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# Synthesis of 7-Hydroxy-4-methyl Coumarin Under Microwave Irradiation

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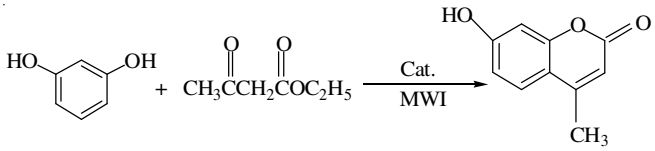
The 1,3-benzenediol and ethyl acetoacetate as raw materials were used to synthesize 7-hydroxy-4-methyl coumarin under microwave irradiation with zirconium sulfate tetrahydrate as the catalyst. Experiment showed that the yield reached up to 87.5 %, when the reaction conditions were as follow: the molar ratio of phenolic and ester was 1.0:1.0, 0.4 g of $Zr(SO_4)_2{\cdot}4H_2O$, 10 mL of cyclohexane, the mixtures react 12 min under 500 W microwave radiation.

**Keywords: 7-Hydroxy-4-methyl coumarin, Microwave irradiation, Zirconium sulfate tetrahydrate.**

## INTRODUCTION

7-Hydroxy-4-methyl coumarin is a white acicular crystal. It has many uses such as medicine, pesticide and as the important chemical intermediates[1-3]. Sulfuric acid as catalyst used in the synthesis methods of coumarin in industry, but it corrode the equipment and pollution the environment seriously. In recent years, new type of catalysts appeared in the synthesis of coumarin, such as ion exchange resin, solid super acid and ionic liquids[4-7]. However, they present some issues *e.g.*, high cost, harsh reaction conditions and complex operation. Microwave technique is widely used in organic synthesis. It has many advantages such as the conventional conditions, shorter reaction time and higher yields compared with other organic reactions. In this paper, the 1,3-benzenediol and ethyl acetoacetate as raw materials $Zr(SO_4)_2{\cdot}4H_2O$ as catalyst by microwave radiation technology were used to synthesize 7-hydroxy-4-methyl coumarin. The results showed that the catalyst has good catalytic activity. Furthermore, the 7-hydroxyl-4-methyl coumarin reaction has the characters: simple operation, short reaction time and high yield under microwave radiation. The reaction principle is as follows:




## EXPERIMENTAL

$Zr(SO_4)_4{\cdot}4H_2O$, 1,3-benzenediol, ethyl acetoacetate (Chemical pure, Sinopharm Chemical Reagent Co., Ltd.).

**Method of synthesis of 7-hydroxy-4-methyl coumarin:** Mix 1,3-benzenediol (4.4 g, 0.04 mol ), ethyl acetoacetate (5.6 mL, 0.04 mol) and $Zr(SO_4)_2{\cdot}4H_2O$ 0.4 g, then put into a three mouth bottle. The mixtures were stired and heated in microwave oven under certain power radiation. Then stop heating, cool the reaction liquid to below 90 °C, add a small amount of anhydrous ethanol to reflux the mixed solution then filtering the recovered catalyst. Poured the left thermal liquid into the ice water and filtered to collect the crystalline, then recrystallized by 67 % alcohol. Finally, get a milky white acicular crystal. The fusion process was 188-192 °C, the theoretical value is 186-192 °C.

The products were dried, then grinded with potassium bromide and pressed into tablets, they were put into the Nicolet Impact-670 FTIR spectrometer to analysis of product structure.

## RESULTS AND DISCUSSION

Fig. 1 showed that 3493 $cm^{-1}$ is the characteristic absorption peak of -OH; 3121 $cm^{-1}$ is the characteristic absorption peak of $-CH_3$; 1683 $cm^{-1}$, 1605 and 1450 $cm^{-1}$ are the absorption peak of benzene skeleton vibration; 845 $cm^{-1}$ is the bending vibration of C=C-H outside the phencyclidine.

**Effect of microwave irradiation power on the yield:** Mix 1,3-benzenediol (4.4 g ,0.04 mol ), ethyl acetoacetate (5.6 mL , 0.04 mol), 0.4 g $Zr(SO_4)_2{\cdot}4H_2O$ and 10 mL cyclohexane. The mixtures reacted 12 min. The effect of changing the microwave radiation power upon the yield was shown in Fig. 2. The yield was low within the specified time for reaction was not complete when microwave irradiation power was small. When the power was so large that reaction temperature was elevated

