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

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ABSTRACT

1-(6, 8-dimethylcoumarin-4-yl)-2-(chroman-3-yl)ethenes **(3)** were prepared by MW assisted Knoevanagel condensation of 3-formyl chromones **(1)** with 1-(6,8-dimethylcoumarin-3-yl)-4-acetic acid **(2)** under solvent free conditions. New compounds were scanned for antimicrobial activities.

KEYWORDS

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

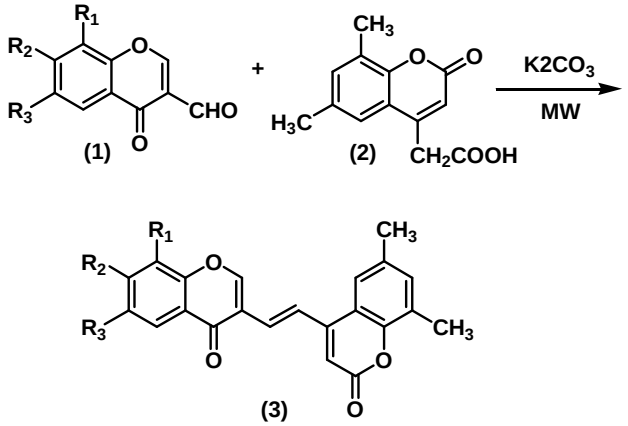
INTRODUCTION

Owing to the widespread applications of chromones[1-13] and coumarins[14-23], it was thought worthwhile to synthesise 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 up till now 1-[(6,8-dimethylcoumarin-4-yl)-2-(chroman-3-yl)]ethenes **(3)** have not been synthesised using MW assistance and solvent free conditions. Condensation reactions of active methylene compounds with 3-formyl chromones are well known[25]. Karale[26] synthesised such compounds by conventional method.

In the present investigation 1-[(6,8-dimethylcoumarin-4-yl)-2-(chroman-3-yl)]ethenes (**3**) have been synthesised 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



Scheme 1

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those obtained by conventional method[26]. The time required for completion of reaction is also less than the conventional method[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[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}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 δ ppm. Elemental analysis was carried on Perkin-Elmer 2400 microanalyser. Microwave oven (800watt) of Bajaj (India) was used.

General procedure

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_2CO_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 1

Comp	R_1	R_2	R_3	M P °C	Yield %		C %		H %	
					M W	Normal	Calc	Found	Calc	Found
3a	H	H	Cl	296	73	60	69.75	69.76	3.95	3.97
3b	H	H	CH_3	254	70	48	77.00	77.08	5.00	5.06
3c	CH_3	H	CH_3	301	71	58	77.57	77.61	5.11	5.16
3d	H	H	Br	291	65	52	62.38	62.43	3.50	3.57
3e	H	CH_3	Cl	322	70	63	70.28	70.32	4.33	4.36
3f	H	CH_3	H	298	60	46	77.00	77.08	5.00	5.06
3g	Cl	H	H	302	65	53	69.71	69.76	3.93	3.99
3h	Cl	H	Cl	318	79	69	63.90	63.94	3.36	3.41
3i	H	H	H	252	62	53	76.74	76.75	4.65	4.68
3j	CH_3	CH_3	H	278	77	57	77.47	77.98	5.37	5.33

Discussion of spectra

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

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

There are no bands corresponding to –CHO of formylchromone and –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 –COOH.

^{1}HNMR (TMS), **(3a)** δppm: 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}HNMR (TMS), **(3d)** δppm: 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).

Mass (**3a),** m/e 378(M^+), 349, 224, 196(100%); (**3d**), m/e 431, 392, 286, 193(100%)

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