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Synthesis of coumarin-3-carboxylic acids in waste curd water: A green approach

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ABSTRACT

An efficient and green protocol has been developed for the synthesis of derivatives of coumarin-3-carboxylic acid using waste curd water as a catalytic solvent. Curd water successfully catalyzes the reaction of 2-hydroxybenzaldehydes with dimethyl malonate under ultrasonic irradiation (40 °C) to construct different scaffolds of coumarin-3-carboxylic acid, with good to outstanding yields. The use of biodegradable solvents, sustainability, low reaction duration, mild reaction conditions without metals and Lewis acids, excellent yields, and compatibility with a wide range of electronically diverse substrates are all advantages of this synthesis process. Acidic curd water, which acts as a biological catalyst as well as a solvent for the reaction under ultrasonic irradiation, may be a better green alternative to some standard methods for synthesizing coumarin-3-carboxylic acids.

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1. Introduction

New catalytic synthetic strategies in the field of chemical science that meet increasingly stringent environmental constraints are in high demand within the pharmaceutical and chemical industries. Developing cleaner, safer, and more environmentally friendly chemical approaches is a crucial objective for chemists [1]. As a result of the presence of this heterocyclic nucleus in numerous natural compounds, the synthesis of coumarins and their derivatives has garnered significant interest from organic and medicinal chemists for many years. These compounds are widely used as precursors for the synthesis of crucial organic compounds in the pharmaceutical industry. Coumarin and its derivatives showcase a wide range of biological activities, including antioxidative, anti-Alzheimer, antidiabetic, anti-HIV, antiallergic, antihelmintic, sedative, and hypnotic [2-5]. Furthermore, they function as anticancer agents by inhibiting the monocarboxylate transporter, act as anticoagulants (targeting the coagulation enzymes FXa and Thr involved in thrombosis), and display antimicrobial efficacy against *Staphylococcus aureus*, *Bacillus subtilis*, and *Escherichia coli* [6,7] (Figure 1). In addition, they have applications in materials science, agrochemicals, food industry, perfumery, and the cosmetic sector [8].

Coumarins containing a carboxyl group in a heterocyclic backbone, namely, coumarin-3-carboxylic acids (also known as 3-carboxycoumarins), represent an important class of biologically valuable pharmacological compounds, as well as have some specific applications in a wide range of possibilities over other coumarin derivatives (esters and amides). In particular, derivatives of coumarin-3-carboxylic acid are utilized for the following purposes: (i) detecting the hydroxyl radical (·OH) generated by γ-irradiation or by chemical reactions in aqueous solutions [9], (ii) addressing neurological disorders such as neuropathic pain, epilepsy, and depression [10], and (iii) serving as fluorescent probes and sensitizers for triplet oxygen [11]. Thus, such chemical compounds can be considered promising new achievements for further innovative work.

Numerous pathways are known in the literature for the synthesis of coumarin-3-carboxylic acids. A two-step method developed by Fringuelli *et al*. in 2003 involved the Knoevenagel

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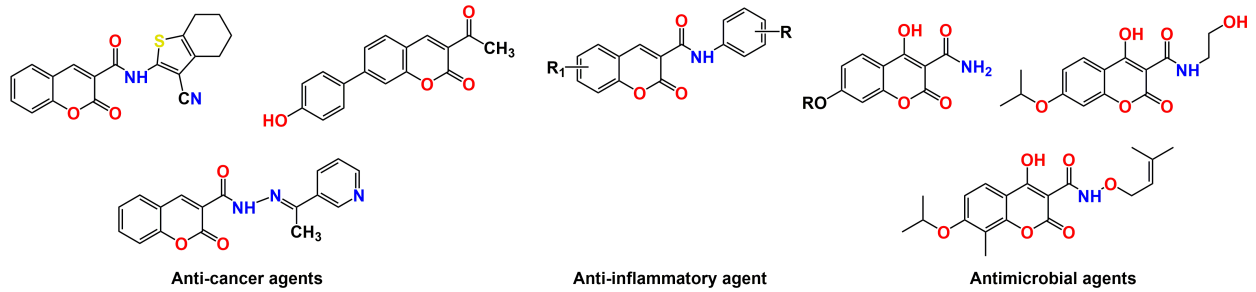


Figure 1. Coumarins containing a carboxyl group in a heterocyclic backbone.

