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Section A: Green Chemistry

Research Article

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Tannic acid: An Efficient Catalyst for the Synthesis of Bis-(4-hydroxycoumarin-3-yl)methanes

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Abstract: Tannic acid catalyzed one-pot synthesis of bis-(4-hydroxycoumarin-3-yl)methanes, from aromatic aldehyde, and 4- hydroxycoumarine in the presence of tannic acid (5mol %) as a catalyst was stirred at reflux temperature in ethanol:water (1:1) for specified period of time. The notable advantages of this method are the experimental simplicity, inexpensive reagents, short reaction times and easy workup procedure.

Keywords: Multi-component reactions, aromatic aldehyde, Bis-(4-hydroxy coumarin-3-yl)methanes, Tannic acid.

INTRODUCTION

Recently, coumarin derivatives have received attention because of their biological importance and numerous pharmacological activities like anticoagulant, anti-HIV and anticancer agents[1]. Coumarin and its derivatives are widely used as additives to food, cosmetics, and optical brightening agents[2].

These compounds are also utilized as urease inhibitors[3]. A number of methods have been reported for the synthesis of these compounds in the presence of various catalysts like molecular iodine like molecular iodine[4], tetrabutylammonium bromide (TBAB)[5] Manganous chloride ($MnCl_2$ $4H_2O$) [6] sodium dodecyl sulfate(SDS) [7], tetrabutylammoniumhexatungstate ($[TBA]_2[W_6O_{19}]$)[8], sulfated titania(TiO_2/SO_4) [9], ruthenium(III) chloride hydrate ($RuCl_3 \cdot nH_2O$)[10], Cobalt(II) chloride hexahydrate [11], tungstate sulfuric acid[12], $NaHSO_4.SiO_2$/ Indion 190 resin[13], Fe_3O_4 nanoparticles[14] Nano TiO_2@KSF [15] Boron Sulfonic Acid [16]. Although various procedures are reported for the synthesis of bis-(4-hydroxycoumarin)methanes, disadvantages including low yields of products, long reaction times, nonrecyclable catalyst, use of an excess of reagents or catalysts, and harmful and corrosive solvents.

Hence, many organic reactions have been carried out using tannic acid as catalyst, such as in the synthesis of Synthesis of 2,4,5-Triaryl-1H-Imidazole[17], 12-aryl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one[18], 1-amidoalkyl-2-naphthols catalyzed[19], 2,3-dihydroquinazolin-4(1*H*)-ones[20]. Tannic acid was found to be non-toxic, cheap and efficient catalyst for many organic reactions. In view of the emerging importance of tannic acid as a catalyst, we wish to report a mild and highly efficient method for the synthesis of Bis-(4-hydroxycoumarin-3-yl) methane.

EXPERIMENTAL

Chemicals were purchased from Merck, Fluka and Aldrich chemical companies. All yields refer to isolated products unless otherwise stated. Melting points were determined in an open capillary. ^1H nuclear magnetic resonance (NMR) (500 MHz) with tetramethylsilane as internal standard and dimethylsulfoxide DMSO-d6 as solvent. Fourier transform infrared (IR) spectra were obtained as KBr discs on a Shimadzu spectrometer. Mass spectra (MS) were determined on a Varion-Saturn 2000 GC/MS instrument.

General Procedure: A mixture of subsutited aromatic aldehyde (1mmol), and 4- hydroxycoumarine (1mmol) in the presence of tannic acid (5mol %) as a catalyst was stirred at reflux temperature in ethanol: water (1:1) (10 ml) for 25-40 minutes. After the appropriate time, the mixture was cool than poor on ice cold water solidified the product filtered its 3(a-o). The crude solid material was purified by recrystallization from ethanol.

RESULTS AND DISCUSSION

In continuation of our previous studies on catalysed organic reactions, we found that the condensation reaction of 4-hydroxycoumarin (1) and aromatic aldehyde, (2) in the presence of catalytic amounts of tannic acid leads to bis-(4-hydroxycoumarin-3-yl) methanes derivatives (3) **(Scheme 1).**

Initially, we used 4-hydroxycoumarin (1) and 4- chlorobenzaldehyde as the model reaction system to investigate the reaction at 0, 2.5, 5, 7.5 and 10 mol% of tannic acid in ethanol:Water (1:1 v:v)at reflux temperature. The product was obtained in 0, 65, 96 and 96% yield, respectively. This indicates that the use of 5 mol% of tannic acid is sufficient to promote the reaction forward (Table 1) conditions.

