

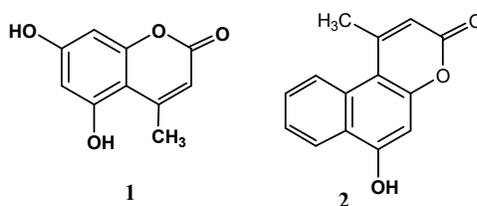
# Synthesis Two Coumarin Derivatives Using Heterogeneous Catalyst

Joumaa Merza

Central Laboratory in organic chemistry, Department of Chemistry, Al-Baath University Homs, Syria

## Abstract

Two coumarin derivatives: 5,7-di Hydroxy-4-Methyl Coumarin (**1**) and 6-hydroxy-1-methyl-3H-benzo[f]chromen-3-one (**2**) have been synthesized via Pechmann condensation using Amberlyst-15 as a green catalyst. The coumarin **1** was synthesized by the condensation of phloroglucinol **3** with the ethyl acetoacetate **4**, while the coumarin **2** was synthesized from the condensation of  $\beta$ -keto esters **4** with the 1,3-dihydroxy naphthalene **5**. The conditions of reactions were as following: (1:1) the molar ration of reagents, (10mol.%, 0.2 g) Amberlyst-15 at 110°C in solvent-free conditions. The yields in this conditions were (95%) for the compounds **1** and (88%) for the compounds **2**. The possibility of recycling the heterogenous catalyst (amberlyst -15) adds an advantage to the studied reactions. The purified products were characterized by spectral methods: FT-IR,  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$ .



**Keywords:** Coumarin, Pechmann Condensation, phloroglucinol, Amberlyst-15

## 1. INTRODUCTION

The coumarins are heterocyclic organic compounds, they are known as benzo- 2-pyrone derivatives, and constitute an important class of natural products which received a significant attention from many pharmaceutical and organic chemists, because of its broad spectrum of biological and pharmaceutical properties such as: antibacterial, anticancer and the inhibitor of HIV-1 protease. Furthermore, these compounds are used as additives in food, perfumes, agrochemicals, cosmetics, pharmaceutical and in the laser technologies due to its useful properties in spectroscopic analysis [1-7]. Several synthetic methods, like Pechmann condensation [15], Perkin, Reformatsky, Wittig reaction, Knoevenagel condensation and Claisen rearrangement have been investigated for the synthesis of coumarins [8-14]. Pechmann reaction is well known, it is a simple method and has been widely used to synthesize the coumarins from activated phenols, such as *m*-substituted phenols and acetoacetic esters or an unsaturated carboxylic acid in presence of an acid catalyst. In addition, the use of various conventional homogeneous acids such as  $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{CF}_3\text{COOH}$ , *p*-toluene sulfonic acid,  $\text{P}_2\text{O}_5$ ,  $\text{POCl}_3$  and metal halides, different solid acid catalysts [16–24] have also been studied for the synthesis of the hydroxy derivatives of 4-methyl coumarin. However, to obtain high yield by using acidic heterogeneous catalysts, a long time is required in these reactions. The use of microwave irradiation has been employed for a number of organic syntheses to reduce the reaction time, rate enhancement and to increase the selectivity and yields.

The use of microwave irradiation in the coumarin synthesis via Pechmann reaction in presence of homogeneous liquid acid as catalyst has been also used by using the sulfuric acid, *p*-toluene sulfonic acid and ionic liquid as homogeneous liquid acids [20]. However, sulfuric acid and *p*-toluene sulfonic acid are corrosive, hazardous and require careful handling in microwave system. The separation of ionic liquid catalyst to recover from reaction mixture by solvent extraction adds an extra step in synthesis and the use of solid acids for microwave-accelerated synthesis of coumarins is scanty [16-24]. Singh et al. studied the synthesis of coumarins on solid support K-10 montmorillonite clay using domestic microwave oven and observed higher selectivity, however, with poor yields of coumarins. But they obtained a good yield (55–85%) of other coumarin derivatives using montmorillonite K-10 clay, however, the reaction was promoted with the addition of one drop of concentrated sulfuric acid and high power of microwave irradiation (640 W) was required. Frère et al. [16-24] obtained good yields (66%) of coumarin derivatives in 30 min on solid support graphite/K-10 using a focused microwave reactor (300 W, monomode system), however, they observed that the use of appropriate solvent is required for controlled microwave reactions.

Recently, we have reported excellent catalytic activity of Amberlyst-15 as a solid acid catalyst for the synthesis of 7-substituted 4-methyl coumarins by Pechmann condensation [22-26], with high yield (95%, 110 °C, 120 min) of 7-hydroxy 4-methyl coumarin.

