

Research Article

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Green synthesis of 3-(1-naphthyl), 4-methyl-3-(1-naphthyl) coumarins and 3-phenylcoumarins using dual-frequency ultrasonication

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Abstract: Green synthesis of 3-(1-naphthyl), 4-methyl-3-(1-naphthyl) coumarins and 3-phenylcoumarins has been carried out in one step by reacting 2-hydroxybenzaldehydes and 2-hydroxyacetophenones with 1-naphthylacetic anhydride and phenylacetic anhydride, respectively, using dual-frequency ultrasonication, i.e. ultrasonic bath of 40 kHz and probe of 20 kHz. The compounds were obtained in very high yield (80–90%) and their structures were confirmed by infrared and nuclear magnetic resonance data.

Keywords: ultrasonication, naphthyl coumarins, 1-naphthylacetic anhydride, 3-phenylcoumarins, phenylacetic anhydride

1 Introduction

Pyrone ring fuses with benzene nucleus to form a class of heterocyclic compounds known as benzopyrones, of which benzo- α -pyrones, commonly called coumarins, comprise a vast class of compounds. Coumarin was first extracted from tonka beans [1] and its derivatives are known to exhibit a variety of medicinal, physicochemical and phytochemical properties [2–5]. 3-(1-Naphthyl) coumarins were first reported by Spenger et al. [6] and are known for their anticoagulant properties. 3-Phenylcoumarins have diverse applications. They play significant role in photoconduction [7] and exhibit fungicidal

[8], anti-HIV6 [9], anti-oxidant, anti-proliferative [10], vasorelaxant and platelet anti-aggregatory activities [11] and also inhibitory activities like inhibition of thromboplastin-induced disseminated intravascular coagulation [12], monoamine oxidase inhibition, [13] etc. Recently, 3-phenylcoumarins have also been studied for their antibacterial properties [14].

Naphthyl coumarins have been synthesised earlier by condensation of 2-methoxybenzaldehydes, 2-hydroxybenzaldehydes or 2-hydroxyacetophenone with 1-naphthylacrylonitrile [15], 1-*N,N*-diethyl(1-naphthyl)acetamide [16] or 1-naphthylacetic anhydride [17]. Phenyl coumarins have been synthesised by condensation of phenyl acetic acid or phenyl acetic anhydride or acetothiomorpholide with 2-hydroxybenzaldehydes using different bases like $\text{PhPOCl}_2/\text{Et}_3\text{N}$, K_2CO_3 , etc. and solvents like benzene [18–20]. Microwave irradiation has also been used for the synthesis of 3-phenyl and 3-naphthylcoumarins using DMSO as solvent [21]. Another method involves esterification of 2-hydroxybenzaldehydes in the presence of POCl_3 -pyridine followed by cyclisation of 2-arylacetoxysalicylaldehyde with KOH in pyridine [22]. The methods above have disadvantages like the use of hazardous solvents, longer reaction time, lower yields, etc.

In continuation of our work on the development of simple and efficient routes for the green synthesis of naturally occurring compounds using ultrasonication, we propose to report our efforts towards one-pot green synthesis of 3-(1-naphthyl), 4-methyl-3-(1-naphthyl) coumarins and 3-phenylcoumarins using ultrasound irradiation. The reaction rates of various chemical transformations like synthesis of α , β unsaturated compounds [23], 3-substituted indoles [24], oxidation and reduction reactions [25], Mannich-type reactions [26], triazole derivative synthesis [27,28], nanomaterial synthesis [29], Michael addition reactions [30], coupling reactions [31], extraction of caffeine [32], etc. have been enhanced using ultrasound activation.

