, 0.001 mole) in dry acetone (25 mL) was added ethyl propiolate (0.098 g, 0.0001 mole) and the mixture was heated at reflux for 18 hr. The solvent was removed under reduced pressure and the residue was recrystallised from ethanol, yield 0.3 g (72%), m.p. 220-21°C (pale yellow granules); IR (KBr): 3399 (alcoholic OH); 3304 (triazole CH), 1733 (triazole ester CO), 1684 cm-1 (C3-ester CO); 1H NMR (CDCl3/TMS): δ 1.37 (t, J = 7.1 Hz, 3H, triazole ester CH3), 1.45 (t, J = 7.1 Hz, 3H, C3-ester CH3), 2.41 (s, 3H, C2-CH3), 3.89 (s, 3H, C5-OCH3), 4.39-4.40 (m, 4H, C3-ester CH2 and triazole ester CH2), 4.66 (t, J = 7.1 Hz, 2H, indole NCH2), 4.78 (t, J = 7.1 Hz, 2H, triazole NCH2), 6.86-7.44 (m, 3H, C6, C7 and C4-H), 7.69 (s, 1H, triazole CH); FABMS (m/z, relative intensity): 400 (M+ 70), 355(100), 327(4), 246(12), 187(6), 154(100). Anal. Found: C, 60.14; H, 6.26; N, 13.63. Calcd for C20H24N6O5: C, 59.99; H, 6.04; N, 13.99%.
1-[4-Ethoxycarbonyl-5-phenyl-1,2,3-triazol-1-yl]-ethyl-3-ethoxy carbonyl-5-methoxy-2-methylindole 8 and 1-[4-phenyl-5-ethoxy carbonyl-1,2,3-triazol-1-yl]ethyl-3-ethoxy carbonyl-5-methoxy-2-methylindole 9. To the solution of indole azide 4 (0.4 g, 0.0014 mole) in dry acetone (25 mL) was added ethyl phenylpropiolate (0.24 g, 0.0014 mole). The mixture was refluxed for 12 hr. Evaporation of solvent afforded an oil which was chromatographed on silica gel column (eluting system benzene-ethyl acetate 9:1). Evaporation of the eluate afforded a solid residue which was recrystallised from ethanol, yield 0.31 g (47%), m.p. 189°C (brown granules); IR (KBr): 3449 (alcoholic OH), 1662 cm⁻¹ (C 3-ester CO); ¹H NMR (CDCl₃ / TMS): δ 1.08 (t, J = 7.1 Hz, 3H, triazole ester CH₃), 1.43 (t, J = 7.1 Hz, 3H, C₃-ester CH₃), 2.64 (s, 3H, C₂-CH₃), 3.84 (s, 3H, C 5- OCH₃), 3.99 (q, J = 7.1 Hz, 2H, triazole ester CH₂), 4.38 (q, J = 7.1 Hz, 2H, C₃-ester CH₂), 4.61 (t, J = 7.1 Hz, 2H, indole NCH₂), 5.31 (t, J = 7.1 Hz, 2H, triazole NCH₂), 6.81 (dd, J = 8.5 Hz and 2.5 Hz, 1H, C₆-H), 6.98 (d, J = 8.5 Hz, 1H, C₇-H), 7.34-7.53 (m, 5H, Ar-H), 7.63 (d, J = 2.5 Hz, 1H, C₄-H); ¹³C NMR (CDCl₃): δ 12.0 (C₃-ester CH₂-C), 13.9 (triazole ester CH₂-C), 14.98 (C₂-CH₃-C), 43.8 (triazole NCH₂-C), 49.2 (indole NCH₂-C), 56.15 (C₂-OCH₃-C), 59.8 (C₃-ester CH₂-C), 62.3 (triazole ester CH₂-C), 104.5 (C₇), 105.2 (C₈), 109.5 (C₉), 112.4 (C₃), 125.5 (C₈), 127.9 (junction[b]C), 128.2 (C₄′ of phenyl), 129.4 (phenyl C₃′ and C₅′), 129.9 (phenyl C₂′ and C₆′), 130.3 (junction[a]), 131.3 (phenyl C′), 145.1 (C₂), 150.6 (triazole C₅′), 156.2 (C₄), 158.9 (triazole ester carbonyl C), 166.2 (C₃-ester carbonyl C). Anal. Found: C, 65.84; H, 5.83; N, 11.91. Calcd for C₂₆H₂₈N₄O₅: C, 65.53; H, 5.92; N, 11.76%.

