

Synthesis of 3,3-Arylidene Bis(4-Hydroxycoumarin) Catalyzed by *p*-Dodecylbenzenesulfonic Acid (DBSA) in Aqueous Media and Microwave Irradiation

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Abstract

A series of 3,3-arylidene bis(4-hydroxycoumarins) were synthesized by the reaction of aromatic aldehydes with 4-hydroxycoumarin using dodecylbenzenesulfonic acid as Brønsted acid-surfactant catalyst in aqueous media and under microwave irradiation. The present method is operationally simple and the use of water as the reaction medium makes the process environmentally benign.

Keywords

3,3-Arylidene Bis(4-Hydroxycoumarin), 4-Hydroxycoumarin, Microwave Irradiation, *p*-Dodecylbenzenesulfonic Acid (DBSA), Aqueous Media

1. Introduction

Many of coumarin derivatives are biologically active [1] [2]. A great volume of studies have attempted to inhibit bacterial growth using naturally occurring coumarins, such as herniarin, umbelliferone and scopoletin on the antifungal activity of umbelliferone, scopoletin and coumarin itself [3] [4]. Some coumarin derivatives, including novobiocin and analogues, have been demonstrated to be very active as antibiotics [5]-[7]. Among synthetic derivatives, several antibacterial 3-acyl and 3-carba-moyl-4-hydroxycoumarins [8]-[12] have been described.

Bis-coumarins are generally prepared by condensing carbonyl compounds with 4-hydroxycoumarin in organic solvents [13] [14], which applied a large number of hazardous and toxic solvents related to catalysts. Several

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methods have been recently reported for such synthesis which includes use of different catalysts such as molecular iodine [15], MnCl_2 [16], strong tertiary amine base (DBU) [17], POCl_3 [18], diethyl aluminum chloride (Et_2AlCl_3) [19], LiClO_4 [20], SO_3H functionalized, ionic liquids [21], SDS [22], TBAB [23], $\text{Zn}(\text{Proline})_2$ [24], [bmim] $[\text{BF}_4]$ [25], sulfamic acid [26], $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ [27], SiO_2Cl [28], $\text{SiO}_2\text{-OSO}_3\text{H}$ NPs [29], Sulfated titania [30] refluxing in ethanol or acetic acid [31], thermal solvent-free microwave, ultrasound condition [32] [33] etc.

With the growing public concern about the environment, several synthesis methods using 4-hydroxycoumarin have been recently proposed for preparing biscoumarins in aqueous media. Despite the efficacy and eco-friendliness of these methods, they use catalysts including TEBA [34] and I_2 [35] and have long reaction times. Thus, it is still required to propose efficient and novel methods based on green methodology.

p-Dodecylbenzenesulfonic acid (DBSA) is a Brønsted acidsurfactant-combined catalyst, which is composed of an acidic group and a hydrophobic moiety. It could be explained that the inside of emulsion droplets composed of substrate and DBSA is hydrophobic enough to exclude water molecules. Therefore, surfactant-catalyzed organic reactions in water have turned to be one of the most challenging research issues. The behavior of DBSA as a catalyst has been studied in Mannich type reactions, Biginelli reaction, synthesis of bis (indol-3-yl) alkanes, tetrahydrobenzo [*b*] pyrans, dihydropyrano [*c*] chromens, xanthenes derivatives and esterification of various carboxylic acids and alcohols [36]-[42]. In the present work, these results were reported for the synthesis of 3,3-Arylidene bis(4-hydroxycoumarin) derivatives by DBSA in environmentally benign conditions and under microwave irradiation.

2. Result and Discussion

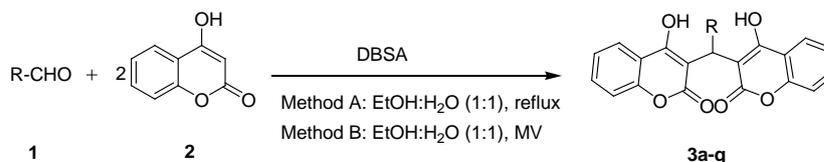
In this paper, efficient method was tried to be proposed for the condensation of aldehydes with 4-hydroxycoumarin, which led to the corresponding 3,3-arylidene bis(4hydroxycoumarin) in the presence of DBSA as a homogeneous catalyst in two methods (A, B) (Scheme 1). DBSA was used as a source of H^+ to catalyze this reaction and found to be a good catalyst for the preparation of 3,3-arylidene bis(4-hydroxycoumarin).