To determine the effect of solvent, various solvents such as dioxane, tetrahydrofuran, dichloromethane, acetonitrile, methanol, ethanol, water, ethanol: water (1:3,v:v), ethanol:water (1:2,v:v) and ethanol: water (1:1,v:v) were used for the model reaction. Ethanol: water (1:1) stand out as the solvent of choice among the solvents tested because of the rapid conversion and excellent yield

(96%) of desired product, whereas the product formed in lower yields (0~90%) by using other solvents (**Table 2, Entry 1~9**).

To study the generality of this process, variety of examples were illustrated for the synthesis of bis-(4-hydroxycoumarin-3-yl) methane and the results are summarized in Table3. The reaction is compatible for various substituents such as $-CH_3$, $-OCH_3$, -OH, $-N(CH_3)_2$,-Br,-Cl and hetroaldehyde. The formation of desired product has been confirmed by ^1H NMR and IR spectroscopic analysis techniques and compared with the corresponding literature data.

Table 1: Optimization of the amount of tannic acid for the synthesis of bis-(4-hydroxycoumarin-3-yl)methanes.

Entry	Amount of catalyst (mol%)	Time (min)	Yield(%)
1	0	30	0
2	2.5	30	65
3	5	30	96
4	7.5	30	96
5	10	30	96

Table 2: Screening of solvents for the synthesis of of bis-(4-hydroxycoumarin-3-yl)methanes.

Entry	Solvent	Yield (%)
1	Dioxane	Trace
2	Tetrahydrofuran	Trace
3	Dichloromethane	Trace
4	Acetonitrile	25
5	Methanol	75
6	Ethanol	86
7	Water	65
8	Ethanol: water (1:3,v:v)	77
9	Ethanol: water (1:2,v:v)	90
10	Ethanol: water (1:1,v:v)	96

Table 3. Synthesis of Bis(4-hydroxycoumarin-3-yl)methanes using tannic acid

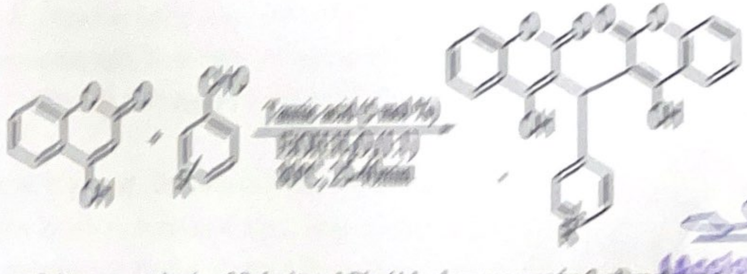
Entry	Ar-CHO	Product	Time (min)	Yield[b] (%)	M.P. °C
1	C_6H_5	3a	30	95	[illegible]
2	4-ClC_6H_4	3b	25	96	[illegible]
3	4-$NO_2C_6H_4$	3c	30	96	[illegible]
4	4-$OCH_3C_6H_4$	3d	30	92	[illegible]
5	4-$CH_3C_6H_4$	3e	35	96	[illegible]
6	4-BrC_6H_4	3f	30	92	[illegible]
7	2-ClC_6H_4	3g	30	90	[illegible]
8	3-$NO_2C_6H_4$	3h	25	91	[illegible]
9	4-$(CH_3)_2NC_6H_4$	3i	40	90	[illegible]
10	4-HOC_6H_4	3j	35	92	[illegible]
11	2-HOC_6H_4	3k	30	96	[illegible]
12	2-BrC_6H_4	3l	25	90	[illegible]
13	3-$CH_3OC_6H_4$	3m	35	91	[illegible]
14	Furan-2-carbaldehyde	3n	30	95	[illegible]
15	Thiophene-2-carbaldehyde	3o	25	95	[illegible]

[a]Reaction conditions: 1 (2 mmol), 2 (1 mmol), Tannic acid (5%), ethanol at reflux temperature;
[b]Isolated yields

Spectral data

Compound 3a: ^1H NMR: (DMSO-d_6) δ= 6.30 (s, 1H), 6.92-7.10 (m, 13H). ^{13}C NMR: (DMSO-d_6) δ= 15.0, 92.0, 106.2, 107.1, 115.0, 117.2, 125.0, 126.4, 127.1, 128.4, 128.7, 131.0, 152.4, 140.0, 164.1, 166.3. IR (KBr): 3040, 1660, 1615, 746.