In the present, we extended this study for the synthesis of 5,7-Dihydroxy 4-methyl coumarin **1** which have anti-inflammatory and antibacterial activity and it present a good smell which can be used in perfume or as additional food using activated phenols (1,3-dihydroxy naphthalene and 1,3,5-trihydroxy phenol (Phloroglucinol)) with ethyl acetoacetate and using Amberlyst-15 as heterogeneous catalyst under solvent free conditions.

Amberlyst-15 is a macro reticular polystyrene based ion exchange resin with strongly acidic sulfonic group. It serves as an excellent source of strong acid. It can also be used as recycled catalyst. Amberlyst-15, Hammett acidity approximately to one sulfonic acid group. It is of specific interest in this study since it has been reported to be a solid superacid catalyzing a variety of organic conversions and reactions. Applications of this catalyst allow mild and highly selective transformations and synthesis in a facile and environmentally friendly conditions [25-26].

## 2. EXPERIMENTAL

### 2.1. Apparatus

The spectra  $^1\text{H}$ ,  $^{13}\text{C}$ -NMR were recorded on a device 400 MHz model Bruker, Switzerland company, optical absorption spectrum infrared device model FT-IR-4100 from Jasco, rotary evaporator 4.91 model from the German company Normschiff, thin layer chromatographic of aluminum coated by Silica Gel 60F254 measuring 20 X 20 from the German company Merck, thin layer chromatographic of preparatory glass coated by Silica Gel 60F254 measuring 20 X 20 from the German company Merck.

### 2.2. Raw materials and reagents

1,3-dihydroxy naphthalene, 1,3,5-trihydroxy phenol (phloroglucinol), ethyl acetoacetate (sigma aldrich & merck), nitric acid, sulfuric acid and solvents (99% by Merck), amberlyst-15 (99% by sigma aldrich)

### 2.3. Experimental Procedure

#### 2.3.1. Synthesis of 5,7-di Hydroxy-4-Methyl Coumarin (**1**):

A mixture of 1,3,5-trihydroxy phenol (phloroglucinol) (1 mmol) **3**, ethyl acetoacetate (1.1 mmol) **4** and acid catalyst (10 mol%) were added, then the reaction mixture was stirred in oil bath and heated to 110°C for the desired time. The reaction was followed by thin layer chromatography (T.L.C). In the end of the reaction, the mixture was filtered to remove the catalyst, then the filtrate cooled to room temperature. The hot methanol was added to the cooled filtrate, a solid (crude product) was obtained, this compound was filtered and then recrystallized with ethanol to obtain pure product. The compound was identified by its spectroscopic spectra: FT-IR,  $^1\text{H}$ ,  $^{13}\text{C}$ -NMR).

#### 2.3.1.2 Synthesis of 6-hydroxy-1-methyl-3H-benzo[f]chromen-3-one (**2**)

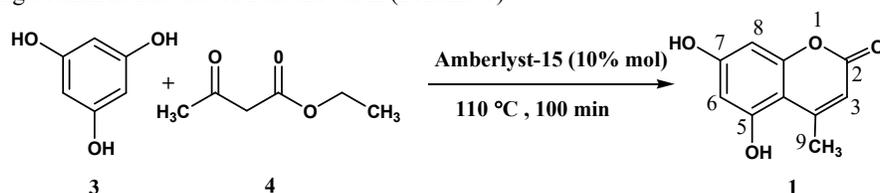
A mixture of 1,3-Dihydroxy naphthalene (1 mmol), ethyl acetoacetate (1.1 mmol) and acid catalyst (10 mol%) were added, then the mixture was stirred in oil bath heated to 110°C for the desired time. The reaction was controlled by thin layer chromatography (T.L.C). In the end of the reaction, the mixture was filtered to remove the heterogeneous catalyst, then filtrate was cooled to room temperature, a hot ethanol was added to the cooled filtrate, a solid (crude product) was filtered and then recrystallized with ethanol to obtain pure product. The physical data (mp, FT-IR,  $^1\text{H}$ -NMR,  $^{13}\text{C}$ -NMR) of these known compounds were found to be identical with those reported in the literature.

## 3. Results and Discussion:

The efficient methods to synthesis the coumarins derivatives **1** and **2** using Amberlyst-15 as a catalyst in the Pechmann reaction are reported herein.