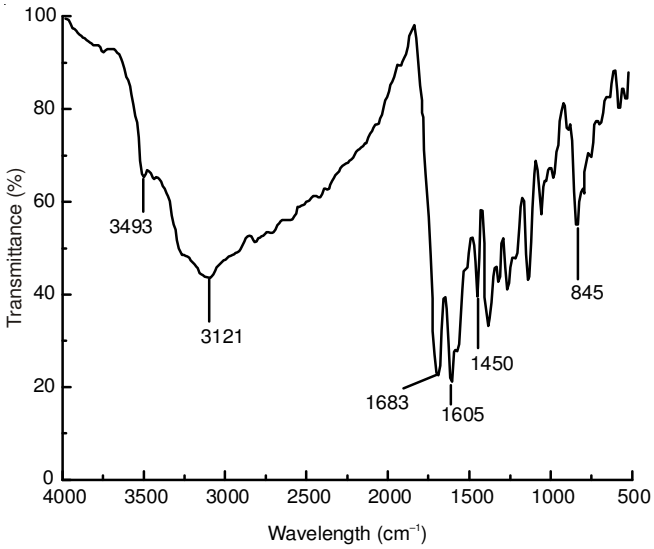



Fig 1. Infrared spectroscopy of 7-hydroxyl-4-methyl coumarin

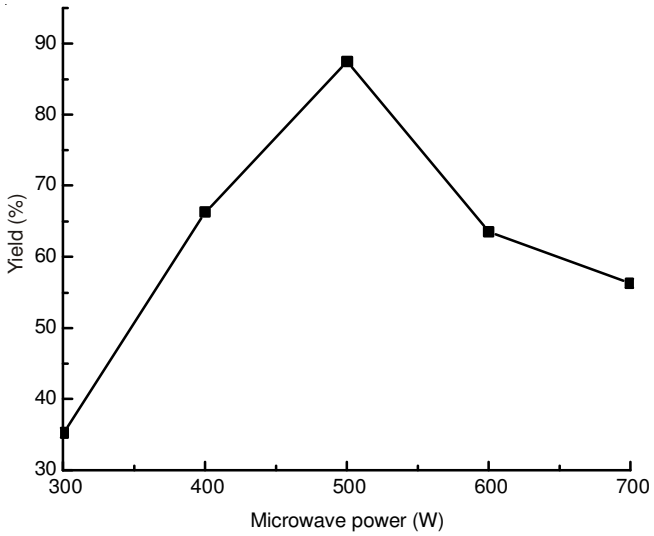



Fig. 2. Effect of microwave irradiation power on the yield

too fast in the short time. It leaded the reactant volatilization so the yield reduced. 500 W was appropriate.

**Effect of microwave time on the yield:** Mixed 4.4 g (0.04 mol) 1,3-benzenediol, 5.6 mL (5.74 g, 0.04 mol) ethyl acetoacetate, 0.4 g $Zr(SO_4)_2{\cdot}4H_2O$ and 10 mL cyclohexane. Investigate the effect of the microwave time on the yield when microwave irradiation power was 500 W. The yield increased with increasing the microwave irradiation time. As the reaction time was increased the product color changed from white to yellow. Under such condition, the yield decreased due to side reaction increased. Fig. 3 shows 12 min was the optimal microwave irradiation time.

**Effect of catalyst quantity on the yield:** Mix 4.4 g (0.04 mol) 1,3-benzenediol, 5.6 mL (5.74g, 0.04 mol) ethyl acetoacetate and 10 mL cyclohexane. The mixtures reacted 12 min under 500 W microwave irradiation power. The catalyst quantities was changed. Fig. 4 shows 0.4 g is the optimal catalyst dosages. With the increase of catalyst dosage the yield increased significantly. But when it reached 0.4 g and then increase the dosage of catalyst, the yield basically unchanged, so the optimum amount of catalyst was 0.4 g.