Compound 3b: ^1H NMR: (DMSO-d_6) δ = 6.17 (s, 1H), 7.22-7.92 (m, 12H). ^{13}C NMR: (DMSO-d_6) δ = 16.7, 91.2, 103.3, 107.5, 115.5, 118.7, 124.5, 125.5, 126.1, 127.3, 128.1, 131.0, 134.4, 139.6, 165.0, 167.1. IR (KBr): 3038, 1660, 1607, 755.



Scheme: synthesis of Substituted Bis(4-hydroxycoumarin-3-yl)methanes

Table 3. Synthesis of bis-(4-hydroxycoumarin-3-yl)methanes using tannic acid

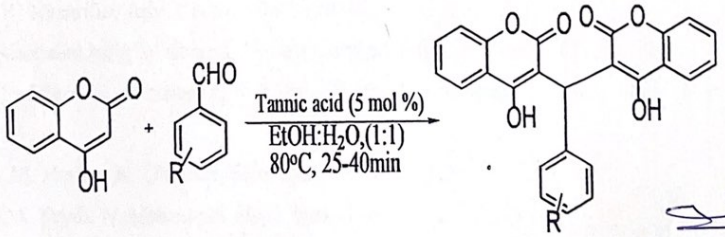
Entry	Ar-CHO	Product	Time (min)	Yield (%)	M.P °C
1	C_6H_5	3a	30	93	228-230
2	4-ClC_6H_4	3b	25	96	252-254
3	4-$NO_2C_6H_4$	3c	20	96	232-234
4	4-$CH_3OC_6H_4$	3d	30	95	242-244
5	4-$CH_3C_6H_4$	3e	35	94	271-273
6	4-BrC_6H_4	3f	30	92	266–268
7	2-ClC_6H_4	3g	30	90	224–226
8	3-$NO_2C_6H_4$	3h	25	91	234–236
9	4-$(CH_3)_2NC_6H_4$	3i	40	90	222–224
10	4-HOC_6H_4	3j	35	92	222-224
11	2-HOC_6H_4	3k	30	94	254-256
12	2-BrC_6H_4	3l	25	90	257-259
13	3-$CH_3OC_6H_4$	3m	35	91	238-240
14	Furan-2-carbaldehyde	3n	30	95	199-201
15	Thiophene-2-carbaldehyde	3o	25	93	212 (d)

[a]***Reaction conditions:*** **1 (2 mmol), 2 (1 mmol), Tannic acid (5%) ethanol at reflux temperature;**
[b]**Isolated yields**

Spectral data

Compound 3a: ^{1}H NMR: (DMSO-d_6): δ= 6.30 (s, 1H), 6.82–7.42 (m, 13H). ^{13}C NMR: (DMSO-d_6): δ= 15.0, 92.0, 106.2, 107.1, 115.0, 117.2, 125.0, 124.4, 127.1, 128.0, 128.7, 131.0, 132.4, 140.0, 164.1, 166.3. IR (KBr): 3040, 1660, 1615, 744.

Compound 3b: ^{1}H NMR: (DMSO-d_6): δ = 6.17(s,1H), 7.22–7.92 (m, 12H). ^{13}C NMR: (DMSO-d6): δ = 16.7, 91.2, 105.3, 107.5, 115.5, 118.7, 124.5, 125.5, 126.1, 127.3, 128.1, 131.0, 134.4, 139.6, 163.0, 167.1.IR (KBr): 3038, 1660, 1607, 755.



Scheme: synthesis of Substituted Bis-(4-hydroxycoumarin-3-yl)methanes

CONCLUSION

Tannic acid is an easily available, inexpensive and efficient catalyst for the synthesis of Bis-(4-hydroxycoumarin-3-yl)methanes derivatives from various aryl aldehyde and 4- hydroxycoumarine (1mmol) in the presence of tannic acid (5mol %) as a catalyst was stirred at reflux temperature in ethanol: water (1:1) (10 ml) for 25-40 minutes. The remarkable advantages offered by this method are the use of safer catalyst, short reaction times, ease of product isolation, and high yields. We believe that this method is a useful addition to the present methodology for the synthesis of Bis-(4-hydroxycoumarin-3-yl)methanes.

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