Initially, the systematic evaluation of different solvents for the model reaction of 3-nitro benzaldehyde and 4-hydroxycoumarin in the presence of DBSA in water at reflux was focused on. Attempts were made to study and optimize the reaction conditions in order to show that performing the reaction in H_2O with low yield while using the amounts of EtOH in the media produced satisfactory results (Table 1, entry 6). These results revealed that the highest yield was obtained with the water/ethanol (1:1) solvent system (Table 1, entry 6).

Since DBSA was emerged as a suitable catalyst for the reaction in 1:1 ethanol/water media, then efforts were made to optimize the catalyst load for the condensation reaction, leading to the rapid formation of 3,3-arylidene bis(4-hydroxycoumarin). The present optimization studies revealed that the yield smoothly increased with the catalyst load up to 25 mol% and the use of larger amounts of the catalyst did not improve the yields, while its decreasing amount decreased the yields. The negligible amount of the product was formed in the absence of catalyst.

To find the specific effect of microwave irradiation on the reaction, these reactions were carried out under the same conditions in a microwave oven (Table 1, entry 13) and it was observed that, while the reaction time considerably decreased, the yields of the product slightly increased. Thus, MW conditions had a beneficial effect on this reaction. Afterward, concentration was within the scope of this reaction with the variety of aldehydes (Scheme 1) in order to check the viability of this protocol in obtaining a library of 3,3-arylidene bis(4-hydroxycoumarin) derivatives in two methods (Table 2).

As can be seen in Table 2, a range of dicoumarols was synthesized using different aldehydes and 4-hydroxycoumarin under the standardized reaction. The results are summarized in Table 2. Regardless of the nature of the substitution (electron donating and electron withdrawing) of the aromatic aldehydes, the products were obtained in good to excellent yields (entries 1 - 17). Similar results were also obtained in the microwave condition



Scheme 1. Synthesis of 3,3-arylidene bis(4-hydroxycoumarin).

Table 1. Optimization of reaction condition on the yield of 3,3-arylidene bis(4-hydroxycoumarin).

Entry	Catalyst	Solvent	Temperature	Time (min)	Yield (%) ^a
1	without DBSA	H ₂ O	reflux	240	trace
2	DBSA (25%)	H ₂ O	reflux	75	85
3	DBSA (25%)	EtOH	r.t.	120	trace
4	DBSA (25%)	EtOH	reflux	60	87
5	DBSA (25%)	MeOH	reflux	105	80
6	DBSA (25%)	EtOH:H ₂ O (1:1)	reflux	40	94
7	DBSA (25%)	MeOH:H ₂ O (1:1)	reflux	65	90
8	DBSA (25%)	EtOH:H ₂ O (1:1)	r.t.	40	trace
9	DBSA (10%)	EtOH:H ₂ O (1:1)	reflux	40	68
10	DBSA (15%)	EtOH:H ₂ O (1:1)	reflux	40	70
11	DBSA (20%)	EtOH:H ₂ O (1:1)	reflux	40	72
12	DBSA (30%)	EtOH:H ₂ O (1:1)	reflux	40	93
13	DBSA (25%)	EtOH:H ₂ O (1:1)	MV condition	12	95

^aIsolated yield.**Table 2.** Synthesis of 3,3-arylidene bis(4-hydroxycoumarin) by condensation of aldehydes and 4-hydroxycoumarin using DBSA (25 mol%) as catalyst.

