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Several new pyrazolino[3',4':5,4]cyclopent[b]indoles 2a-e have been synthesized from the reaction of 2-(4'-methoxy)benzylidene-1-oxo-1H, 8H-2,3-dihydrocyclopent[b]indoles 1a-e with hydrazine hydrate in ethanol in good yield.

Indole is the main constituent unit in many of the alkaloids of the natural origin. Indole and its derivatives are shown to exhibit antitumour1,2, antiinflammatory3, antibacterial4,5, and antifungal6,7 activities. Pyrazolines have also been reported to possess excellent antibacterial8,9, antifungal7,10, and antiviral11 activities. These compounds owe their activities to the heterocyclic ring present in the structure. The structural and biosignificance of indoles as well as pyrazolines has infused interest in us to synthesize some hitherto unknown pyrazolino[3',4':5,4]cyclopent[b]indole derivatives 2a-e utilizing 2-(4'-methoxy)benzylidene-1-oxo-1H, 8H-2,3-dihydrocyclopent[b]indoles12 1a-e as synthons to construct pyrazolinoannelated rings on the cyclopent[b]indole skeleton. The new products have been characterized by C, H, N analysis, IR, 1H NMR and mass spectral studies.

Results and Discussion

Hydrazine hydrate was added to a solution of 2-(4'-methoxy)benzylidene-5-methyl-1-oxo-1H, 8H-2,3-dihydrocyclopent[b]indole 1a in ethanol to yield the compound 2,3,3a,4-tetrahydro-6-methyl-3-(4'-methoxy)phenyl-2H-pyrazolino[3',4':5,4]cyclopent[b]indole 2a in 76% yield (Scheme I). The IR spectra of 2a showed remarkable changes in comparison with that of the parent compound 1a. Amongst them, the following are significant. The band due to C=O disappeared and a new band appeared at 1601 cm⁻¹ attributed to C=N vibrations. In addition, the absorptions due to pyrazolino NH13 and indole NH13 were observed as a broad band centered at 3385 cm⁻¹ (broad band starts from 3350 to 3400). Its 1H NMR spectrum in CDCl₃ showed a three proton singlet at δ 2.44 corresponding to C₆ methyl group. The multiplet observed in the region δ 2.47-3.85 is assigned to C₃a and C₃ protons. The signal due to C₄ methylene protons appeared as a multiplet at δ 3.72-3.78. The resonance due to pyrazolino NH appeared as a broad singlet at δ 4.47-4.51 and that of indole NH was found at δ 8.47 as a singlet. A singlet observed at δ 3.87 and a multiplet appeared in the region δ 6.92-7.58 have been assigned to methoxy and aromatic protons based on their integrations corresponding to three and seven protons, respectively.

The electron impact mass spectrum of the compound 2a showed the molecular ion(M⁺) peak at m/z 317 (68.1%) with several fragment ions at m/z values, 302 due to loss of methyl radical (34%), 316 due to

![Scheme I](image-url)
loss of hydrogen radical (56%), 286 due to loss of methoxy radical ion (20%). The mass spectrum also registered many other fragments along with the base peak at m/z 134 due to formation of protonated aryl nitrile ion (100%). A definite proof for the structure of 2a was derived from its satisfactory microanalytical (C,H,N) data in accordance with the molecular formula C₂₀H₂₁N₃O₅. Based on the above discussion, the compound 2a was identified as 2,3,3a,4-tetrahydro-6-methy 1-3-(4'-methoxy)phenyl-2H-pyrazolino[3'¿4¿5¿4¿cyclopent[b]indoles 2. The compounds 2b-e were synthesized similarly from 2-(4'-methoxy)benzylidene-1-oxo-1H. 8H-2,3-dihydrocyclopent[b]indoles 1b-e. The characterization data of compounds 2a-e are given in Table I.