This great technique has proved to be extraordinary in terms of operational simplicity, selectivity, reaction

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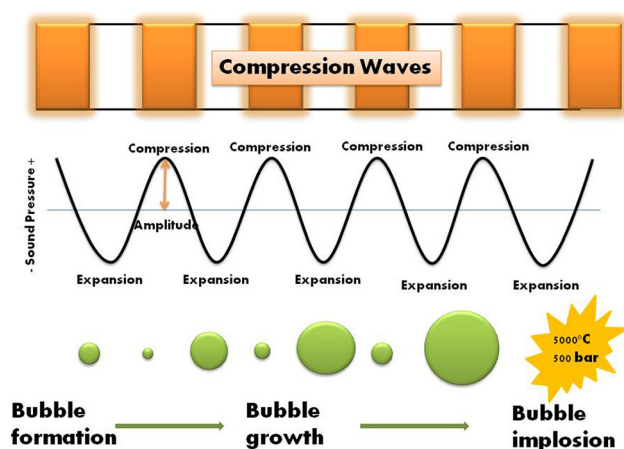


Figure 1: Cavitation process.

time, and yield and excludes the use of hazardous chemicals. During the propagation of ultrasonic waves, compressions and rarefactions, i.e. an alternating zone of high pressure and low pressure, are produced due to longitudinal vibrations of molecules. The formation of cavities or bubbles takes place due to low pressure, which expand and finally collapse ferociously during the compression phase producing shock waves. This phenomenon of bubble formation and violent collapsing is referred to as cavitation (see Figure 1) and is responsible for most of the ultrasonic physical and chemical effects [33]. Dual frequency has synergistic effects in comparison to simple ultrasonication as it reduces reaction time [34] and also enhances cavitation effect [35].

2 Materials and methods

All starting materials and common laboratory chemicals were purchased from commercial sources and used without any purification. Melting points were determined in open capillary tubes and were uncorrected. Proton nuclear

magnetic resonance (^1H NMR) spectra were recorded on Baker advance (400 MHz) instruments using trimethyl silane (TMS) as an internal standard. Infrared (IR) spectra were recorded on PerkinElmer Fourier transform IR (FT-IR) spectrophotometer. Sonication was performed using an Oscar-make probe sonicator of 20 kHz and Labsoul-make ultrasonic bath of 40 kHz. When combined ultrasound experiments were performed, the probe was immersed in the test tube placed in ultrasonic bath.

2.1 General procedure for the synthesis of 3-(1-naphthyl), 4-methyl-3-(1-naphthyl) coumarins and 3-phenylcoumarins

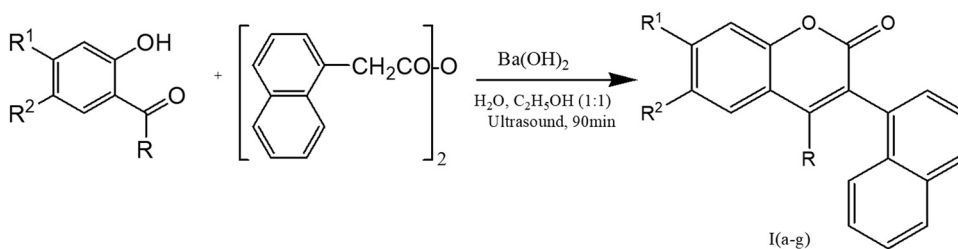
A mixture of salicylaldehyde (4.0 mmol), 1-naphthylacetic anhydride (4.0 mmol) and activated $\text{Ba}(\text{OH})_2$ (C-200-0.5 g) in equimolar mixture of ($\text{C}_2\text{H}_5\text{OH}-\text{H}_2\text{O}$) (1:1) (30 mL) was irradiated with dual-frequency ultrasound by keeping the above mixture in ultrasonic bath operating at 40 kHz and simultaneously irradiating 20 kHz frequency from probe-type ultrasonicator in the same test tube containing the mixture for 90 min. The progress and completion of reaction were checked by thin-layer chromatography. Then the mixture was poured into cold water and acidified with hydrochloric acid. So formed, the precipitates were filtered, dried and recrystallised from methanol to get 3-(1-naphthyl) coumarin as a colourless solid. A similar reaction between 2-hydroxyacetophenone and 1-naphthylacetic anhydride provided 4-methyl-3-(1-naphthyl) coumarin. Substituted 3-(1-naphthyl) coumarins and 4-methyl-3-(1-naphthyl) coumarins were synthesised, whose structures were confirmed by IR and ^1H NMR (CDCl_3).