condensation of salicylaldehydes with malononitrile in basic medium followed by a pinner reaction and acid hydrolysis [12]. Scott *et al.* developed a one-pot green synthesis of coumarin-3-carboxylic acid from 2-hydroxybenzaldehydes and Meldrum's acid at room temperature with catalytic amounts of ammonium acetate [13]. A variety of catalytic approaches have been adopted for Knoevenagel aldehyde condensation with an active methylene compound such as K10-$ZnCl_2$ [14], $Yb(OTf)_3$ [15], potassium 1,2,3,6-tetrahydrophthalimide [16], silica gel [17], K_2CO_3, NaN_3 [18], $SnCl_2$ [19] and $ZrOCl_2{\cdot}8H_2O$ [20]. In recent years, great effort has been expended to produce coumarin derivatives using greener approaches using ionic liquid [21], deep eutectic solvent (DES) [22], natural kaolinitic clay (EPZG, EPZ10) [23], aqueous extract of pods of *acacia concinna* [24], water extract of *Nilgiri bark* ash (WENBA) [25], and water extract of banana (WEB) [26]. Although these protocols reported by others definitely deserve of their own, still they suffer from a variety of demerits, such as a long reaction time, low yields, and the need of action for purification of adducts. Therefore, the exploration for a lot of general, clean, efficient, and high-yielding routes for synthesis remains a sound exercise in organic chemistry and represents a field of research of current and growing interest.

The dairy industry stands out as one of India's most polluting sectors. The dairy industry in India has experienced rapid growth due to the growing demand for milk and other dairy products. Consequently, this growth has led to the disposal of large amounts of waste in nearby water bodies. Dairy wastewater contains substantial quantities of bio-chemical oxygen demand, chemical oxygen demand, as well as organic and inorganic chemicals. The improper discharge of this wastewater into water bodies without proper treatment can cause significant environmental problems [27]. Recently, we have investigated the effective utilization of waste curd water as a catalytic solvent in organic synthesis. Curd water, a liquid by-product of the curdling process that is separated from curd during the cheese or yogurt production process, is being considered. The reaction between 2-hydroxybenzaldehydes (1) and dimethyl malonate (2), facilitated by ultrasound irradiation at 40 °C, produces distinct scaffolds of coumarin-3-carboxylic acid. This process highlights the development of an environmentally friendly synthesis approach for coumarin-3-carboxylic acids, aided by ultrasound (Scheme 1).

2. Experimental

2.1. Instrumentation

Sonication was performed in a Labman Probe Sonicator with a frequency of 25 kHz and a nominal power of 200 W. Melting points were determined in the open capillaries and were not corrected. IR spectra were taken as KBr pellets on a Shimadzu FT-IR spectrophotometer (FT-IR 8400S). The ^1H and ^{13}C NMR spectra were recorded at room temperature on a Bruker Avance II 400 NMR spectrometer at 400 and 100 MHz, respectively, using DMSO-d_6 as NMR solvent. Chemical shifts are given in ppm. The Waters Q-Tof Micromass LC-MS spectrometer was used to record the mass spectra.

2.2. Materials

Dimethyl malonate and 2-hydroxybenzaldehydes were obtained from commercial suppliers of Sigma-Aldrich and used without further purification. Curd water was prepared as a catalytic solvent in the laboratory. Thin layer chromatography (TLC) on silica gel plates (Merck, silica gel $60F_{254}$, ready to use) was used to monitor the progress of the synthesis, with ethyl acetate: *n*-hexane (1:4) used as the eluent.

2.3. Procedure for the preparation of curd water solvent

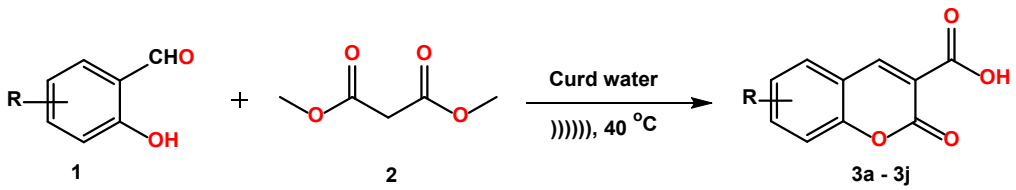
The curd was synthesized under aseptic conditions with a 1% lactic acid bacteria starter culture in 100 mL of pasteurized warm milk and incubated at 37 °C for 48 hours to activate the culture and establish the curd. The water was taken from the freshly made curd by filtering it through a muslin cloth, and the filtered turbid liquid was then collected. The turbid liquid was centrifuged for 15 minutes at 4000 revolutions per minute. The turbid liquid was filtered using ordinary Whatman paper, producing a pale-yellow liquid suitable for further reactions [28].

