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Synthesis of Coumarin Derivatives Using Green Chemistry Approach: A Mini Review

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Abstract:

The present review aims to highlight the current progress achieved in the synthesis of coumarins either linked or fused with diverse bioactive five- and six-membered heterocycles by making the utilization of green chemistry techniques such microwaves irradiation, ultrasound-assisted strategies and solvent free synthesis.

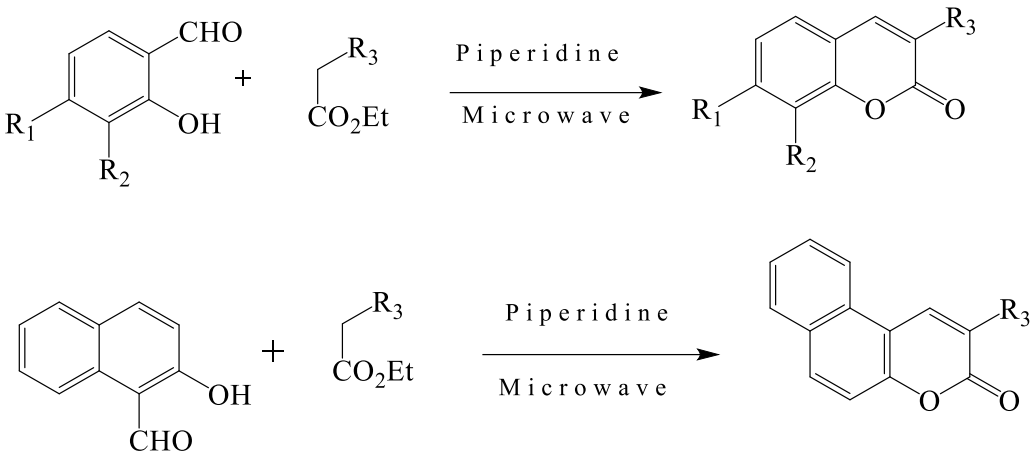
Keywords: Coumarin, Benzocoumarin, Microwave, Ultrasound, Solvent free.

Introduction:

The study of coumarin dates back to 1820 chemically coumarin [2-H- benzopyran-2-one] belongs to subgroup of lactones [1]. Coumarin containing derivatives are used to great extent in pharmacy and medicine. Their properties and biological activities play an important role in the development of new drugs therapy. For this reason, numerous method and techniques have been developed for synthesis of substituted coumarin [2]. Coumarin is within the organic compounds and within the many uses of terms within the cosmetics, dyes and food added. Coumarin derivatives have been used in the medical field as well as HIV and affecting the livers [3], newly formed Coumarin derivatives were screened for anti-inflammatory activity [4], Coumarin derivatives like furano coumarin, pyrano coumarin, isoflavones and benzopyrones have a significant role in the treatment of different cancer conditions [5]. Coumarin derivatives have been used in the medical field as anti-clotting blood pressure depressor muscles loosened [6].

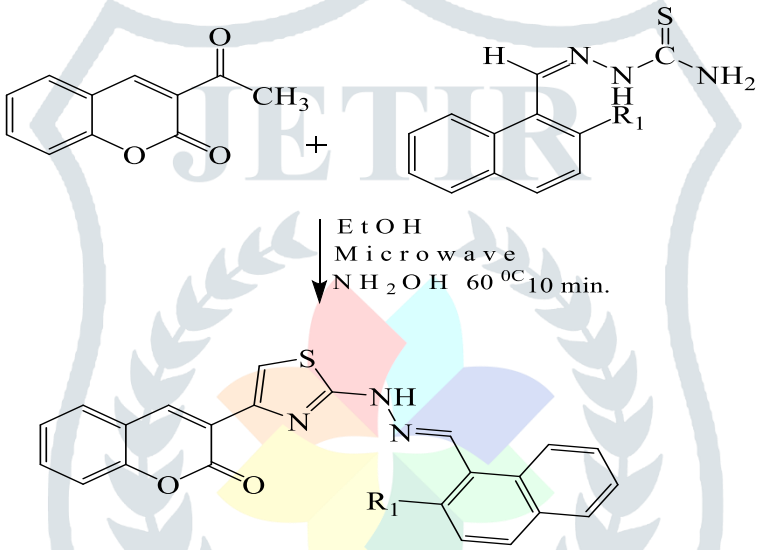
Results and Discussion:

Darek Bogdal et al. [7] reported faster synthesis of coumarin by the Knoevenagel condensation under microwave irradiation of salicylaldehyde or its derivative with various derivative of ethyl acetate in presence of piperidine leads to synthesis of coumarin by solvent free reaction (Scheme-1).



