Microwave assisted synthesis of 1-(6,8-dimethyl coumarin-4-yl)-2-(chroman-3-yl) ethenes under solvent free conditions

M.T. Bachute¹*, C.H. Gill², B.K. Karale³, R.T. Bachute⁴
¹P.G. Dept of Chem, KBP Mahavidyalaya, Pandharapur (MS), (INDIA)
²School of Chemical Sciences, Dr. BAMU, Aurangabad (MS), (INDIA)
³P.G. Dept. of Chemistry, Radhabai Kale Mahila Mahavidyalaya, Ahmednagar, (INDIA)
⁴IPCA, Laboratories, Ratlam (MP), (INDIA)
E-mail: mbachute@gmail.com; chgill50@yahoo.com; bkkarale@gmail.com

KEYWORDS
Chromones; Coumarins; Microwave assisted; Solvent free; Knoevangel condensation.

INTRODUCTION
Owing to the widespread applications of chromones[1-13] and coumarins[14-23], it was thought worthwhile to synthesize heterocyclic compounds containing combination of chromone and coumarin moieties, which would result in added potential.

Among the important tools, the use of microwave radiations[24], as the source of energy for chemical reactions, is an eco-friendly alternative to traditional heating. This results in reduction in time, increase in yield and thus eco-friendly.

A reaction under solvent free conditions is an added factor to minimize the pollution. Literature survey revealed that until now 1-(6,8-dimethylcoumarin-4-yl)-2-(chroman-3-yl)ethenes (3) have not been synthesized using MW assistance and solvent free conditions. Condensation reactions of active methylene compounds with 3-formyl chromones are well known[25]. Karale[26] synthesized such compounds by conventional method.

In the present investigation 1-[(6,8-dimethylcoumarin-4-yl)-2-(chroman-3-yl)]ethenes (3) have been synthesized by MW assisted Knoevangel condensation of variously substituted 3-formyl chromones (1) with 1-(6,8-dimethyl coumarin-3-yl)-4-acetic acid (2) in the presence of potassium carbonate under solvent free conditions as shown in the Scheme 1. The yields of the products obtained are better than...
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those obtained by conventional method\(^2\text{[26]}\). The time required for completion of reaction is also less than the conventional method\(^2\text{[26]}\). The IR, NMR and mass spectra of only representative compounds were scanned. The elemental analysis of all compounds is in good agreement with the molecular formulae.

Antimicrobial activity

The new compounds 3a-3j obtained were scanned for their antimicrobial activity against E.Coli and S. Albus bacteria using streptomycin sulphate as the standard reference. All the compounds showed moderate to good antibacterial activity against both bacteria.

EXPERIMENTAL

3-Formyl chromones and coumarin-4-acetic acid derivatives were synthesised using known procedure\(^2\text{[26]}\). Melting points were determined in open capillary tubes and are uncorrected. IR spectra were scanned on Perkin-Elmer FT spectrophotometer in KBr disc. \(^1\text{H}\) NMR spectra were scanned on Brucker 300 MHz spectrophotometer using DMSO+CDCl\(_3\) mixture as solvent and TMS as an internal standard. Chemical shifts are expressed in \(\delta\) ppm. Elemental analysis was carried on Perkin-Elmer 2400 microanalyzer. Microwave oven (800watt) of Bajaj (India) was used.

Synthesis of 1-(coumarin-4-yl)-2-(chroman-3-yl)ethenes (3)

A mixture of 3-formylchromone (1) (1mmol), coumarin-4-acetic acid (2) (1mmol) was ground with anhydrous K\(_2\)CO\(_3\) and irradiated with MW at 800W for 8-10 minutes continuously (Temperature of the reaction mixture was not recorded). The yellowish coloured residue was cooled and treated with water, filtered, dried and recrystallised from pyridine. The overall yield is in the range of 60-79%. This typical procedure was used to prepare all the compounds in TABLE 1.

<table>
<thead>
<tr>
<th>Comp</th>
<th>R(_1)</th>
<th>R(_2)</th>
<th>R(_3)</th>
<th>M (\degree)C</th>
<th>Yield %</th>
<th>C %</th>
<th>H %</th>
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<td>3a</td>
<td>H</td>
<td>H</td>
<td>Cl</td>
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<td>73</td>
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<td>H</td>
<td>H</td>
<td>CH(_3)</td>
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<tr>
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<td>CH(_3)</td>
<td>H</td>
<td>CH(_3)</td>
<td>301</td>
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<td>H</td>
<td>H</td>
<td>Br</td>
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<td>52</td>
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<td>H</td>
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<td>76.74 76.75</td>
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<td>CH(_3)</td>
<td>H</td>
<td>278</td>
<td>57</td>
<td>57</td>
<td>77.47 77.98</td>
</tr>
</tbody>
</table>

Discussion of spectra

IR (KBr, 3a) v cm\(^{-1}\): 1692 (C=O of coumarin), 1644 (C=O of chromone), 1602 (C=C group), 1457 (\(\gamma\)-pyrone ring) and 3065 (\(=\text{CH}\) group).

IR (KBr, 3d) v cm\(^{-1}\): 1689 (C=O of coumarin), 1639 (C=O of chromone), 1603 (C=C group), 1458 (\(\gamma\)-pyrone ring) and 3063 (\(=\text{CH}\) group).

There are no bands corresponding to \(-\text{CHO}\) of formylchromone and \(-\text{COOH}\) of coumarin-4-yl acetic acid indicating the condensation, of active methylene group of coumarin-4-acetic acid with aldehyde group of 3-formylchromone, with concomitant decarboxylation of \(-\text{COOH}\).

\(^1\text{H}\)NMR (TMS), (3a) \(\delta\) ppm: 2.41(s, 3H, ArCH\(_3\)), 2.44(s, 3H, ArCH\(_3\)), 7.09(d, 1H (J=15Hz), ethylenic proton), 7.58(d, 1H (J=15Hz), ethylenic proton) and 6.55-8.40 (m, 7H, aromatic protons and C\(_2\)-H of chromone).

\(^1\text{H}\)NMR (TMS), (3d) \(\delta\) ppm: 2.43(s, 3H, ArCH\(_3\)), 2.46(s, 3H, ArCH\(_3\)), 7.11(d, 1H (J=15Hz), ethylenic proton), 7.59(d, 1H (J=15Hz), ethylenic proton) and 6.56-8.44(m, 7H, aromatic protons and C\(_2\)-H of chromone).
chromone). Mass (3a), m/e 378(M+), 349, 224, 196(100%); (3d), m/e 431, 392, 286, 193(100%)

ACKNOWLEDGEMENTS

MTB thanks to the Principal Dr. K. N. Ganage, KBP Mahavidyalaya, Pandharpur for encouragement and providing all necessary facilities.

REFERENCES