2.4. General procedure for the synthesis of derivatives of coumarin-3-carboxylic acid

A mixture of 2-hydroxybenzaldehyde (1.0 mmol) and dimethyl malonate (1.0 mmol) in 5 mL of curd water was prepared. The mixture was sonicated at appropriate times and the course of the reaction was monitored using TLC on silica gel with ethyl acetate: *n*-hexane (1:4) as an eluent. After completion of the reaction, the resulting mixture was poured into the ice-water mixture, filtered off, washed with cold water, and the crude product was obtained as a solid. The solid product was recrystallized from methanol and pure derivatives of coumarin-3-carboxylic acid (3a-3j) were obtained. The authenticity of the products was established by comparing their melting points with literature values (Table 1) and by analyzing the spectroscopic data of ^1H and ^{13}C NMR, IR, and MS.

2-Oxo-2H-chromene-3-carboxylic acid (**3a**): Color: White. Yield: 95%. M.p.: 192-194 °C. FT-IR (KBr, ν, cm^{-1}): 3050 (C-H) (aromatic), 1751 (C=O) (ester), 1687 (C=O) (acid), 1500 (C=C) (aromatic). ^1H NMR (400 MHz, DMSO-d_6, δ, ppm): 12.81 (s, 1H, OH), 8.71 (s, 1H, Ar-H), 7.83-7.81 (d, 1H, Ar-H), 7.71-7.67 (t, 1H, Ar-H), 7.37-7.36 (t, 1H, Ar-H), 7.39-7.38 (d, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 115.90, 117.70, 117.85, 124.52, 130.10, 134.80, 147.87, 153.92, 156.81. MS (EI, *m/z*): 191.11 (M^+).

7-(Diethylamino)-2-oxo-2H-chromene-3-carboxylic acid (**3b**): Color: Pale yellow. Yield: 91%. M.p.: 220-222 °C. FT-IR (KBr, ν, cm^{-1}): 3456 (N-C) (amine), 3024 (C-H) (aromatic), 1760



Scheme 1. Green synthesis of coumarin-3-carboxylic acids.

(C=O) (ester), 1685 (C=O) (acid), 1515 (C=C) (aromatic). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 12.24 (s, 1H, OH), 7.58 (s, 1H, Ar-H), 7.57 (s, 1H, Ar-H), 6.76-6.74 (d, 1H, Ar-H), 6.54-6.53 (d, 1H, Ar-H), 3.53-3.48 (m, 4H, $2CH_2$), 1.23-1.20 (m, 6H, $2CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 12.11, 44.04, 105.91, 107.20, 111.24, 131.55, 148.30, 151.85, 160.10, 165.65. MS (EI, *m/z*): 261.15 (M).

7,8-Dihydroxy-2-oxo-2H-chromene-3-carboxylic acid (**3c**): Color: White. Yield: 94%. M.p.: 192-194 °C. FT-IR (KBr, ν, cm^{-1}): 3472-3240 (OH) (aromatic), 3016 (C-H) (aromatic), 1768 (C=O) (ester), 1678 (C=O) (acid), 1517 (C=C) (aromatic). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 12.17 (s, 1H, OH), 11.04 (s, 1H, Ar-H), 8.75 (d, 1H, Ar-H), 8.16 (d, 1H, Ar-H), 6.30 (s, 1H, OH), 6.21 (s, 1H, OH). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 94.01, 98.50, 103.11, 107.20, 145.22, 156.16, 157.88, 160.35, 164.12, 166.18. MS (EI, *m/z*): 245.14 (M^+ + Na).

5,7-Dihydroxy-2-oxo-2H-chromene-3-carboxylic acid (**3d**): Color: White. Yield: 87%. M.p.: 194-196 °C. FT-IR (KBr, ν, cm^{-1}): 3501 (OH) (aromatic), 3018 (C-H) (aromatic), 1778 (C=O) (ester), 1695 (C=O) (acid), 1547 (C=C) (aromatic). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 10.77 (s, 1H, OH), 8.64 (s, 1H, Ar-H), 8.15 (s, 1H, Ar-H), 7.20 (s, 1H, Ar-H), 6.88 (s, 1H, OH), 6.86 (s, 1H, OH). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 94.09, 98.55, 102.83, 107.44, 145.22, 157.34, 158.20, 160.38, 164.18, 165.70. MS (EI, *m/z*): 245.14 (M^+ + Na).