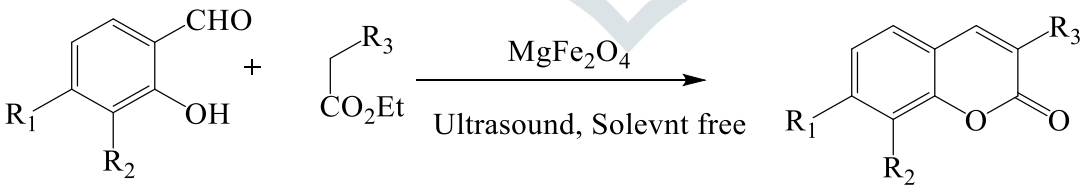
Scheme- 1: Synthesis of coumarin by condensation under microwave irradiation

Osman et al. [8] reported microwave assisted synthesis of hydrazinyl thiazolyl coumarin and its antioxidant activity (Scheme-2).



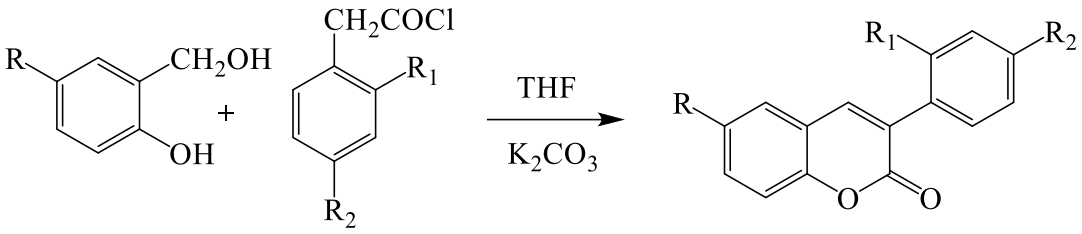
Scheme- 2: Synthesis of hydrazinyl thiazolyl coumarin under microwave irradiation

Ghomi et al. [9] reported Knoevenagel synthesis of 3-substituted coumarins was performed in $MgFe_2O_4$ nanoparticles (4 mol%) catalyzed reaction, of salicylaldehydes and 1,3-dicarbonyl compounds, under ultrasonic irradiation (20 kHz, 35W, 45 °C) (Scheme-3).



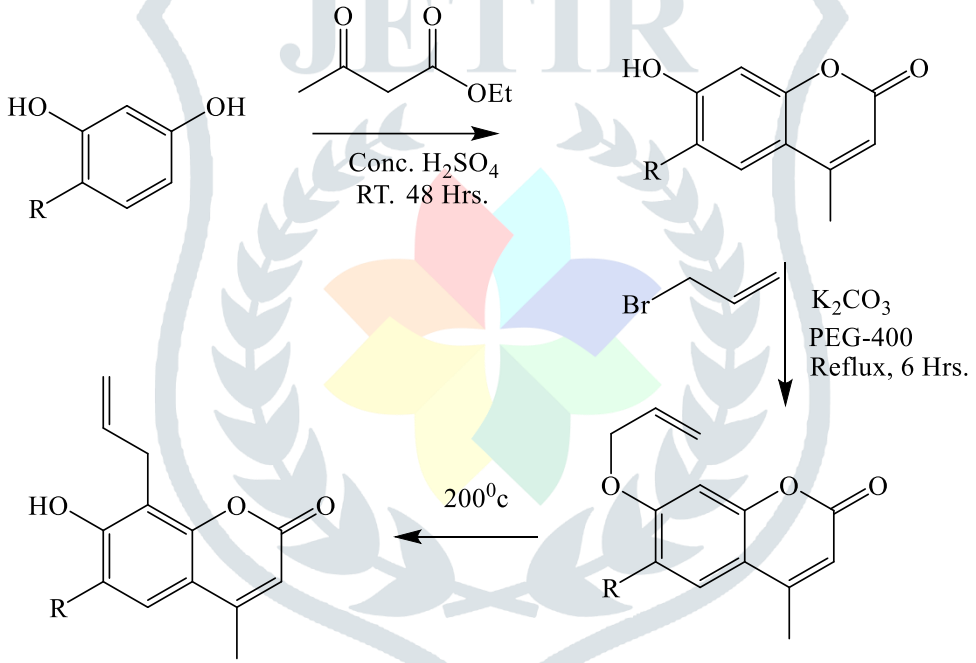
Scheme-3: Synthesis of 3-substituted coumarin under ultrasonic irradiation Cat. by $MgFe_2O_4$.

Sripathi et al [10] reported synthesis of 3-Aryl coumarins were synthesized in one-pot reaction from different salicylaldehydes and phenyl acetyl chlorides, in the presence of K_2CO_3, under ultrasound irradiation (Scheme-4).