### 3.1. Synthesis of Compound **1**

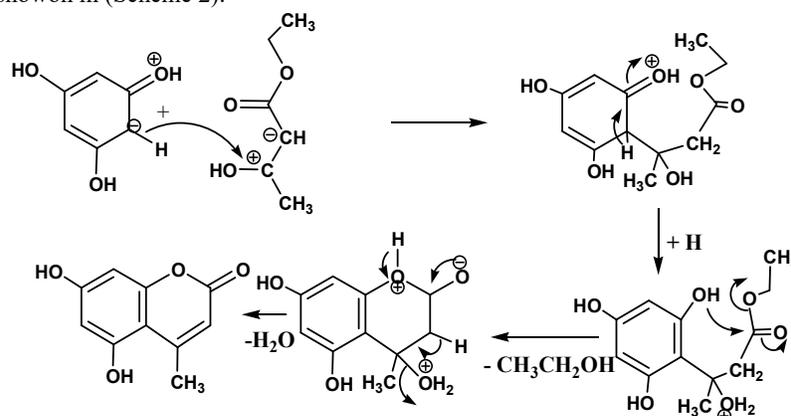
The reaction of phloroglucinol **3** and  $\beta$ -keto esters **4** in presence of catalytic amount of Amberlyst-15 afforded the corresponding coumarin derivatives **1** as shown in (Scheme 1).



**Scheme 1:** Synthesis of coumarin **1** via Pechmann condensation of phloroglucinol with  $\beta$ -keto esters to substituted coumarins.

The coumarin derivative **1** was obtained in high yields in a relatively short time. It is known that the

pechmann reaction proceeds through transesterification and intramolecular hydroxyalkylation, followed by dehydration [18, 24]. These three steps are all typical acid catalyzed reactions. Therefore, the outcome of the pechmann reaction depends on the mechanism of the pechmann condensation of phenols and  $\beta$ -keto esters by amberlyst-15 as shown in (Scheme 2).



**Scheme 2:** suggested mechanism of condensation of phloroglucinol and  $\beta$ -keto esters in presence of Amberlyst-15 catalyst.

At first time, for the optimization of the reaction conditions, a mixture of phloroglucinol and ethyl acetoacetate was investigated as a model reaction and its behavior was studied in a variety of conditions, such as: Temperature, time of reaction, solvents, molar ratio of catalyst and type of catalysts.

The best result was achieved by carrying out the reaction of phloroglucinol and ethyl acetoacetate (with 1:1 mol ratio) in the presence of (0.2g, 10% mol) of Amberlyst-15 at 110°C for 100 min. The reaction mixture was monitored by T.L.C using (ethyl acetate:n.hexane 7:3) under solvent-free conditions, The yield obtained in these conditions was excellent (95%). It is important to say that the incrision the quantity of catalyst didn't affect the yield (Table 1):

**Table 1.** Effect of Amberlyst-15 percentage in Pechmann condensation of phloroglucinol with a ethyl acetoacetate.

Entry	Amount of catalyst (mol.%)	Yield (%)
1	-	Traces
2	10	95
3	20	88
4	30	86
5	40	85

As the using of large quantities of Amberlyst-15 did not affect the yield of the reaction, therfor, it is preferred using the least possible quantity of catalyst. The studying the effect of temperature on the synthesis of was carried out at the temperature range of 40°C – 150°C (Table 2):

**Table 2.** Effect of temperature on the yield of compod 1

Entry	Temperature (°C)	Yield (%)
1	40	20
2	80	40
3	110	95
4	130	80
5	150	55

As indicated in Table 2, It is clear the increasing of the temperature until 110°C the yield improved from 20% to 95%, but the yield was decreased to 55%, when the temperature increased more than 110°C to 150°C, this is probably due to the formation of the secondary products such chromones, the self-condensation of ethyl acetoacetate, isomerization and cleavage of 5,7-di hydroxy-4-methyl coumarin in one side, and in the other side. this is perhabs due to the decreasing of activity of catalyst at high temperature because the low thermal stability of the vinyl based polymers [26b], therfor It is better to prossed the reaction in 110°C.

The time of reaction was optimized to 100 min where the reaction was completely finished with the highest yield (monitored by T.L.C), But the increasing the time up to 100 min, the yield was decreased, it is probably due to the increasing the secondary products (Appearance several spot as checked by TLC), the results are summarized in Table 3:

**Table 3.** effect of the time on Pechmann condensation of phloroglucinol with ethyl ethyl acetoacetate.

Entry	Time (min.)	Yield (%)
1	30	20
2	60	30
3	100	95
4	150	86
5	200	75

The effect of several solvent on the yield of coumarin derivatives was studied. As indicated in the previous three tables (table 1, 2, 3), the yield was found to be significantly higher in solvent-free conditions. when this result was compared with other solvents. it is found that the non-polar solvents, like toluene, were better than polar solvent, it is due to reduce the formation of hydrogen bond (inter- and intra- molecular) in the phenol derivatives and also to form an azeotropic mixture (ethanol and water) which was producing during the reaction which facilitate removing them from the reaction media, in addition, the polar solvents may cause the degradation of the compound [27].

