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GREEN CHEMISTRY APPROACH FOR SYNTHESIS OF DERIVATIVES OF COUMARIN AND COMPARATIVE STUDY BY FLUORESCENCE SPECTROPHOTOMETER

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ABSTRACT

Even though several methods for coumarin synthesis have been reported. While the majority of their earlier syntheses requires reactant material which is expensive, in some methods high amount of energy is required to complete the reaction, some methods produces by products which are hazarded to environment, some methods are not possible in large industrial scale, while some are having low practical yield. One reaction which overcomes all the above things, the well known Pechmann condensation was used for the preparation of 7-hydroxy coumarin followed by O-allylation in polyethylene glycol 400 which is the one step towards green chemistry approach and then Claisen rearrangement afforded the 8-allyl-7-hydroxy-4-methylcoumarin. Fluorescence is very simple and non destructive technique; it is also very sensitive, selective and specific type of technique. As all coumarin molecules are fluorescent and they show different absorption and emission spectra, they are sensitive in different environment so it is interesting to study the effect of different solvents (ethanol, methanol, CCl_4,hexane) on the six different derivatives of coumarin. It was found that the intensity of peak will increase from non-polar to polar solvent and wavelength decreases.

Key words: Pechamann condensation, Green chemistry, Fluorescence.

INTRODUCTION

Coumarins are easily available in various plants in large quantity, and are biologically active compound used in various cosmetics, medicines and pharmaceutical industries, while those molecules are recreantly used in anti tuberculoses and anti AIDS active drugs. So it is interesting to study this molecule and there derivatives. Coumarins are the active photosensitizing drugs widely used in photomedicine[1] in research of various biologically active macromolecules and on DNA repair[2]. Coumarin are also used in ultraviolet therapy known as photopheresis, has recently been used for the treatment of cutanous T-cell lymphona, Sezary syndrome and related diseases[3-4]. Coumarins are well documented as therapeutic agents and have been used as medicines in ancient Egypt and in aboriginal cultures[5-6]. One example, Warfarin, is

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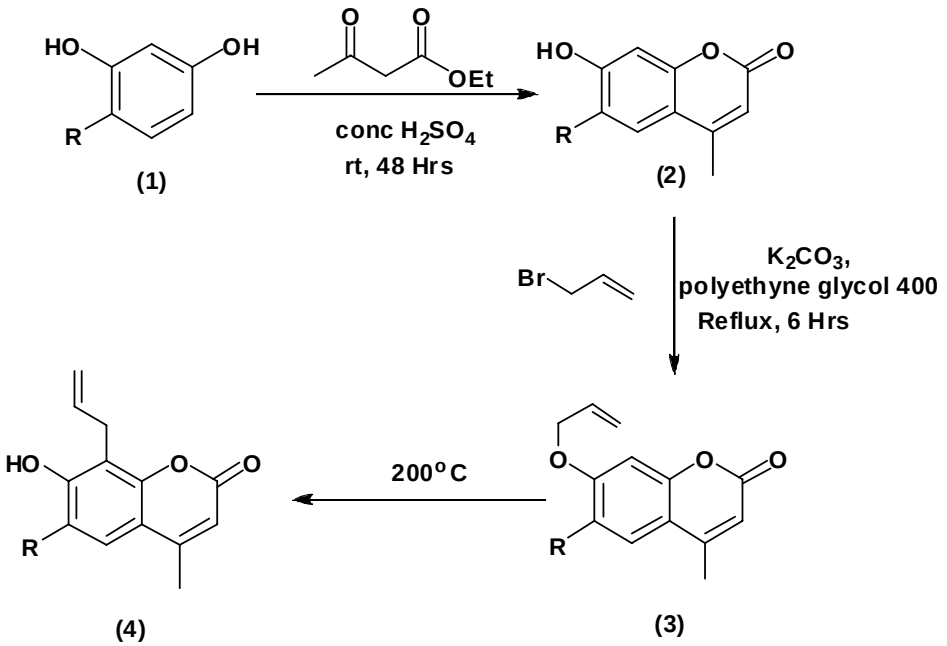
the most prescribed anticoagulant[7-9] on the market. The clinical use of plants containing coumarins for the treatment of skin disease has been known for a long time. The toxic effects and medicinal importance of these plants have been reported over a time span of many years. Coumarins are showing anticoagulant, anti-inflammatory, antimicrobial activity. They also shown antitomoural and CNS active compound.

Recent medicinal research has focused on the use of coumarin derivatives as anti-HIV agents. A recent review by Yu and co-workers described the study of over 150 coumarin derivatives and their efficacy in fighting HIV[10].

EXPERIMENTAL

A valuable method for the synthesis of coumarin is the Pechmann condensation of phenols, using concentrated sulfuric acid as the catalyst. Condensation of resorcinol with ethylacetoacetate yields 4-methyl-7-hydroxy coumarins which are known to give blue fluorescence in UV light.

O-Allylation of 4-methyl-7-hydroxy coumarins with a weak base like K_2CO_3 in polyethylene glycol 400 at 60°C gives an allylated compound which is one step towards green chemistry, Owing to the acidity of the phenolic proton present on 4-methyl-7-hydroxy coumarin, a weak base like K_2CO_3 can also be used for abstracting the proton. This allylated compound when subjected to heat at 200°C undergoes a Claisen rearrangement yielding 8-allyl-7-hydroxycoumarin (**Scheme 1**).