Evaporation of another eluate (eluting system benzene-ethyl acetate; 7:3) afforded a solid residue of compound 9 which was recrystallised from ethanol, yield 2.5 g (80%), m.p. 146°C (colourless needles); IR (KBr): 3449 (alcoholic OH), 1662 cm⁻¹ (C 3-ester CO); ¹H NMR (CDCl₃ / TMS): δ 1.08 (t, J = 7.1 Hz, 3H, triazole ester CH₃), 1.44 (t, J = 7.1 Hz, 3H, C₃-ester CH₃), 2.62 (s, 3H, C₂-CH₃), 3.84 (s, 3H, C 5- OCH₃), 4.38 (q, J = 7.1 Hz, 2H, triazole ester CH₂), 4.70 (t, J = 7.1 Hz, 2H, C₃-ester CH₂), 4.74 (t, J = 7.1 Hz, 3H, C 3-ester CH₃), 4.81 (t, J = 8.5 Hz, 1H, CH₂-SO₂-), 7.46-7.64 (m, 2H, C₇ and C₈-H), 7.73 (s, 1H, C₄-H), 8.16 (d, J = 8.5 Hz, 1H, C₇-H), 8.42 (d, J = 8.5 Hz, 1H, C₉-H). Anal. Found: C, 69.92; H, 6.31; N, 4.43. Calcd for C₁₉H₂₃NO₄: C, 69.71; H, 6.47; N, 4.28%.

1-[2-Hydroxyethyl]-3-ethoxy carbonyl-5-methoxy-2-methylbenz[g]indole 11. Compound 11 was prepared according to the procedure depicted for 2 and recrystallised from ethanol, yield 2.5 g (80%), m.p. 165-66°C (brown granules); IR (KBr): 1537, 1171 cm⁻¹ (asymmetric and symmetric SO₂); ¹H NMR (CDCl₃/TMS): δ 1.50 (t, J = 7.1 Hz, 3H, C₃-ester CH₃), 2.72 (s, 3H, C₂-CH₃), 2.88 (s, 3H, SO₂CH₃), 4.08 (s, 3H, C₂-OCH₃), 4.46 (q, J = 7.1 Hz, 2H, C₃-ester CH₂), 4.66 (t, J = 7.1 Hz, 2H, NCH₂), 4.94(t, J=7.1Hz,2H,CH₂-SO₂-),7.46-7.64(m,2H,C₇ and C₈-H), 7.81 (s, 1H, C₄-H), 8.13 (d, J = 8.5 Hz, 1H, C₉-H), 8.47 (d, J = 8.5 Hz, 1H, C₇-H). Anal. Found: C, 59.38; H, 5.36; N, 3.32. Calcd for C₁₉H₂₃NO₄: C, 59.25; H, 5.72; N, 3.45%.

1-[2-Mesylethyl]-3-ethoxy carbonyl-5-methoxy-2-methylbenz[g]indole 12. Compound 12 was prepared from 11 (2g, 0.006 mole) according to the procedure given for 3 and recrystallised from ethanol, yield 1.8 g (73%), m.p. 165-66°C (brown granules); IR (KBr): (alcoholic OH absent), 1663 (C₃-ester CO), 1357, 1171 cm⁻¹ (asymmetric and symmetric SO₂); ¹H NMR (CDCl₃/TMS): δ 1.50 (t, J = 7.1 Hz, 3H, C₃-ester CH₃), 2.72 (s, 3H, C₂-CH₃), 2.88 (s, 3H, SO₂CH₃), 4.08 (s, 3H, C₂-OCH₃), 4.46 (q, J = 7.1 Hz, 2H, C₃-ester CH₂), 4.66 (t, J = 7.1 Hz, 2H, NCH₂), 4.94(t, J=7.1Hz,2H,CH₂-SO₂-),7.46-7.64(m,2H,C₇ and C₈-H), 7.81 (s, 1H, C₄-H), 8.13 (d, J = 8.5 Hz, 1H, C₉-H), 8.47 (d, J = 8.5 Hz, 1H, C₇-H). Anal. Found: C, 59.38; H, 5.36; N, 3.32. Calcd for C₂₀H₂₃NO₄S: C, 59.25; H, 5.72; N, 3.45%.

