

NOTE

A REVISIT OF PECHMANN REACTION UNDER MICROWAVE RADIATION

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ABSTRACT

A series of coumarins have been prepared by the Pechmann reaction of different phenols with ethyl acetoacetate as well as malic acid using catalytic amount of sulfuric acid under microwave irradiation for few seconds.

Keywords: Pechman reaction, Coumarins, Microwave irradiation

INTRODUCTION

Coumarins and its derivatives exist naturally in grasses, orchids, legumes and citrus fruits. The parent compound is the sweet smelling constitutes of white clover and is present in the Tonkanga beans and in many other plants [1, 2]. Coumarins are responsible for high level of biological activity. These are used commercially as food additives [1,2], in cosmetics [1], as optical brightner [3], dispersed fluorescent, and laser dyes [4].

Coumarins are usually synthesized by several routes including Pechmann [5,6], Perkin [7], Knoevenagel [8], Reformatsky [9] and Wittig reaction [10]. Among these Pechmann reaction is the most widely used method as the reaction involves the use of simple starting materials, which are phenols and β -ketoesters in the presences of acid condensing agents. The various agents are H_2SO_4 , P_2O_5 , $FeCl_3$, $ZnCl_2$, $POCl_3$, $AlCl_3$, PPA, HCl , H_3PO_4 , $F_3CHCOOH$, montmonrillomite and clays [5,11-13].

These methods have sever drawbacks including use of a large amount of catalysts, long reaction time (for some reactions it is several days) and most often temperature above than $150^\circ C$. These methods results in small amount of coumarins and excess of colored dyes which are difficult to remove by crystallization or even by column chromatography.

Recently, coumarins have been synthesized by using microwave irradiation [14-16]. Helavi *et al.* [17] have reported the use of sulfuric acid in quantitative amount for the Pechmann condensation of phenol with malic acid irradiated for four minutes but we carried the reaction of phenol with ethyl aceto acetate as well as malic acid under microwave condition by using smaller amount of sulphuric acid in few seconds and much better yield.

EXPERIMENTAL SECTION

All the chemicals were purchased from market and used as such without further purification. The reactions were carried out in a household microwave oven

(Dawlance DW-162, 1000 W, 2450 MHz). Melting points were noted on Gallonkemp melting point apparatus. 1H NMR was acquired on a Bruker AC-250 (250 MHz) spectrometer. IR spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrometer using KBr discs

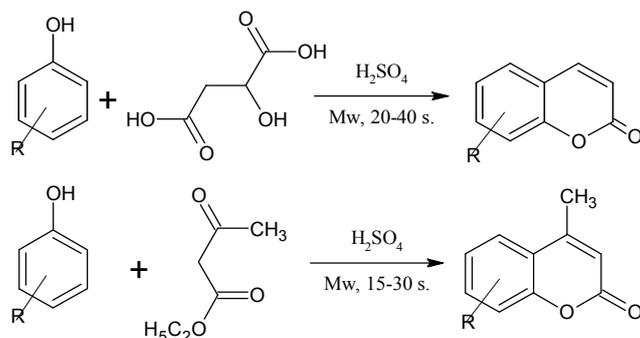
General Procedure

A mixture of a phenol (20 mmol), malic acid or ethyl acetoacetate (20 mmol) and sulfuric acid (few drops) was heated under microwave irradiation for 15-40 seconds. The reaction mixture was cooled to room temperature and treated with chilled water. The precipitate were filtered and recrystallised from appropriate solvents.

RESULT AND DISCUSSION

We have reinvestigated Pechmann reaction (Scheme 1) with a series of phenols and found that only 2-3 drops of sulfuric acid and microwave heating for 15 to 40 seconds are sufficient to produce coumarins in good yields (Table 1).

Different derivatives of phenols were treated with malic acid and ethyl acetoacetate in the presence of catalytic amount of concentrated H_2SO_4 and irradiated with microwave radiations for 15-40 s in open vessel under atmospheric pressure in a household microwave oven. (Scheme 1).



Scheme 1

Table 1. Time required for synthesis of different coumarin derivatives

Phenol	Reagents	Time, (S)	Coumarins	M.p. (°C)	Yield, %
Phenol	Ethyl acetoacetate	30	4-methylcoumarin	83 (83-85) [18]	30
<i>m</i> -Methoxy Phenol	Malic acid	30	7-methoxycoumarin	116 (117-8) [18]	71
<i>m</i> -Methoxy Phenol	Ethyl acetoacetate	15	7-methoxy-4-methylcoumarin	156-157 (156-158) [19]	67
<i>p</i> -cresol	Malic acid	40	6-methylcoumarin	76 (76-78) [18]	60
<i>p</i> -cresol	Ethyl acetoacetate	20	4,6-dimethylcoumarin	151-152 (150) [20]	24
Hydroquinone	Malic acid	20	6-hydroxycoumarin	250 (250) [18]	72
Hydroquinone	Ethyl acetoacetate	30	6-hydroxy-4-methylcoumarin	244 (245) [18]	56
Resorcinol	Malic acid	20	7-hydroxycoumarin	228 (228-230) [18]	64
Resorcinol	Ethyl acetoacetate	20	7-hydroxy-4-methylcoumarin	185 (184-186) [19]	90
Orcinol	Ethyl acetoacetate	20	5-hydroxy-4,7-dimethylcoumarin	248 (248) [18]	88

Table 2. IR and ¹HNMR spectral data of some synthesized coumarins

Products	IR ν_{\max} (KBr/cm ⁻¹)	¹ HNMR (δ)
4-methylcoumarin	1665, 1610, 1445, 1400	(CDCl ₃) 2.62 (s, 3H, CH ₃), 6.48 (s, 1H, 3-H), 7.30-7.65 (m, 4H, 5-H, 6-H, 7-H, 8-H)
7-hydroxy-4-methylcoumarin	3260-3080, 1690	(CDCl ₃) 2.65 (s, 3H, CH ₃), 6.41 (s, 1H, 3-H), 6.90-7.70 (m, 4H, 5-H, 6-H, 7-H, 8-H), 10.21 (s, 1H, OH)
7-methoxy-4-methylcoumarin	1684	(CDCl ₃) 2.59 (s, 3H, CH ₃), 4.21 (s, 3H, OCH ₃), 6.50 (s, 1H, 3-H), 7.00-7.50 (m, 3H, 5-H, 6-H, 8-H)
4,6-Dimethylcoumarin	1685	(CDCl ₃) 2.45 (s, 3H, CH ₃), 2.48 (s, 3H, CH ₃), 6.31 (s, 1H, 3-H), 7.24 (d, J _{7,8} = 8.4, 8-H), 7.44 (dd, J _{7,8} = 8.4, J _{5,7} = 1.8, 7-H), 7.57 (7.24 (d, J _{5,7} = 1.8, 5-H
5-hydroxy-4,7-Dimethylcoumarin	1670	(CDCl ₃) 1.89 (s, 3H, CH ₃), 2.14 (s, 3H, CH ₃), 6.02 (s, 6-H), 6.31 (s, 1H, 3-H), 6.58 (s, 8-H)

The structures of the synthesized coumarins were established by comparing the melting points with those reported in literature (table-I) and their spectral studies (Table 2.). This method gave better yields with less side products unlike conventional method which gives small yields of coumarins.

CONCLUSION

It is concluded that microwave irradiation method is an efficient tool of green chemistry that uses no solvent, short time and less energy consumption. It produces less side products, which reduces pollution hazards

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