• 3-(1-Naphthyl)coumarin (**Ia**)

IR (KBr) cm^{-1} : 1,718 ($\text{C}=\text{O}$), ^1H NMR (CDCl_3) δ , ppm: 7.27–7.94 (m, 12H, Ar-H and H-4).

• 7-Methyl-3-(1-naphthyl)coumarin (**Ib**)

IR (KBr) cm^{-1} : 1,719 ($\text{C}=\text{O}$), ^1H NMR (CDCl_3) δ , ppm: 2.38 (s, 3H, CH_3) and 7.31–7.92 (m, 11H, Ar-H and H-4).

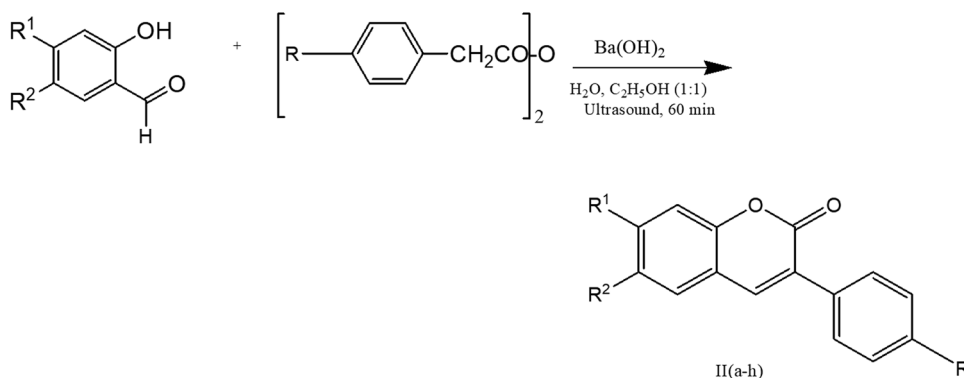


Scheme 1: Synthesis of 3-(1-naphthyl), 4-methyl-3-(1-naphthyl) coumarins.

Table 1: Characterisation of data of compounds I (a–g)

Compound	R	R ¹	R ²	M.Pt. (lit) (°C)	IR (cm ⁻¹): (C=O)	Yield (%)	¹ H NMR (CDCl ₃) δ (ppm)
Ia	H	H	H	153–154 (154–155) [17]	1,718	85	7.27–7.94 (m, 12H, Ar–H and H-4)
Ib	H	H	CH ₃	131–132 (132–133) [17]	1,719	80	2.38 (s, 3H, CH ₃) and 7.31–7.92 (m, 11H, Ar–H and H-4)
Ic	H	OCH ₃	H	149–150 (151–153) [17]	1,718	80	3.82 (s, 3H, OCH ₃) and 7.1–7.84 (m, 11H, Ar–H and H-4)
Id	H	H	Cl	152–154 (153–154) [17]	1,719	84	7.28–7.96 (m, 11H, Ar–H and H-4)
Ie	H	H	Br	123–125 (126–127) [17]	1,720	82	7.21–7.95 (m, 11H, Ar–H and H-4)
If	CH ₃	H	H	187–189 (188–90) [17]	1,718	82	2.16 (s, 3H, CH ₃) and 7.30–7.93 (m, 11H, Ar–H and H-4)
Ig	CH ₃	H	Cl	184–186 (185–186) [17]	1,718	84	2.14 (s, 3H, CH ₃) and 7.39–7.96 (m, 10H, Ar–H and H-4)