**Table 4.** Effect of solvent on Pechmann condensation of phloroglucinol with ethyl acetoacetate .

Entry	Solvents	Yield (%)
1	Toluene	85
2	THF	70
3	1,4-Dioxan	50
4	EtOH	20
5	MeOH	30
6	H <sub>2</sub> O	20
7	-	95

Several acidic catalysts were examined to compare it with Amberlyst -15 (Table 5). When using homogenous catalysts, it is necessary to use a large quantity of catalyst to have the same yield, but if the same molar percentage was used, the yield will be very low (Table 5, entries 1, 4, 6). In other hand, when the Silic catalysts were used (Table 5, entries 2, 5), the yield was not improved, it may due to their high surface polarity which attract the water molecules and causing the poisoning of the active sites of catalyst. While non -polar surface catalyst (Amberlyst-15) (Table 5, entry 7) was stayed active and no poisoning active sites was observed, so the best yield was obtained, in addition, it is easy to isolate the catalyst from the reaction media without any supplementary treatment.

**Table 5.** Effect the type of catalyst on condensation of phloroglucinol with ethyl acetoacetate.

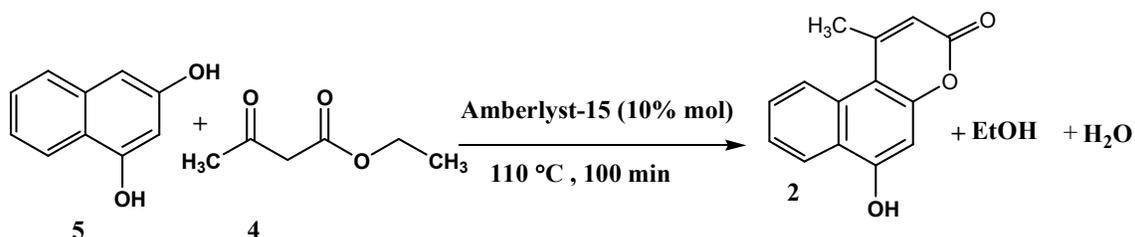
Entry	Catalyst	Yield (%)
1	H <sub>2</sub> SO <sub>4</sub>	30
2	SiO <sub>2</sub> -SO <sub>4</sub> H	30
3	CH <sub>3</sub> -SO <sub>3</sub> H	45
4	<i>p</i> -TSA	50
5	HMS-SO <sub>3</sub> H	10
6	AlCl <sub>3</sub>	55
3. 7	2. Amberlyst 15	1. 95

The best result was achieved by carrying out the reaction of phloroglucinol and ethyl acetoacetate (with 1:1 mol ratio) in the presence of 0.2 g of Amberlyst-15 at 110 °C under solvent-free conditions and 5,7-di Hydroxy-4-Methyl Coumarin was obtained in very high yields up to 95% .

From our point of view, Amberlyst-15 was successfully recycled at least 5 times without apparent decrease of activity, selectivity giving and high yield nearly 95% at every cycle after 5 cycles, the color of the Amberlyst-15 changed which is presumably due to the partial deposit of carbonaceous materials .

### 3.2. Synthesis of Compound 2:

The optimal conditions obtained during the synthesis of the compound **1** were applied to the synthesis of 6-hydroxy-1-methyl-3H-benzof[*f*]chromen-3-one **2**. The high yields up to 88 % during 2 hours was obtained. by condensation 1,3-Di hydroxy naphthalen with ethyl acetoacetate under the same reaction conditions



**Scheme 3:** Synthesis the coumarin derivative **2** via Pechmann condensation of 1,3-di hydroxy naphthalen **5** with  $\beta$ -keto esters **4**

The compound **2** is characterized with pretty smell wich can be studied and used as a perfume after investigated its properties.

#### 4. Conclusion

A green and efficient procedure to synthesis two coumarin derivatives **1** and **2** by Pechmann methode using Amberlyst-15 as acidic catalyst under solvent free conditions was achived. This catalyst is stable and can promote the yields and reaction times over eight runs without any loss of activity. Moreover, heterogeneous reaction conditions, high yields of products, short reaction times, ease of work-up and clean procedure will make this procedure a useful addition to the available methods.