6-Chloro-2-oxo-2H-chromene-3-carboxylic acid (**3e**): Color: Pale yellow. Yield: 92%. M.p.: 120-122 °C. FT-IR (KBr, ν, cm^{-1}): 3021 (C-H) (aromatic), 1751 (C=O) (ester), 1682 (C=O) (acid), 1512 (C=C) (aromatic), 875 (C-Cl). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 8.68 (s, 1H, OH), 7.99 (s, 1H, Ar-H), 7.89 (s, 1H, Ar-H), 7.66-7.63 (d, 1H, Ar-H), 7.39-7.36 (d, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 117.84, 119.11, 119.22, 128.26, 128.82, 133.48, 147.09, 152.97, 156.16, 163.51. MS (EI, *m/z*): 225.11 (M^+).

8-Hydroxy-2-oxo-2H-chromene-3-carboxylic acid (**3f**): Color: Pale yellow. Yield: 92%. M.p.: 200-202 °C. FT-IR (KBr, ν, cm^{-1}): 3482 (OH) (aromatic), 3031 (C-H) (aromatic), 1781 (C=O) (ester), 1686 (C=O) (acid), 1527 (C=C) (aromatic). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 11.57 (s, 1H, OH), 8.61 (s, 1H, Ar-H), 7.60 (t, 1H, Ar-H), 6.80-6.79 (d, 1H, Ar-H), 6.77 (d, 1H, Ar-H), 6.69 (s, 1H, OH). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 107.85, 145.06, 157.46, 158.08, 159.58, 165.63. MS (EI, *m/z*): 226.12 (M^++ Na).

6-Bromo-2-oxo-2H-chromene-3-carboxylic acid (**3g**): Color: Pale creamy solid. Yield: 93%. M.p.: 192-194 °C. FT-IR (KBr, ν, cm^{-1}): 3028 (C-H) (aromatic), 1752 (C=O) (ester), 1680 (C=O) (acid), 1518 (C=C) (aromatic), 878 (C-Br). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 8.74 (s, 1H, OH), 8.10 (s, 1H, Ar-H), 7.49 (s, 1H, Ar-H), 7.19-7.17 (d, 1H, Ar-H), 3.48-3.46 (d, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 116.37, 118.67, 119.50, 123.52, 131.09, 131.29, 147.01, 153.37, 159.29, 163.46. MS (EI, *m/z*): 268.77 (M^++ Na).

5-Isopropyl-8-methyl-2-oxo-2H-chromene-3-carboxylic acid (**3h**): Color: White. Yield: 90%. M.p.: 216-218 °C. FT-IR (KBr, ν, cm^{-1}): 3022 (C-H) (aromatic), 3045-2914 (C-H) (aromatic, methyl), 1764 (C=O) (ester), 1679 (C=O) (acid), 1530 (C=C) (aromatic). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 12.43 (s, 1H, OH), 9.29 (s, 1H, Ar-H), 7.60-7.58 (d, 1H, Ar-H), 7.31-7.29 (d, 1H, Ar-H), 3.57-3.52 (m, 1H, Ar-H), 2.43 (s, 3H, CH_3), 1.36-1.34 (d, 6H, $2CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 116.37, 118.67, 119.50, 123.52, 131.09, 131.29, 147.01, 153.37, 159.29, 163.46. MS (EI, *m/z*): 247.23 (M^++ Na).

8-Isopropyl-5-methyl-2-oxo-2H-chromene-3-carboxylic acid (**3i**): Color: White. Yield: 86%. M.p.: 170-172 °C. FT-IR (KBr, ν, cm^{-1}): 3051 (C-H) (aromatic), 3034-2894 (C-H) (aromatic, methyl), 1758 (C=O) (ester), 1682 (C=O) (acid), 1510 (C=C) (aromatic). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 8.69 (s, 1H, OH), 8.14 (s, 1H, Ar-H), δ 7.95-7.94 (d, 1H, Ar-H), 7.68 (d, 1H, Ar-H), 7.66 (m, 1H, CH), 7.42 (s, 3H, CH_3), 2.54 (d, 6H, $2CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 11.65, 22.11, 25.95, 113.23, 116.44, 125.18, 130.91, 133.01, 135.46, 145.19, 152.32, 163.07, 168.39. MS (EI, *m/z*): 247.23 (M^++ Na).