- 8-Methoxy-3-(1-naphthyl)coumarin (**Ic**)
IR (KBr) cm⁻¹: 1,718 (C=O), ¹H NMR (CDCl₃) δ, ppm: 3.82 (s, 3H, OCH₃) and 7.1–7.84 (m, 11H, Ar–H and H-4).
- 7-Chloro-3-(1-naphthyl)coumarin (**Id**)
IR (KBr) cm⁻¹: 1,719 (C=O), ¹H NMR (CDCl₃) δ, ppm: 7.28–7.96 (m, 11H, Ar–H and H-4).
- 7-Bromo-3-(1-naphthyl)coumarin (**Ie**)
IR (KBr) cm⁻¹: 1,720 (C=O), ¹H NMR (CDCl₃) δ, ppm: 7.21–7.95 (m, 11H, Ar–H and H-4).
- 4-Methyl-3-(1-naphthyl)coumarin (**If**)
IR (KBr) cm⁻¹: 1,718 (C=O), ¹H NMR (CDCl₃) δ, ppm: 2.16 (s, 3H, CH₃) and 7.30–7.93 (m, 11H, Ar–H and H-4).
- 7-Chloro-4-methyl-3-(1-naphthyl)coumarin (**Ig**)
IR (KBr) cm⁻¹: 1,718 (C=O), ¹H NMR (CDCl₃) δ, ppm: 2.14 (s, 3H, CH₃) and 7.39–7.96 (m, 10H, Ar–H and H-4).
3-Phenylcoumarins were synthesised by reacting 2-hydroxybenzaldehydes with phenylacetic anhydride in activated Ba(OH)₂/water-ethanol medium under ultrasound irradiations for 60 min. The method has been used efficiently for preparing various substituted 3-phenylcoumarins whose structures were confirmed by IR and ¹H NMR (CDCl₃) spectral data.
- 3-Phenylcoumarin (**Ila**)
IR (KBr) cm⁻¹: 1,716 (C=O), ¹H NMR (CDCl₃) δ, ppm: 7.10–7.66 (m, 10H, Ar–H and H-4).
- 7-Chloro-3-phenylcoumarin (**Ilb**)
IR (KBr) cm⁻¹: 1,720 (C=O), ¹H NMR (CDCl₃) δ, ppm: 7.31–7.95 (m, 9H, Ar–H and H-4).
- 7-Bromo-3-phenylcoumarin (**Ilc**)
IR (KBr) cm⁻¹: 1,719 (C=O), ¹H NMR (CDCl₃) δ, ppm: 7.28–7.89 (m, 9H, Ar–H and H-4).
- 7-Methyl-3-phenylcoumarin (**Ild**)
IR (KBr) cm⁻¹: 1,719 (C=O), ¹H NMR (CDCl₃) δ, ppm: 2.23 (s, 3H, CH₃), 7.21–7.65 (m, 9H, Ar–H and H-4).
- 8-Methoxy-3-phenylcoumarin (**Ile**)
IR (KBr) cm⁻¹: 1,720 (C=O), ¹H NMR (CDCl₃) δ, ppm: 3.85 (s, 3H, OCH₃), 6.70–7.72 (m, 9H, Ar–H and H-4).
- 3-(*p*-Methoxyphenyl)coumarin (**IIf**)
IR (KBr) cm⁻¹: 1,720 (C=O), ¹H NMR (CDCl₃) δ, ppm: 3.84 (s, 3H, OCH₃), 6.87–7.79 (m, 8H, Ar–H and H-4).
- 7-Chloro-3-(*p*-methoxyphenyl)coumarin (**Ilg**)
IR (KBr) cm⁻¹: 1,714 (C=O), ¹H NMR (CDCl₃) δ, ppm: 3.91 (3H, OCH₃), 6.99–7.81 (m, 8H, Ar–H and H-4).
- 7-Bromo-3-(*p*-methoxyphenyl)coumarin (**Ilh**)
IR (KBr) cm⁻¹: 1,718 (C=O), ¹H NMR (CDCl₃) δ,



Scheme 2: Synthesis of 3-phenylcoumarins.

ppm: 3.86 (3H, OCH₃), 6.98–7.67 (m, 8H, Ar–H and H-4).

- 7-Methyl-3-(*p*-methoxyphenyl)coumarin (**III**)

IR (KBr) cm⁻¹: 1,718 (C=O), ¹H NMR (CDCl₃) δ, ppm: 3.85 (s, 3H, OCH₃), 2.22 (s, 3H, CH₃), 6.95–7.82 (m, 8H, Ar–H and H-4).

- 8-Methoxy-3-(*p*-methoxyphenyl)coumarin (**IIj**)

IR (KBr) cm⁻¹: 1,716 (C=O), ¹H NMR (CDCl₃) δ, ppm: 3.84, 3.90 (2s, 3H each, 2 OCH₃), 6.89–7.77 (m, 8H, Ar–H and H-4).