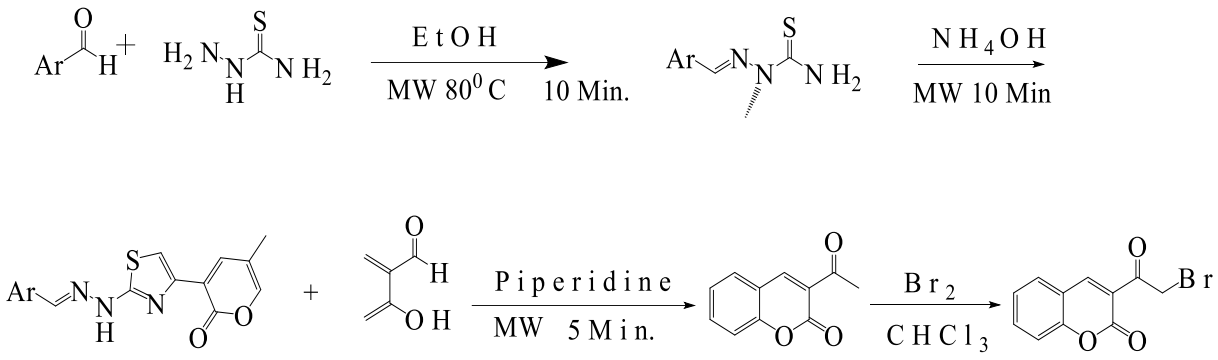
Scheme- 4: Synthesis of 3-aryl coumarin under ultrasonic irradiation.

M. M. Kodape et al. [11] reported the synthesis of coumarin is the Pechmann condensation of phenols, using concentrated sulfuric acid as the catalyst. Condensation of resorcinol with ethyl acetoacetate 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-5).



Scheme- 5: Synthesis of 8-allyl-7-hydroxycoumarin under PEG-400 solvent.

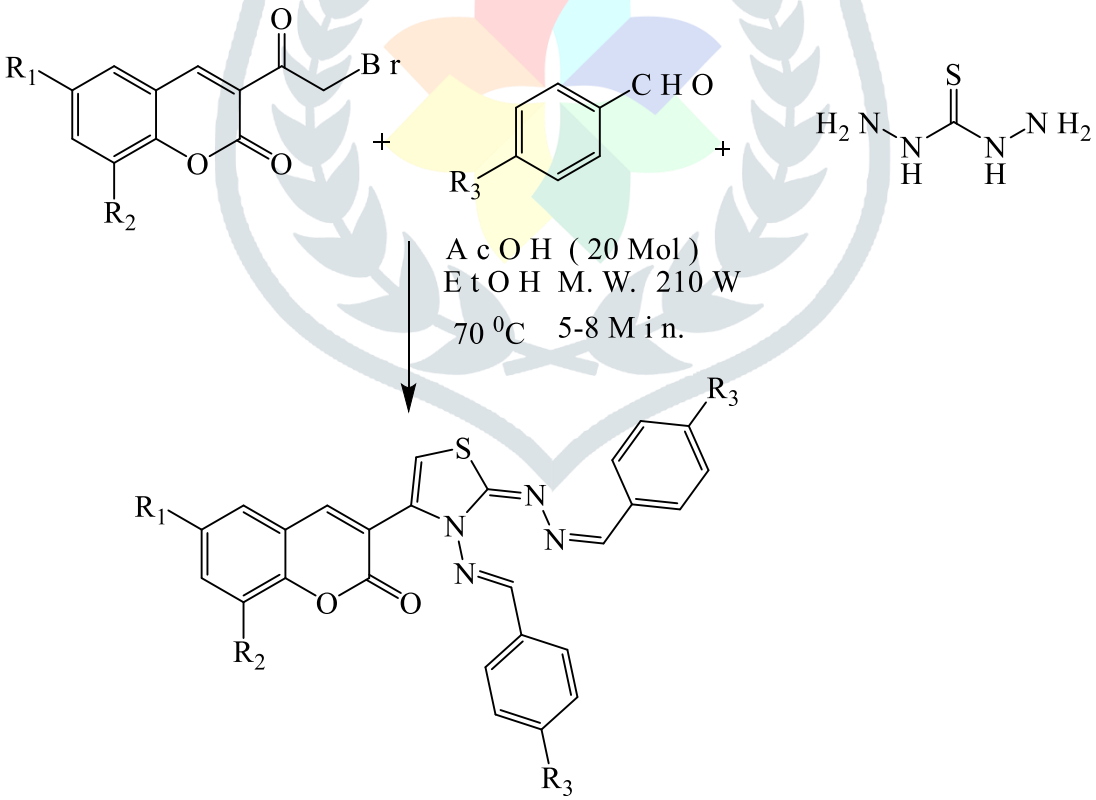
Gabr et al. [12] reported synthesis of novel coumarin-thiazole derivatives under microwave irradiation. In which the reaction of aryl aldehydes with thiosemicarbazide in ethanol under microwave irradiation at 80°c provides 2-arylidene-hydrazinocarbothioamides in good yield within 10 min. Similarly, the treatment of salicylaldehyde with ethyl acetoacetate in presence of piperidine as the base catalyst was found to proceed under microwave irradiation at 45°c to form 3-acetylcoumarin which on reacting with bromine furnished 3-bromoacetyl coumarin. Consequently, the reaction of an equimolar amount of 2-arylidene-hydrazinocarbothioamides and 3-bromoacetyl coumarin in presence of ammonium hydroxide as the catalyst under the influences of microwave irradiation at 100°c afforded the corresponding product coumarin - thiazole derivatives (Scheme-6).