6-Allyl-8-methoxy-2-oxo-2H-chromene-3-carboxylic acid (**3j**): Color: White. Yield: 85%. M.p.: 172-174 °C. FT-IR (KBr, ν, cm^{-1}): 3068 (C-H) (aromatic), 1764 (C=O) (ester), 1692 (C=O) (acid), 1510 (C=C) (aromatic)., 1654 (C=C) (alkene), 1034 (C-O) (methoxy). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 8.60 (s, 1H, OH), 7.15 (s, 1H, Ar-H), 6.01 (s, 1H, Ar-H), 6.00 (s, 1H, Ar-H), 5.98-5.94 (m, 1H, =CH), 5.92 (d, 2H, $=CH_2$), 3.93 (s, 3H, CH_3), 3.42 (d, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 39.31, 55.92, 116.33, 116.42, 118.89, 119.91, 136.52, 142.67, 146.07, 148.49, 156.65, 163.75. MS (EI, *m/z*): 261.21 (M^++ Na).

3. Results and discussion

3.1. Synthesis of 3-carboxycoumarin derivatives

Our contribution aims to broaden the range of methods that can be used to synthesize coumarin-3-carboxylic acids and to describe how a new catalytic system can be used in their synthesis. According to our research, substituted benzaldehydes react with dimethyl malonate in the presence of curd water under ultrasonic radiation to produce the respective derivatives of coumarin-3-carboxylic acid in good to outstanding yields (Scheme 1).

We first evaluated the viability of this reaction using a model condensation of 2-hydroxybenzaldehyde and dimethyl malonate under a variety of reaction conditions. As part of our research on the use of curd water as a catalytic solvent in synthesis, we attempted a curd-water-catalyzed condensation reaction by conventional heating. However, only good yields of the preferred product were obtained because of the difficult reaction conditions, which included high temperatures and a long reaction time. We performed the same reaction under ultrasonic irradiation as an intriguing method to speed up chemical reactions. The results were striking: an enhancement in the yield of the target product was observed, and the entire transformation was achieved within a mere hour.

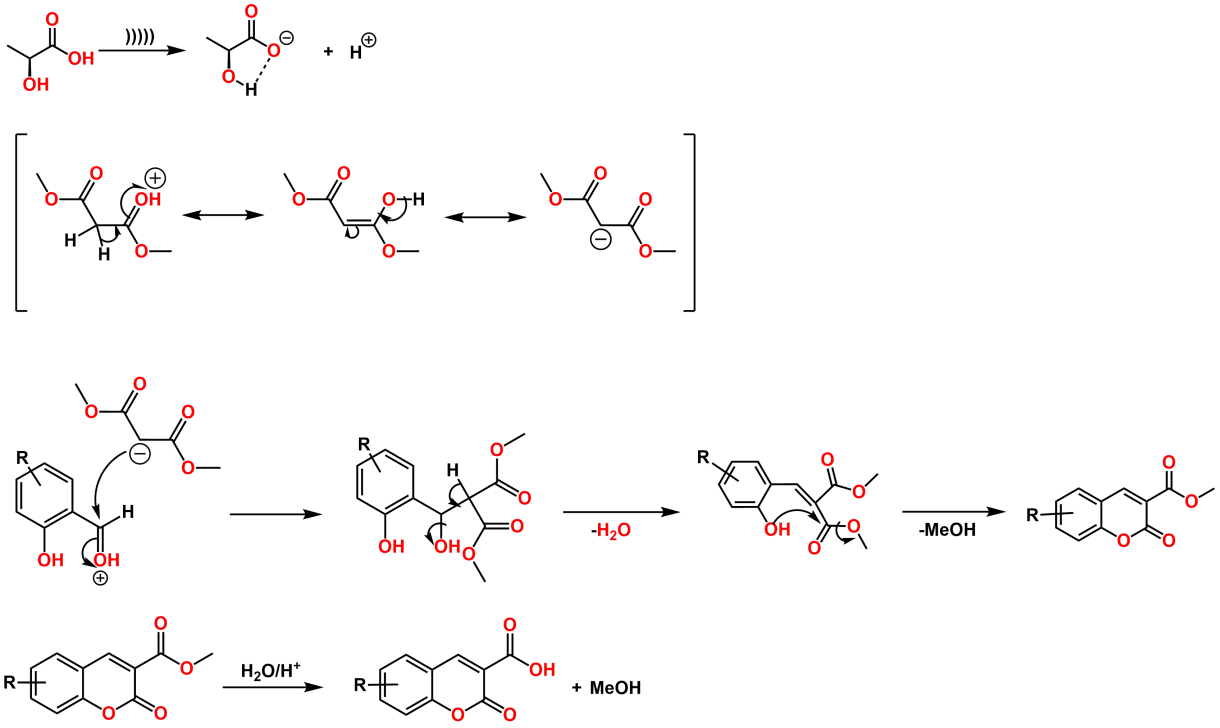
We coupled the catalyst and ultrasonic irradiation in this process to accelerate both the rate of the chemical reaction and the catalyst efficiency. Different aromatic aldehydes were exposed to this technique to investigate the scope of the reaction. All of the reactions went well, yielded high volumes, and created no unwanted byproducts. According to a standard approach, the reaction of 2-hydroxybenzaldehyde (1 mmol) and dimethyl malonate (1 mmol) in the presence of curd water (5 mL) under ultrasonic irradiation (1 hour) produces compound 3a with a 95% yield (Table 1, entry 1).