#### 6. Characterization of the products:

**6.1. 5,7-di hydroxy-4-Methyl Coumarin (1)** yield 95% ( ethyl aceto acetate: *n*-hexane-6:4)

**IR(KBr)** ( $\nu$ , cm<sup>-1</sup>):1680(C=O), 2938 (C<sub>sp3</sub>-H), 3116(C<sub>sp2</sub>-H), 1277 (C-O), 1518-1455 (C=C aromatic), 1670 (C=Calken).

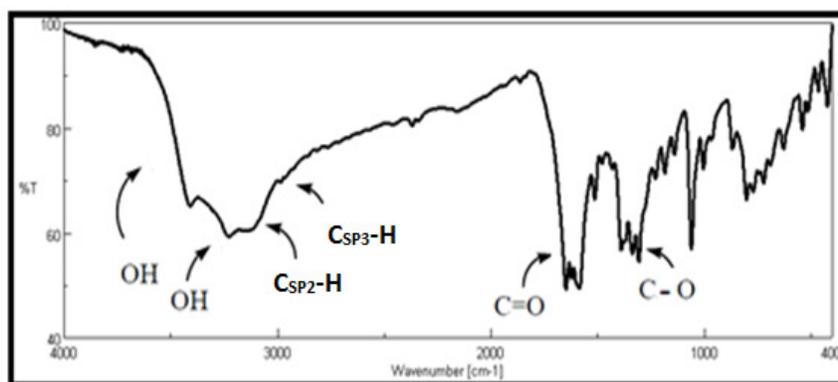


Figure 1: IR specter of compound **1**

**<sup>1</sup>H-NMR (DMSO-d<sub>6</sub>, 400MHz)** ( $\delta$ , ppm):  $\delta$  2.345(s, 3H, CH<sub>3</sub>), 6.128(s, 1H, 3-H), 7.087(s, 1H, 5-H), 6.829(s, 1H, 7-H), 9.371(s,H), 10.007(s,H), **<sup>13</sup>C-NMR(DMSO-d<sub>6</sub>)**  $\delta$ 160.67, 115.95, 154.40, 113.23, 112.58, 110.65, 132.62, 18.72, 149.88, 143.79. Melting point: 282–285 °C

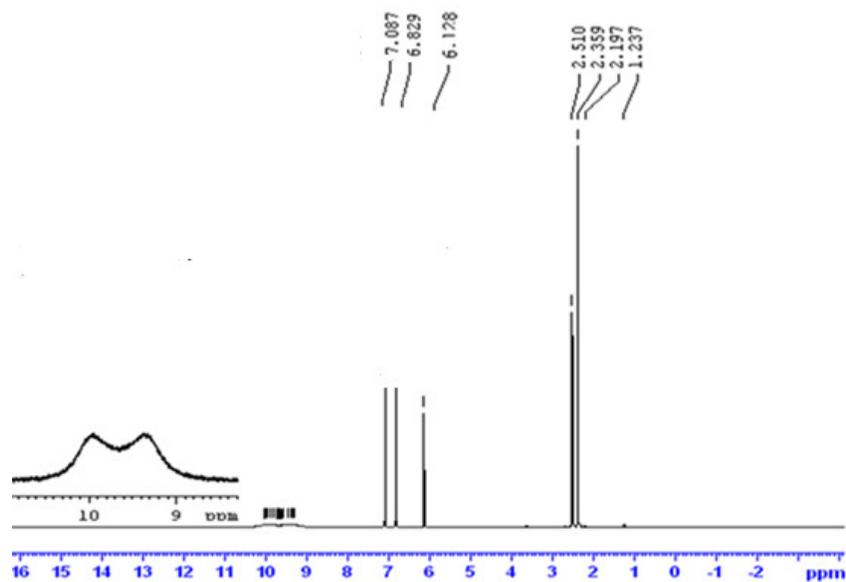


Figure 2:  $^1\text{H-NMR}$  specter (400 MHz,  $\text{CDCl}_3$ ,  $\delta\text{TMS} = 0$  ppm) of compound 1