1-[2-Azidoethyl]-3-ethoxy carbonyl-5-methoxy-2-methylbenz[g]indole 13. Compound 13 was prepared from 12 (1.5g, 0.33 mole) as per the procedure given for the compound 4 and recrystallised from ethanol, yield 1.1g (85%), m.p.193-94°C (brown needles); IR(KBr): 2103(N₃) and 1689 cm⁻¹ (C 3-ester CO); ¹H NMR (CDCl₃/TMS): δ 1.51(t, J=7.1Hz,3H,C₃-ester CH₃),2.89(s,3H,C₂-CH₃),3.85(t,J=7.1Hz,CH₂- N₃),4.09(s,3H,C₃-OCH₃),4.46(q,J=7.1Hz,2H,C₃-ester CH₂),4.74(t,J=7.1Hz,2H,NCH₂),7.46-7.64(m,2H,C₇ and C₈-H), 7.83 (s, 1H, C₉-H), 8.14
(d, J=8.5 Hz, 1H, C_6-H) and 8.48 (d, J=8.5 Hz, 1H, C_7-H). Anal. Found: C, 63.82; H, 5.86; N, 15.43. Calcd for C_{18}H_{20}N_{4}O_{3}: C, 64.76, H, 5.72; N, 15.89%.

1-[4,5-Dimethoxycarbonyl-1,2,3-triazol-1-yl]ethyl-3-ethoxycarbonyl-5-methoxy-2-methylbenz[g]indole 14. Compound 14 was prepared from 13 (0.35g, 0.001 mole) according to the procedure given for the compound 5 and recrystallised from ethanol, yield 0.38g (78%), m.p. 129°C (dark brown prism); IR(KBr): 1739 (triazole ester CO), 1681 cm^{-1} (C_3-ester CO); \( ^{1}H\) NMR (CDCl_3 + DMSO-d_6): \( \delta \) 1.46 (t, \( J=7.1 \) Hz, 3H, C_3-ester CH_3), 1.40 (t, \( J=7.1 \) Hz, 3H, C_7-ester CH_3), 2.50 (s, 3H, C_2-CH_3), 7.46-7.66 (m, 2H, C_7 and C_8-H), 7.50 (d, \( J=8.5 \) Hz, 1H, C_9-H), 8.46 (s, 1H, triazole CH). Anal. Found: C, 62.64; H, 5.92; N, 12.12. Calcd for C_{27}H_{26}N_{4}O_{7}: C, 60.72; H, 5.38; N, 11.15.

1-[4-ethoxycarbonyl-1,2,3-triazol-1-yl]ethyl-3-ethoxycarbonyl-5-methoxy-2-methylbenz[g]indole 15. Compound 15 was prepared from 13 (0.35g, 0.001 mole) as per the procedure given for the compound 6 and recrystallised from ethanol, yield 0.32g (73%), m.p. 210°C (colourless granules); IR(KBr): 3105, 1727 (triazole ester CO), 1686 cm^{-1} (C_3-ester CO); \( ^{1}H\) NMR (CDCl_3 + DMSO-d_6): \( \delta \) 1.27 (t, \( J=7.1 \) Hz, 3H, triazole ester CH_2), 1.40 (t, \( J=7.1 \) Hz, 3H, C_7-ester CH_2), 2.50 (s, 3H, C_2-CH_3), 4.01 (s, 3H, C_5-OCH_3), 4.27 (q, \( J=7.1 \) Hz, 4H, triazole ester CH_2 and C_7-ester CH_2), 4.97 (t, 2H, indole NCH_2), 5.13 (t, 2H, triazole NCH_2), 7.45-7.66 (m, 2H, C_7 and C_8-H), 7.72 (s, 1H, C_3-H), 8.33 (d, J=8.5 Hz, 1H, C_7-H), 8.46 (s, 1H, triazole CH). Anal. Found: C, 62.74; H, 5.81; N, 12.44%.

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References