Table 1. Synthesis of coumarin-3-carboxylic acids in waste curd water with ultrasonic irradiation.

Entry	Aldehyde	Product	Yield (%)	Melting point (°C)		Reference
				Found	Reported	
1	2-Hydroxybenzaldehyde	3a	95	192-194	190-191	[9]
2	4-(Diethylamino)-2-hydroxybenzaldehyde	3b	91	220-222	224-225	[20]
3	2,3,4-Trihydroxybenzaldehyde	3c	94	192-194	190-192	[26]
4	2,4,6-Trihydroxybenzaldehyde	3d	87	194-196	190-192	[25]
5	5-Chloro-2-hydroxybenzaldehyde	3e	92	120-122	121-122	[9]
6	2,3-Dihydroxybenzaldehyde	3f	92	200-202	204-206	[26]
7	5-Bromo-2-hydroxybenzaldehyde	3g	93	192-194	191-193	[23]
8	2-Hydroxy-6-isopropyl-3-methylbenzaldehyde	3h	90	216-218	212-214	[6]
9	2-Hydroxy-3-isopropyl-6-methylbenzaldehyde	3i	86	170-172	167-169	[25]
10	5-Allyl-2-hydroxy-3-methoxybenzaldehyde	3j	85	172-174	172-174	[26]

Table 2. Comparison of our results with some previously reported data for the synthesis of compound 3a.

Catalyst	Condition	Yield %	Reference
K_2CO_3 (10 mol%)/H_2O	Stirring at RT for 20 hours	79	[18]
$SnCl_2{\cdot}2H_2O$	Solvent free 80 °C, 60 minutes	80	[19]
WEB (5%)	Ethanol, 440 minutes	94	[22]
Natural clay, EPZ10	M.W./5 minutes	71	[23]
WENBA	3.5 hours	90	[25]
Curd water	))))), 40 °C, 1 hour	95	This work



Scheme 2. Plausible mechanism for the synthesis of 3-carboxycoumarin derivatives using curd water.

A Knoevenagel condensation of substituted benzaldehydes and dimethyl malonate followed by intramolecular cyclization can be used to outline the mechanism for the formation of coumarin-3-carboxylic acids. We believe that the lactic acid present in the curd water solution coordinates with carbonyl oxygen and activates the carbonyl group for nucleophilic attack (Scheme 2).

Numerous substituted benzaldehydes were examined to investigate the impact of various substituents on the generality of the reaction. The results are summarized in Table 1 (entries 3a-3j). The results demonstrated how broadly applicable the suggested methodology is. In terms of catalyst, temperature, reaction time, and % yields, some previously published data for the synthesis of 3a (Table 1, entry 1) were compared with our findings. As can be seen, our results in terms of yields and reaction times demonstrate a very strong comparability with previously reported data (Table 2).

3.2 Spectroscopic studies

The isolated products were fully characterized on the basis of their analytical data and detailed spectral studies including FT-IR, ^{1}H NMR, ^{13}C NMR, and TOF-MS. All known compounds had physical and spectroscopic data identical to those reported in the literature [18-26].