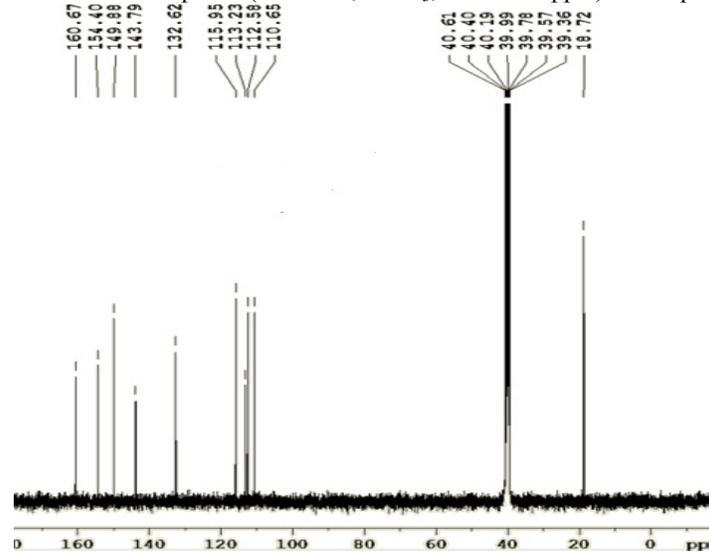


Figure 3:  $^{13}\text{C-NMR}$  specter (100 MHz,  $\text{CDCl}_3$ ,  $\delta\text{TMS} = 0$  ppm) of compound 1

**6.2. 6-hydroxy-1-methyl-3H-benzo[f]chromen-3-one (2)** yield 90% ( ethyl aceto acetate: n.hexane-6:4  
**IR(KBr) ( $\nu$ ,  $\text{cm}^{-1}$ ):**1730( $\text{C}=\text{O}$ ), 2925 ( $\text{C}_{\text{sp}^3}\text{-H}$ ), 3075( $\text{C}_{\text{sp}^2}\text{-H}$ ), 1068 ( $\text{C-O}$ ), 1535+1626 ( $\text{C}=\text{C}$  aromatic).

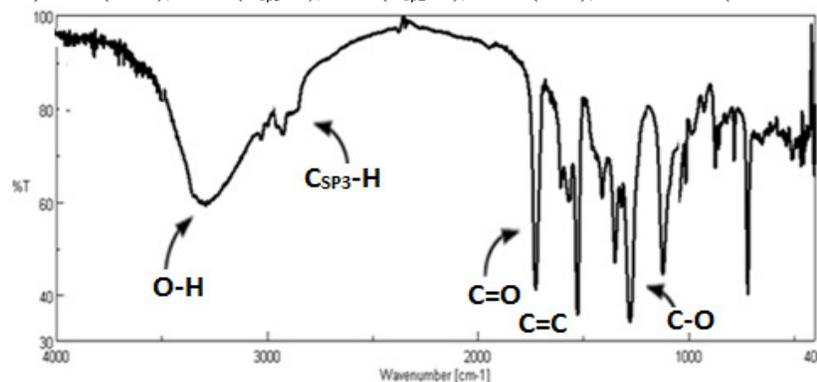


Figure 4: IR specter of compound 2

<sup>1</sup>H-NMR(DMSO-d<sub>6</sub>) (δ, ppm): 2.85 ppm (3H, s, CH<sub>3</sub>), 6.21 ppm (1H, s, H-2), 6.83(1H,s, H-3), 7.54 ppm (1H, t, 10 Hz, H-6), 7.69 (1H, t, 10 Hz, H-5), 8.23 (1H,d,8 Hz, H-7), 8.6 (1H,d, 8 Hz, H-4), 11.48 (s,OH),

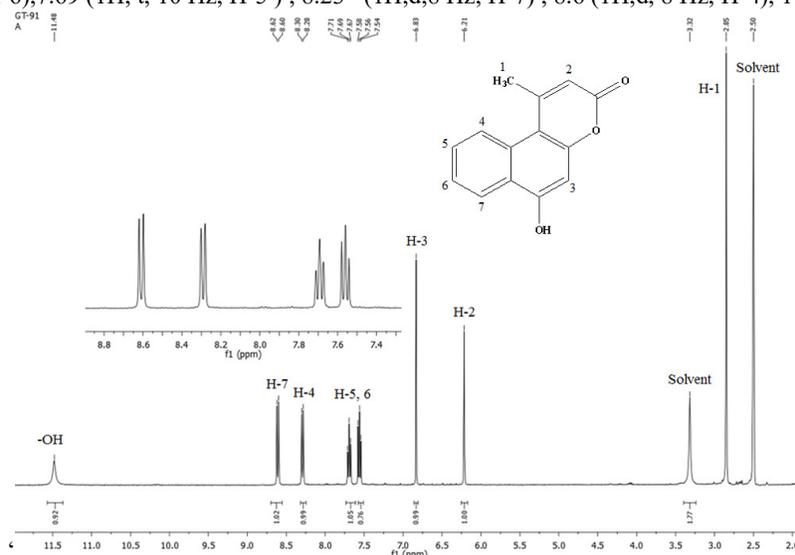


Figure 5: <sup>1</sup>H-NMR specter (400 MHz, CDCl<sub>3</sub>, δTMS = 0 ppm) of compound **1**  
<sup>13</sup>C -NMR (DMSO-d<sub>6</sub>): δ 26.10, 99.32, 107.47, 112.08, 123.55, 123.79, 125.01, 125.68, 129.03, 131.35, 155.41, 156.58, 158.28, 160.08. Melting point: 251–255 °C