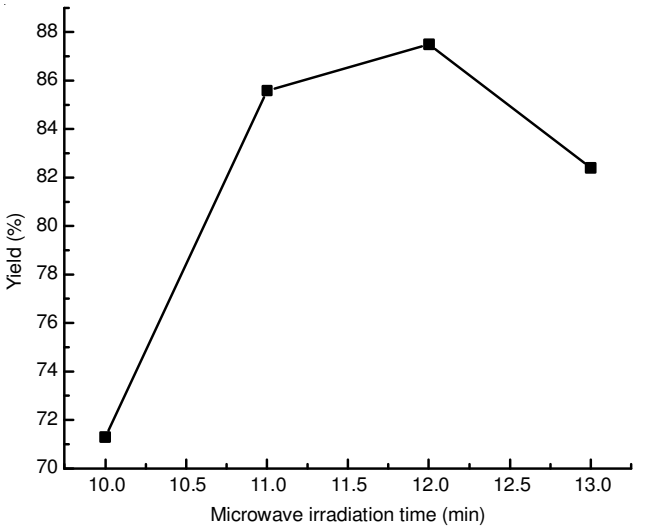



Fig. 3. Effect of microwave irradiation time on the yield

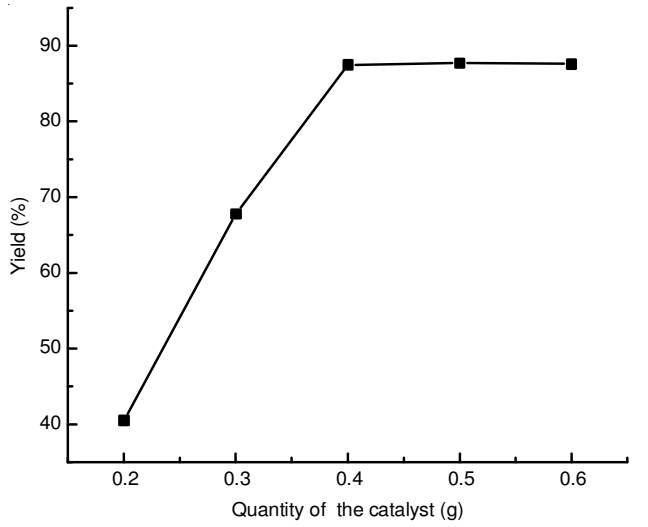



Fig. 4. Effect of quantity of catalyst on the yield

Effect of molar ratio of phenolic and ester on the yield. Chang the reactant molar ratio, the other reaction conditions were the same. Fig. 5 shows that when the molar ratio was 1:1, the yield was the maximum. But as increasing the proportion, this product further reacted with ethyl acetoacetate so the yield decreased.

**Effect of different water retaining agent on yield:** Mixed 4.4 g (0.0 4 mol) 1,3-benzenediol, 5.6 mL (5.74 g, 0.04 mol) ethyl acetoacetate , 0.4 g $Zr(SO_4)_2{\cdot}4H_2O$ and 10 mL dehydrating agent. The mixtures reacted 12 min under 500 W microwave irradiation power. Use different dehydrating agent the yield was significantly different. Table-1 showed it had the maximum yield when cyclohexane was as the dehydrating agent.

TABLE-1
EFFECT OF DIFFERENT WATER RETAINING AGENT ON THE YIELD

| Dehydrating agent | Yield (%) |
|---|---|
| – | 40.5 |
| Benzene | 30.2 |
| Toluene | 24.3 |
| Cyclohexane | 87.5 |

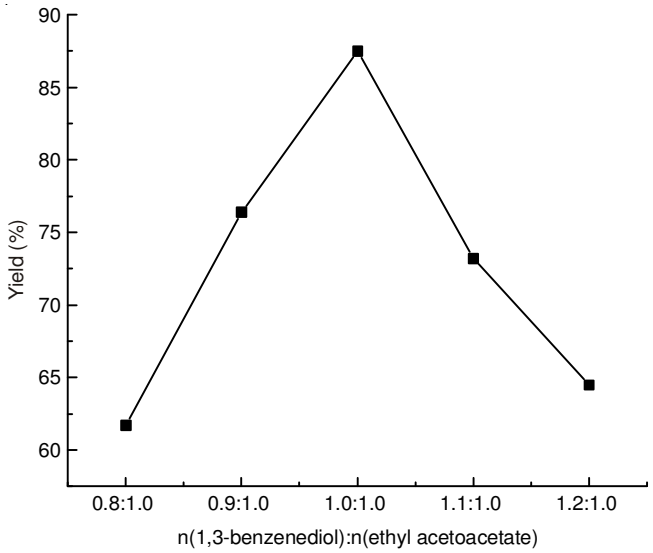



Fig. 5. Effect of phenolic ester molar ratio on the yield

**Compare microwave technology with general synthesis method:** Mix 4.4 g (0.04mol ) 1,3-benzenediol, 5.6 mL (5.74 g, 0.04 mol) ethyl acetoacetate. The mixtures reacted with sulfuric acid and $Zr(SO_4)_2 \cdot 4H_2O$ as catalyst respectively under microwave irradiation and conventional heating method. Table-2 shows microwave irradiation heating method is better than the ordinary heating method with $Zr(SO_4)_2 \cdot 4H_2O$ as catalyst. Layered zirconium sulfate four water structure is stable. Crystal water and laminated zirconium sulfate has strong interactions, resulting form a stronger B acid catalytic activity center in the layer[8]. That is allowing the catalytic reaction to go on smoothly.

TABLE-2
COMPARISON MICROWAVE TECHNOLOGY
WITH GENERAL SYNTHESIS METHOD

| Catalyst | Heating method | Reaction time | Yield (%) |
|---|---|---|---|
| $H_2SO_4$ | Microwave radiation | 24 min | 57.80 |
| | Ordinary heating | 10 h | 42.38 |
| $Zr(SO_4)_2 \cdot 4H_2O$ | Microwave radiation | 12 min | 87.57 |
| | Ordinary heating | 1.5 h | 66.38 |

## Conclusion

**Experiment shows that $Zr(SO_4)_2 \cdot 4H_2O$ was a effective catalyst when the reaction conditions were as follow:** The molar ratio of phenolic and ester was 1:1, the weight of $Zr(SO_4)_2 \cdot 4H_2O$ was 0.4 g, 10 mL cyclohexane, the reaction time was 12 min, microwave radiation power was 500 W, the yield reached up to 87.5 %. $Zr(SO_4)_2 \cdot 4H_2O$ as catalyst has many advantages under microwave irradiation.

## ACKNOWLEDGEMENTS

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