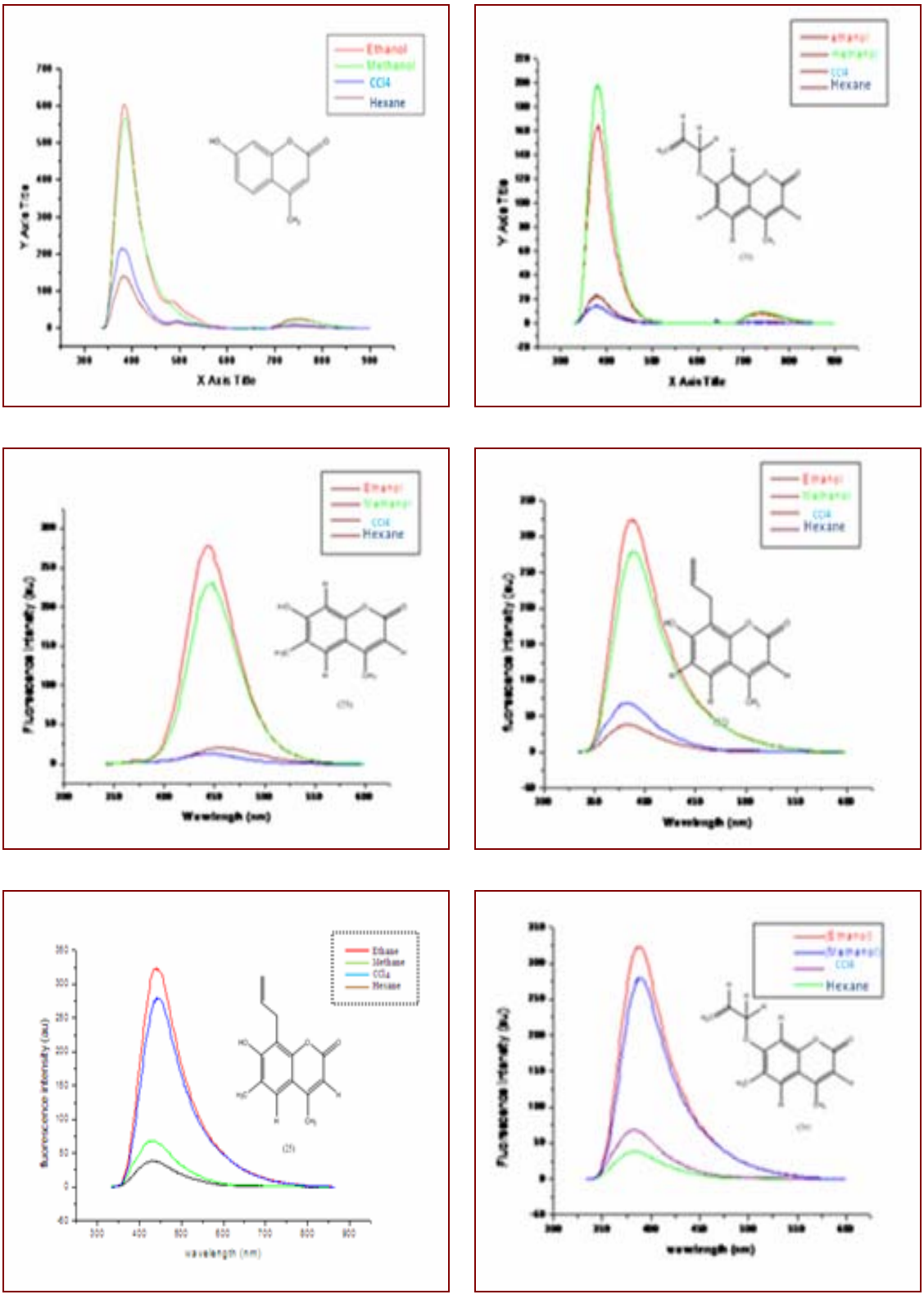


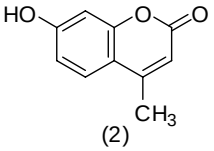
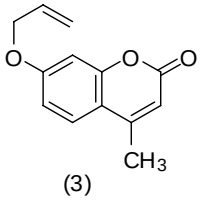
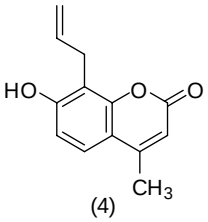
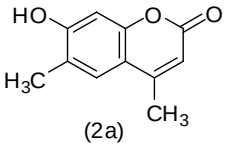
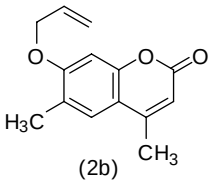
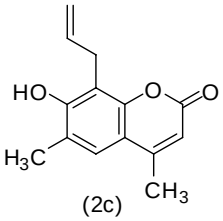
Scheme 1

RESULTS AND DISCUSSION

Pechmann condensation gives coumarin which on O-Allylation yields an allylated coumarins. This allylated compound compounds undergoes a Claisen rearrangement yielding 8-allyl-7-hydroxycoumarin, there are two probable positions for a Claisen to occur (C6 and C8) but only one product was obtained. This reaction is Regiospecific pertaining to the fact that the C8 proton is more acidic than the proton present on C6 carbon.

Solvent study of coumarin derivatives were carried out by taking fluorescence in different solvent like ethanol, methanol, carbontetrachloride, hexane, it was observed that the intensity of the peak will increase and wavelength decreases from non-polar to polar solvent.



R No.	Compound	Parameters	Ethanol	Methanol	CCl_4	Hexane
1	 (2)	Intensity	602.5	570.5	211	138.4
		Wavelength	384	384	379	379
2	 (3)	Intensity	198	164	23	14
		Wavelength	381	379	376	376
3	 (4)	Intensity	322	297	68	39
		Wavelength	376	377	382	382
4	 (2a)	Intensity	277	23	19	12
		Wavelength	442	446	447	454
5	 (2b)	Intensity	199	165	22	14
		Wavelength	430	430	433	438
6	 (2c)	Intensity	322	277	70	38
		Wavelength	439	439	441	441

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