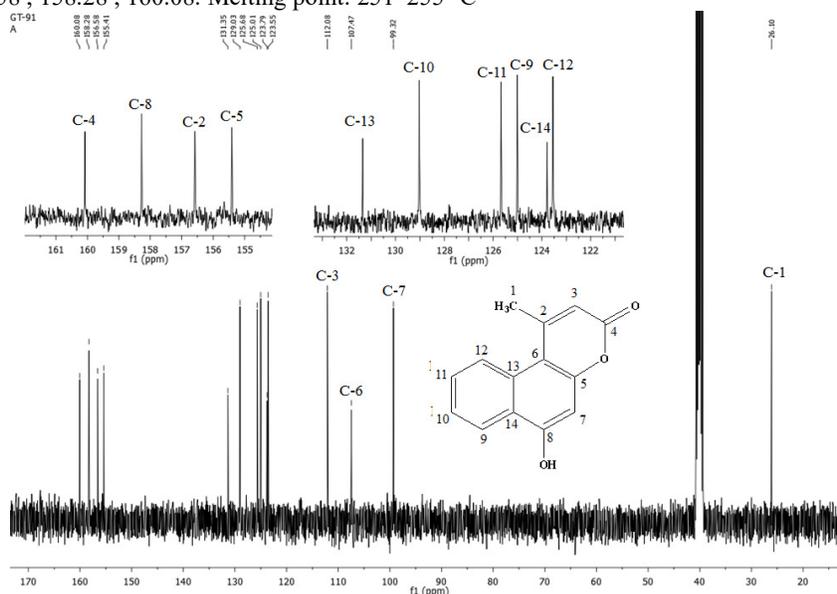


Figure 6: <sup>13</sup>C-NMR specter (100 MHz, CDCl<sub>3</sub>, δTMS = 0 ppm) of compound **1**

## 6. Acknowledgement

The author express his thanks to central laboratory in organic chemistry, department of chemistry, AL Baath University, faculty of sciences, for their assistance during the work.

## 7. References

- [1] R.I. Al-Bayati, A.A. Hussain Al-Amiery, Y.K. Al-Majedy, (2010). Design, synthesis and bioassay of novel coumarins, *J. African Pure and Applied Chemistry*. 4, 74-86.
- [2] G. Cravotto, G.M. Nano, G. Palmisano, S. Tagliapietra. (2001). An asymmetric approach to coumarin anticoagulants via hetero-Diels–Alder cycloaddition, *J. Tetrahedron: Asymmetry*. 12, 707–709.
- [3] O. Kayser, H. Kolodziej, (1997). Antibacterial Activity of Extracts and Constituents of *Pelargonium sidoides* and *Pelargonium reniforme*, *J. Planta Med.* 63, 508–510.
- [4] C. J. Wang, Y. J. Hsieh, C.Y. Chu, Y.L. Lin, T.H. Tseng, (2002). Inhibition of cell cycle progression in