The observation of a distinct absorption peak at 1695-1678 cm^{-1} in FT-IR spectra is consistent with the C=O stretching vibration typically associated with the carboxyl group (COOH) in organic compounds. This suggests the presence of carboxyl functional groups in the synthesized derivatives. The IR bands at 1781-1751 cm^{-1} support the existence of the cyclic ester group within compounds. These spectral bands are indicative of the carbonyl (C=O) stretching vibration in cyclic esters, which is characteristic of coumarin-3-carboxylic acids.

The observed peak in the ^{1}H NMR spectra (δ 12.81-8.60 ppm) aligns with the presence of -OH protons, specifically

carboxyl groups, within the compounds. Variation in chemical shift within this region reflects the diverse chemical environments of these functional groups. In particular, our findings closely resemble data from the literature data (δ 12.26) associated with carboxylic –OH peaks, which confirms the identification of these groups in our compounds [19]. The ^{1}H-NMR spectrum of compound 3j showed the signal for MeO-C at δ (H) 3.93. The two distinct signals in the range of δ (H) 6.01–6.00 corresponded to HC (5, 7), whereas the signal for HC (4) appeared deshielded as s at δ (H) 7.15, in agreement with its *β* -position with respect to the CO group. The two distinct signals in the range of δ (H) 5.98–5.92 and the strongly shielded signal at δ (H) 3.42 corresponded to the allyl group (6). The ^{13}C NMR spectrum revealed two distinct peaks at δ 168.39–163.46 ppm for the carboxyl C=O groups, and δ 163.07–156.81 ppm for the carbonyl of lactone in coumarin skeleton which was closely resemble literature [29].

The theoretical molecular masses of some derivatives are perfectly obtained in the LC mass spectrum with loss of electron pattern. M^+ = 191.11 *m/z* for compound 3a, M^+ = 261.15 *m/z* for compound 3b, and M^+ = 225.11 *m/z* for compound 3e that matches with the calculated mass. In some spectra, M+Na contamination peaks also appear, M+Na = 245.14 *m/z* for compound 3c, M+Na = 245.14 *m/z* for compound 3d, M+Na = 226.12 *m/z* for compound 3f, M+Na = 268.77 *m/z* for compound 3g, 247.23 *m/z* for compound 3h, M+Na = 247.23 *m/z* for compound for 3i and M+Na = 261.21 *m/z* shows excessive mass in LC-ESI-MS experiments involving both organic and aqueous (H_2O-based).

4. Conclusions

The present study introduced a new synthetic protocol for the derivatives of coumarin-3-carboxylic acid, where the lactic acid-induced acidity provides the catalytic support for the reaction. Waste curd water has been demonstrated to work as an excellent catalyst for the reaction of dimethyl malonate with a variety of substituted benzaldehydes under ultrasonic irradiation in aqueous media. The catalyst-free condition, low reaction times, high yields, environmentally friendly conditions, and operational simplicity are the advantages of this protocol, achieving a green alternative to existing protocols. The prepared molecules were characterized by HR-MS, FT-IR, and NMR spectroscopy.

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Disclosure statement

Conflict of interest: The authors declare that they have no conflict of interest.
Ethical approval: All ethical guidelines have been adhered.
Sample availability: Samples of the compounds are available from the author.

CRediT authorship contribution statement

Conceptualization: Nitin Bhaidas Sonawane, Dilip Ramsing Patil; Methodology: Nitin Bhaidas Sonawane, Jamatsing Darbarsing Rajput; Software: Jamatsing Darbarsing Rajput; Validation: Nitin Bhaidas Sonawane, Dilip Ramsing Patil; Formal Analysis: Nitin Bhaidas Sonawane; Investigation: Nitin Bhaidas Sonawane, Jamatsing Darbarsing Rajput; Resources: Nitin Bhaidas Sonawane, Dilip Ramsing Patil; Data Curation: Nitin Bhaidas Sonawane; Writing - Original Draft: Nitin Bhaidas Sonawane,; Writing - Review and Editing: Dilip Ramsing Patil, Nitin Bhaidas Sonawane; Visualization: Nitin Bhaidas Sonawane; Funding acquisition: Nitin Bhaidas Sonawane, Dilip Ramsing Patil; Supervision: Dilip Ramsing Patil, Jamatsing Darbarsing Rajput; Project Administration: Nitin Bhaidas Sonawane, Dilip Ramsing Patil.

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