### Experimental Section

Melting points were determined on mettler FP-5 instrument and are uncorrected. IR spectra of the new compounds have been recorded as KBr pellets on a Perkin-Elmer model 1600 FT-IR instrument in the region 4000-400 cm⁻¹ and ¹H NMR spectra were recorded on a varian AMX-400 instrument using TMS as an internal standard. C, H, N analyses were performed on carlo erba 1108 model elemental C H N analyser. Electron impact mass spectrum was recorded using Jeol(D)-300 EI mass spectrometer.

<table>
<thead>
<tr>
<th>Compd</th>
<th>mp °C</th>
<th>Yield (%)</th>
<th>Mol.formula</th>
<th>Calcd% (Found)</th>
<th>H NMR(CDC1₃) (8,ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>163</td>
<td>88</td>
<td>C₂₀H₂₁N₃O₅ (317)</td>
<td>75.68 06.03 13.24</td>
<td>2.44(s, 3H, Cα-CH₃), 2.47-3.85(m, 2H, C₁-H, Cα-H), 3.87(s, 3H, OCH₃), 3.72-3.78(m, 2H, C₇-H), 4.57-4.51(br s, 1H, pyrazolino NH), 6.92-6.95(d, 2H, C₁'-H, and C₇'-H J₆₇=8.56 Hz), 7.02-7.37(m, 3H, C₁-H,C₇-H and C₇'-H) 7.50-7.58(d, 2H, C₁'-H and C₇'-H J₆₇=8.56 Hz), 8.47 (br s, 1H, indole NH)</td>
</tr>
<tr>
<td>2b</td>
<td>170</td>
<td>83</td>
<td>C₂₀H₂₁N₃O₅ (317)</td>
<td>75.68 06.03 13.24</td>
<td>2.46(s, 3H, Cα-CH₃), 2.54-2.68(m, 2H, C₁-H, Cα-H), 3.83(s, 3H, OCH₃), 3.60-3.87(m, 2H, C₇-H), 4.56(br s, 1H, pyrazolino NH), 6.87-7.60(m, 7H, C₁-H, C₇-H, C₁'-H, C₇'-H, C₁'-H, C₇'-H, and C₇'-H), 8.49(s, 1H, indole NH)</td>
</tr>
<tr>
<td>2c</td>
<td>165</td>
<td>85</td>
<td>C₂₀H₂₁N₃O₅ (317)</td>
<td>75.68 06.03 13.24</td>
<td>2.46(s, 3H, Cα-CH₃), 2.49-2.55(m, 2H, C₁-H, Cα-H), 3.79(s, 3H, OCH₃), 3.80-3.86(m, 2H, C₇-H), 4.09(br s, 1H, pyrazolino NH), 6.87-7.61(m, 7H, C₁-H, C₇-H, C₁'-H, C₇'-H, C₁'-H, C₇'-H, and C₇'-H), 8.46(s, 1H, indole NH)</td>
</tr>
<tr>
<td>2d</td>
<td>160s</td>
<td>85</td>
<td>C₁₈H₂₁N₃O₅ (303)</td>
<td>75.23 05.65 13.85</td>
<td>2.17-2.52(m, 2H, C₁-H and C₇-H), 3.85(s, 3H, OCH₃), 3.86-3.90(m, 2H, C₇-H), 4.56-4.59(br s, 1H, pyrazolino NH), 6.85-7.61(m, 7H, C₁-H, C₇-H, C₁'-H, C₇'-H, C₁'-H, C₇'-H, and C₇'-H), 8.99(s, 1H, indole NH)</td>
</tr>
<tr>
<td>2e</td>
<td>181</td>
<td>91</td>
<td>C₁₉H₁₆N₁OCl (337)</td>
<td>67.56 04.77 12.44</td>
<td>2.11-2.32(m, 2H, C₁-H and C₇-H), 3.61-3.78(m, 2H, C₇-H), 3.79(s, 3H, OCH₃), 4.56-4.57(br s, 1H, pyrazolino NH), 6.84-7.37(m, 7H, C₁-H, C₇-H, C₁'-H, C₇'-H, C₁'-H, C₇'-H, and C₇'-H), 8.49(s, 1H, indole NH)</td>
</tr>
</tbody>
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References

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