- human leukemia HL-60 cells by esculetin, *J. Cancer Lett.* 183, 163–168.
- [5] G.J. Fan, W. Mar, M.K. Park, E. Wook Choi, K. Kim, S. Kim, (2001), A novel class of inhibitors for steroid 5 $\alpha$ -Reductase: synthesis and evaluation of umbelliferone derivatives, *J. Bioorg. Med. Chem. Lett.* 11, 2361–2363.
- [6] S. Kirkiacharian, D.T. Thuy, S. Sicsic, R. Bakhchinian, R. Kurkjian, T. Tonnaire, (2002), Structure–activity relationships of some 3-substituted-4-hydroxycoumarins as HIV-1 protease inhibitors, *J. Il Farmaco.* 57, 703–708.
- [7] S.M. Sethna, N.M. Shah, (1945), The Chemistry of Coumarins, *J. Chem. Rev.* 36, 1–62.
- [8] R.S. Overmann et.al, Studies on The Hemorrhagic Sweet Clover Disease: XIII. Anticoagulant Activity and Structure in The 4-Hydroxycoumarin Group, (1944) , *J. Biol.Chem.* 5, 153-158.
- [9] E. Werner, XXXVIII. (1887), Researches on chrom-organic acids, *J. Chem. Soc. Trans.* 51, 383-389, 1887.
- [10] J.D. Hepwarh, A. J. Boulton, A. McKillop, (1984), *Comprehensive Heterocyclic Chemistry Pergamon, Oxford.* 3 881.
- [11] R.S. Mali, V.J. Yadav, (1977), Convenient Synthesis of Naturally Occurring Coumarins, (2-Oxo-2H-benzopyrans) and 4-Methylcoumarins (4-Methyl-2-oxo-2H-benzopyrans), *J. Synthesis.* 12, 464-465.
- [12] R.L. Shriner, The Reformatsky Reaction, *J. Organic Reactions.* 1 (1942) 1–37.
- [13] S.E. Drewes, N.D. Emslie, N. Karodia, G. Loizou, (1990), Synthesis of Useful Intermediates from the Claisen-Rearrangement of  $\alpha$ -Hydroxy Alkyl Acrylate Precursors, *J. Synth.Comm.* 20, 1437-1443.
- [14] G. Speranza, A.D. Meo, S. Zanzola, G. Fontanna, P. Manitto, (1997), Uncatalyzed Reaction of Phenols and Naphthols with Methyl Cinnamates. A Simple Synthesis of 4-Arylchroman-2-ones and 1-Arylbenzo[f]chroman-3-ones, *J. Synthesis.* 931-936.
- [15] V. H. Pechmann, C. Duisberg, (1884), Neue Bildungsweise der Cumarine Synthese des Daphnetins, *J. Chem. Ber.* 17, 9, 29.
- [16] S. Trenor, A. Shultz, B. Love, T. Long, (2004), Coumarins in Polymers: From Light Harvesting to Photo-Cross-Linkable Tissue Scaffolds, *Chemical Reviews.* 104, 3059-3078.
- [17] J. Singh, S. Kaur, S. Nayyar, G. Kad, (1998), Highly Efficient and Single Step Synthesis of 4-Phenylcoumarins and 3,4-Dihydro-4-phenylcoumarins Over Montmorillonite K-10 Clay, Under Microwave Irradiation†, *J. Chem. Res.* 5, 280-281.
- [18] A. Khandekar, B. Khadilkar, (2002), Pechmann Reaction in Chloroaluminate Ionic Liquid, *J. Synlett.* 1, 0152-0154.
- [19] A. Ramani, B. Chanda, S. Velu, S. Sivasanker, (1999), One-pot synthesis of coumarins, *J. Green Chemistry,* 1, 163-165.
- [20] D. Subhas Bose, A. Rudradas, M. Hari Babu, (2002), The indium (III) chloride-catalyzed von Pechmann reaction: a simple and effective procedure for the synthesis of 4-substituted coumarins, *J. Tetrahedron Letters,* 43, 9195-9197.
- [21] D. Bogdał, Coumarins, (1998), Fast Synthesis by Knoevenagel Condensation under Microwave Irradiation, *J. Chem. Res.* 8, 468-469.
- [22] A. Hoefnagel, E. Gunnewegh, R. Downing, H. van Bekkum, (1995), Synthesis of 7-hydroxycoumarins catalysed by solid acid catalysts, *J. Chemical Society, Chemical Communications,* 2, 225.
- [23] Y. Rao, S. Kulkarni, M. Subrahmanyam, A. Rao, (1993), A novel acylative cyclization reaction of phenol over modified Y zeolites, *J. the Chemical Society, Chemical Communications.* 18, 456.
- [24] A. Hoefnagel, E. Gunnewegh, R. Downing, H. van Bekkum, (1995), Synthesis of 7-hydroxycoumarins catalysed by solid acid catalysts, *J. the Chemical Society, Chemical Communications.* 2, 225.
- [25] R. Pal, T. Sarkar, SH. Khashobis, Amberlyst-15-in organig synthesis, *J. arkivoc.* 1 (2012) 570-609.
- [26] K. Tanaka, F. Toda, (2000), Solvent-Free Organic Synthesis, *J. Chemical Reviews.* 100, 1025-1074.
- [27] A. Olah, G.K.S. Prakash, A. Molnar, J. (2009), *Sommer in Superacid Chemistry,* John Wiley & Sons, Inc.:Hoboken, NJ,.
- [28] R. Sabou, W. Hoelderich, D. Ramprasad, R. Weinand, (2005), Synthesis of 7-hydroxy-4-methylcoumarin via the Pechmann reaction with Amberlyst ion-exchange resins as catalysts, *J. Catalysis.* 232, 34-37.