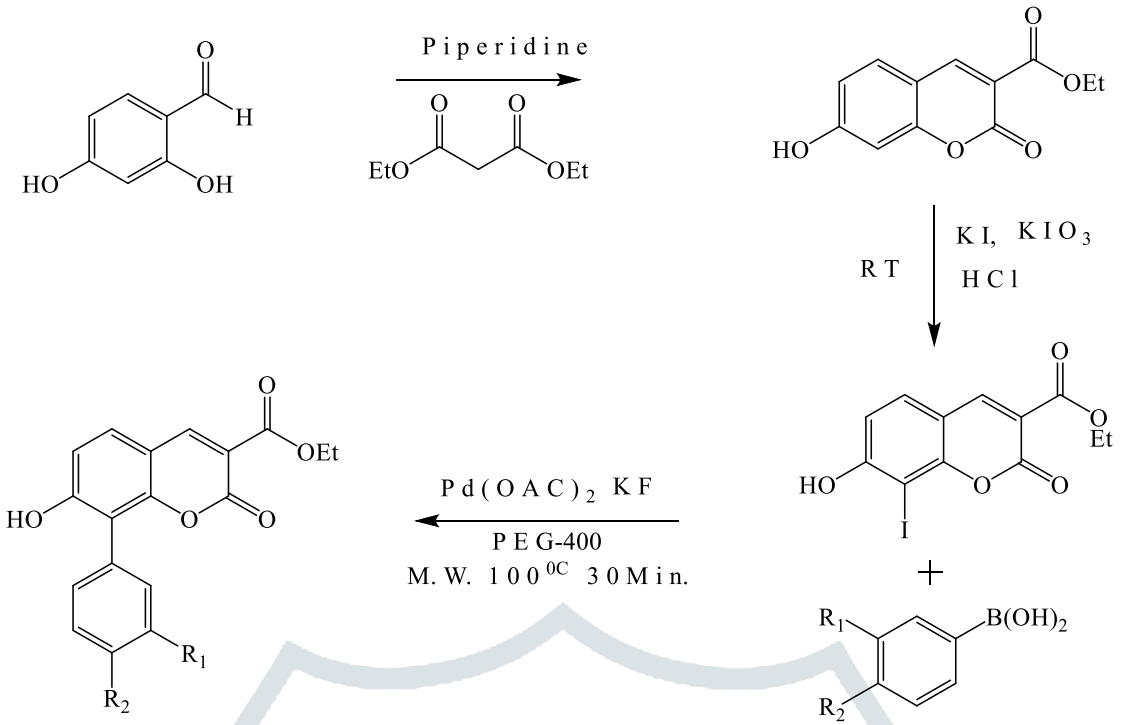
Scheme -6: Microwave assisted construction of coumarin -thiazole derivatives.

Mamidala et al. [13] reported the synthesis of coumarin -thiazole derivatives. The synthesis was one pot three component reaction of coumarin, aldehyde and thiocarbohyrazide using 20 mol % of acetic acid as the catalyst under microwave irradiation with 210 w power at temperature of 70°c. Under this standard condition the corresponding product were obtained (Scheme-7).

Vieira et al. [14] reported synthesis of coumarin derivative via suzuki coupling, using PEG-400 as a solvent, 10 mol % of Pd $(OAC)_2$ as a catalyst; KF as a base under microwave irradiation from 8-iodocoumarin with different phenyl boronic acid. 8-iodocoumarin was synthesized in knoevenagel condensation between 2-hydroxy benzaldehyde and diethylmalonate, followed by the iodination (Scheme-8).



Scheme -7: Three components microwave -irradiated synthesis of coumarin –thiazole derivatives.



Scheme -8. Synthesis of coumarin derivative via Suzuki coupling reaction.

Conclusion

In conclusion, this review summarizes an application of different methodology in coumarin derivative synthesis by green approaches and techniques. The chemistry of coumarin derivative has a very high richness due to the presence of several reactive sites in their structures likely to be engaged in quite a lot of reactions. The results of all these methods are useful and significant to know the suitable method for synthesis of future research coumarin derivative.

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