3 Results

A mixture of salicylaldehyde, 1-naphthylacetic anhydride and Ba(OH)₂ in equimolar mixture of (C₂H₅OH–H₂O) (1:1) (30 mL) was irradiated with dual-frequency ultrasound for 90 min using an ultrasonic bath (40 kHz) and probe (20 kHz; see Scheme 1). The progress of reaction was checked with the help of thin-layer chromatography. After workup, the compound was separated out and recrystallised with methanol. The melting point of the compound thus obtained was 153–154°C; and in IR, it showed absorption at 1,718 cm⁻¹, which are assigned to C=O stretching frequency. In ¹H NMR, it showed multiplet at 7.27–7.94 due to 12 protons (Ar–H and H-4). Based on the data, it was found that the compound was 3-(1-naphthyl) coumarin and its derivatives were prepared (see Table 1).

A similar reaction between 2-hydroxyacetophenone and 1-naphthylacetic anhydride provided 4-methyl-3-(1-naphthyl) coumarin. 3-Phenylcoumarins were also prepared by reacting 2-hydroxybenzaldehydes with phenylacetic anhydrides (Scheme 2). 3-Phenylcoumarin showed IR absorption at 1,716 cm⁻¹ and ¹H NMR multiplet at 7.10–7.66 due to 10

protons. Using the above procedure, various compounds were synthesised (see Table 2).

4 Conclusions

To sum up, we have developed an effective procedure for one-pot green synthesis of 3-(1-naphthyl), 4-methyl-3-(1-naphthyl) coumarins and 3-phenylcoumarins, without the use of toxic reagents and solvents. The synergistic effect of the combined use of 40 kHz ultrasonic bath and 20 kHz probe resulted in only one final purification step, reduced reaction time, and increased yields. It is conclusively observed that rapid synthesis of coumarins is one of the potential applications of this method.

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Table 2: Characterisation of data of compounds II(a–j)

Compound	R	R ¹	R ²	M.Pt. (lit) (°C)	IR (cm ⁻¹): (C=O)	Yield (%)	¹ H NMR (CDCl ₃) δ (ppm)
Ila	H	H	H	139–40 (140–141) [21]	1,716	86	7.10–7.66 (m, 10H, Ar–H and H-4)
Ilb	H	H	Cl	194–196 (195–196) [21]	1,720	90	7.31–7.95 (m, 9H, Ar–H and H-4)
Ilc	H	H	Br	195–196 (194–196) [21]	1,719	87	7.28–7.89 (m, 9H, Ar–H and H-4)
Ild	H	H	CH ₃	141–44 (144–45) [21]	1,719	85	2.23 (s, 3H, CH ₃), 7.21–7.65 (m, 9H, Ar–H and H-4)
Ile	H	OCH ₃	H	121–123 (122–123) [36]	1,720	80	3.85 (s, 3H, OCH ₃), 6.70–7.72 (m, 9H, Ar–H and H-4)
Ilf	OCH ₃	H	H	141–142 (143–144) [21]	1,720	82	3.84 (s, 3H, OCH ₃), 6.87–7.79 (m, 8H, Ar–H and H-4)
Ilg	OCH ₃	H	Cl	190–191 (190–192) [21]	1,714	83	3.91 (3H, OCH ₃), 6.99–7.81 (m, 8H, Ar–H and H-4)
Ilh	OCH ₃	H	Br	200–202 (201–202) [21]	1,718	84	3.86 (3H, OCH ₃), 6.98–7.67 (m, 8H, Ar–H and H-4)
Ili	OCH ₃	H	CH ₃	140–142 (142–143) [21]	1,718	82	3.85 (s, 3H, OCH ₃), 2.22 (s, 3H, CH ₃), 6.95–7.82 (m, 8H, Ar–H and H-4)
Ilij	OCH ₃	OCH ₃	H	184–185 (185–186) [21]	1,716	80	3.84, 3.90 (2 s, 3H each, 2 OCH ₃), 6.89–7.77 (m, 8H, Ar–H and H-4)

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