Entry	R	Product	Method A Time (min)/yield (%)	Method B Time (min)/yield (%)	M.P. (°C) Found	M.P. (°C) Reported
1	C ₆ H ₅ -	3a	60/80	6.5/84	232 - 234	230 - 232 [22]
2	3-NO ₂ C ₆ H ₄ -	3b	45/90	7.5/80	234 - 236	234 - 236 [22]
3	4-NO ₂ C ₆ H ₄ -	3c	60/90	4.5/90	237 - 240	232 - 234 [22]
4	3-BrC ₆ H ₄ -	3d	60/87	7.0/92	225 - 228	287 [12]
5	4-ClC ₆ H ₄ -	3e	60/85	5.5/76	258 - 260	256 - 258 [22]
6	2,4-(Cl) ₂ C ₆ H ₃ -	3f	90/88	8.0/85	190 - 195	198 - 200 [29]
7	2,6-(Cl) ₂ C ₆ H ₃ -	3g	45/90	6.0/93	125 - 130	178 - 180 [28]
8	2-MeC ₆ H ₄ -	3h	90/85	8.5/83	218 - 220	221 - 223 [22]
9	4-MeC ₆ H ₄ -	3i	78/85	6.5/85	266 - 265	266 - 268 [22]
10	2-MeOC ₆ H ₄ -	3j	90/80	8.0/82	213 - 215	214 - 215 [13]
11	4-MeOC ₆ H ₄ -	3k	90/87	8.0/90	249 - 251	246 - 248 [22]
12	2,4-(MeO) ₂ C ₆ H ₃ -	3l	120/75	10.0/75	203 - 205	197 - 198 [13]
13	3,4,5-(MeO) ₃ C ₆ H ₂ -	3m	120/70	9.0/68	240 - 245	241 - 243 [13]
14	2-HOC ₆ H ₄ -	3n	90/86	8.5/88	250 - 255	254 - 256 [15]
15	4-(Me ₂ N)C ₆ H ₄ -	3o	90/80	8.5/87	210 - 215	216 - 217 [26]
16	Propionaldehyde	3p	60/87	6.0/92	140 - 142	144 - 146 [27]
17	2-(Prop-2-ynyloxy)-C ₁₀ H ₆ -	3q	150/60	15/78	168 - 172	-

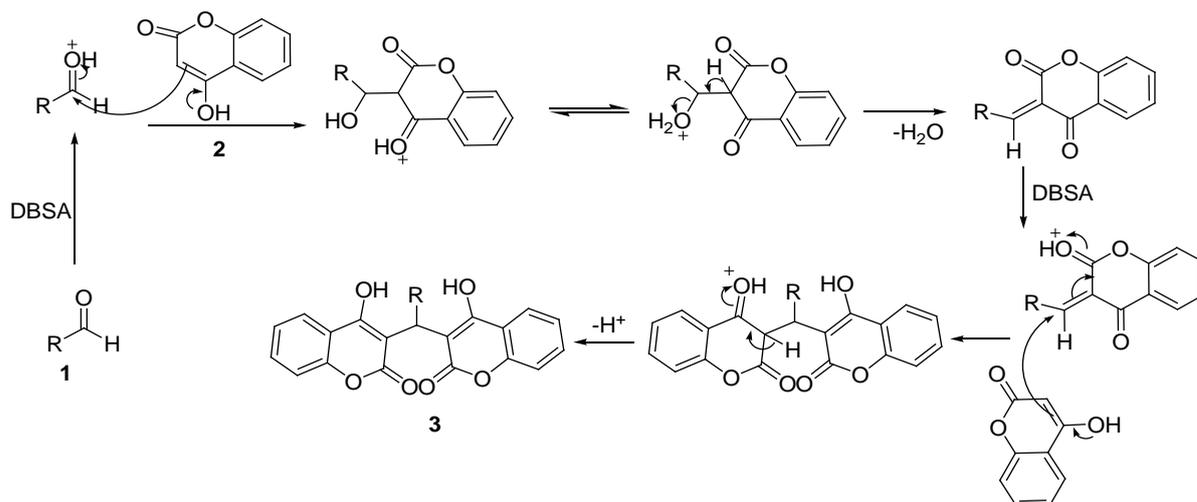
Method A: EtOH:H₂O (1:1), reflux; Method B: EtOH:H₂O (1:1), MV.

(Method B). All the reactions were completed within 45 - 150 min and 4.5 - 15 min in Methods A and B, respectively. In these reactions, there was no need for the column purification of the products. The obtained solid products were just filtered off from the reaction mixture, dissolved in hot ethanol, refiltered to separate any contaminated catalyst with the product and finally recrystallized from the filtrate to obtain pure dicoumarols.

According to the proposed mechanism, the formation of 3,3-arylidene bis(4-hydroxycoumarin) could be rationalized from the Knoevenagel condensation of aromatic aldehydes with 4-hydroxycoumarin in the presence of DBSA and followed by Michele addition of the second 4-hydroxycoumarin (**Scheme 2**).

To show the advantage of the present work in comparison with the reported results in the literature, the results of DBSA with reflux in ethanol or acetic acid, iodine, DBU, SDS, TBAB, $\text{TiO}_2/\text{SO}_4^{2-}$ and SiO_2/Cl were compared in terms of the synthesis of biscoumarin derivatives. As shown in **Table 3**, DBSA can act as an effective catalyst with respect to reaction time, yields and the obtained products.

In conclusion, DBSA was demonstrated a new efficient catalyst for the synthesis of dicoumarols, prepared via the condensation reaction of aromatic aldehyde and 4-hydroxycoumarin using DBSA as a homogeneous catalyst under aqueous media and microwave conditions. These conditions had advantages such as shorter reaction time, simpler work-up, inexpensive and non-toxic catalysis, environmental benignity and excellent yields.



Scheme 2. Proposed mechanism.

Table 3. Comparison of our results with some of those reported in the literature for the reaction of 4-nitro benzaldehyde, malononitrile and 4-hydroxycoumarin.

Entry	Reaction condition	Yield (%)	Time	Ref.
1	Reflux ethanol or acetic acid	71	5 - 6 h	[30]
2	I ₂ (10 mol%), H ₂ O, 100°C, 1.01 × 10 ⁵ Pa	71	28 min	[15]
3	DBU, r.t.	-	-	[32]
4	SDS (20 mol%), water, 60°C	98	3	[22]
5	TBAB, water	91	25 min	[23]
6	TBAB, solvent-free	91	21 min	[23]
7	TiO ₂ /SO ₄ ²⁻ , H ₂ O, 80°C	88	30	[30]
8	SiO ₂ Cl, CH ₂ Cl ₂ , 40°C	85	3.5	[28]
9	DBSA (25 mol%), H ₂ O:Ethanol, 80°C	90	60 min	this work
10	DBSA (25 mol%), H ₂ O:Ethanol, MV	90	4.5 min	this work

3. Experimental

3.1. Instruments and Characterization

IR spectra were recorded on a Perkin-Elmer FT-IR 240-C spectrophotometer (KBr). $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were run on Bruker spectrometers at 400 MHz for $^1\text{H-NMR}$ and 100 MHz for $^{13}\text{C-NMR}$. The melting points were determined using an Electrothermal 9100 apparatus. The reactions were monitored by thin layer chromatography and the products were identified either fully or in the comparison of melting points and spectroscopic data with the previously reported ones.

3.2. General Procedure for the Synthesis of 3,3-Arylidene Bis(4-Hydroxy-2Hchromen-2-Ones) Derivatives (Method A)

A mixture of 4-hydroxycoumarin (2 mmol, 0.324 g), substituted benzaldehydes (1 mmol, 0.106 g), and DBSA (0.25 mmol, 0.326 g) was stirred at reflux in 5 ml ethanol-water mixture (1:1). The progress of the reaction was monitored by TLC. After the reaction completion and upon its cooling, the solid material was precipitated from the solution. The precipitates were filtered off, washed with water, and were recrystallized from EtOH to obtain pure 3,3-arylidene bis(4-hydroxy-2Hchromen-2-ones) derivatives as yellow-white solids (60% - 90% yields).

3.3. General Procedure (Method B)

A mixture of 4-hydroxycoumarin (2 mmol, 0.324 g), substituted benzaldehydes (1 mmol, 0.106 g), and DBSA (0.25 mmol, 0.326 g) in 5 ml ethanol-water mixture (1:1) was inserted in a microwave oven (Samsung, Model KE300R) at 450 W for an appropriate period of time (Table 1, Method B). The reaction was followed by TLC. After the reaction completion, its mass was cooled down to 25°C. The solid residue were filtered off, washed with water, and were recrystallized from EtOH (68% - 93% yields).

3.4. The Spectral Data of Unreported Compound 3q

4-hydroxy-3-(((4-hydroxy-2-oxo-2H-chromen-3-yl)(2-(prop-2-ynyloxy)naphthalen-3-yl)methyl)-2H-chromen-2-one (3q): Mp = 168°C - 172°C. IR (KBr, cm^{-1}): 3450, 3271, 3074, 2148, 1661. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ = 1.58 (s, 1H, CH), 2.34 (t, 1H, J = 2.4 Hz, $\equiv\text{CH}$), 4.56 (dd, J = 9.6, 2.4 Hz, $\text{CH}_2\text{-O}$), 6.44 (m, 2H, H-arom), 7.37 - 7.43 (m, 6H, H-arom), 7.64 - 7.69 (m, 4H, H-arom), 8.06 (s, 2H, H-arom), 10.90 (s, 1H, OH), 11.75 (s, 1H, OH). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ : 34.3, 56.9, 116.6, 116.7, 118.0, 118.1, 119.2, 124.3, 124.4, 124.5, 124.7, 124.8, 124.9, 130.9, 132.6, 132.9, 130.1, 132.6, 132.9, 133.1, 133.8, 135.2, 152.1, 152.2.

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