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LEAM as a Natural and Green Catalyst for Knoevenagel Condensation

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Abstract: A straightforward, gentle, and eco-friendly procedure has been established for the Knoevenagel condensation of aromatic aldehydes with malononitrile using LEAM (leaf extract of *Aegle marmelos*) at room temperature. The reaction provides the desired products in excellent yields with high purity. This green approach avoids the use of harmful acidic or basic catalysts, making the process both convenient to handle and environmentally safe.

Keywords: LEAM, Green chemistry, Knoevenagel condensation, natural catalyst.

1. Introduction

The Knoevenagel condensation is regarded as a highly useful and dependable reaction for forming carbon–carbon bonds in organic synthesis. It was first reported by Emil Knoevenagel in 1894 [1]. In this reaction, aldehydes or ketones react with active methylene compounds in the presence of mild bases to generate α, β-unsaturated products through a sequence involving enolate formation, nucleophilic addition, and subsequent removal of water [2,3]. Because the reaction is straightforward to perform and follows a well-understood mechanism, it has become an important method for constructing complex molecules used in pharmaceuticals, dyes, agrochemicals, fragrances, and advanced functional materials [4–6].

Despite its usefulness, conventional Knoevenagel procedures commonly rely on bases such as NaOH, KOH, or organic amines like piperidine, typically carried out in volatile organic solvents including ethanol, toluene, or benzene at higher temperatures for extended reaction periods [7,8]. These conditions create environmental and safety concerns, mainly due to solvent toxicity, increased chemical waste, and significant energy requirements [9]. In addition, the homogeneous catalysts employed in these systems are often difficult to separate and reuse, which raises operational costs and contributes to additional waste generation [10]. The use of harsh conditions can also restrict the applicability of the reaction, particularly when dealing with sensitive or sterically demanding substrates [11].

The concept of green chemistry, proposed by Paul Anastas and John C. Warner, promotes the design of chemical processes that minimize or eliminate hazardous substances and reduce waste while improving overall efficiency [12,13]. Applying these ideas to the Knoevenagel condensation has encouraged the development of alternative strategies. These include aqueous or solvent-free methods that employ water as an environmentally safer medium or avoid solvents entirely through grinding techniques or microwave assistance [14,15]. Another approach involves heterogeneous and recyclable catalysts such as metal oxides, clays, or calcined natural materials, which allow easier separation and repeated use [16,17]. Bio-derived catalysts from plant extracts, fruit ashes, or enzyme-based systems are also being explored as renewable and low-cost options [18,19]. Additionally, ionic liquids and deep eutectic solvents have been introduced as non-volatile and reusable substitutes for conventional solvents [20,21].

Natural materials are particularly attractive for sustainable catalysis. They are generally biodegradable, non-toxic, and readily available, and they often function effectively under mild reaction conditions. Many of these materials contain diverse functional groups that can promote catalytic activity without the need for additional reagents [22]. Converting plant-based resources or agricultural residues into catalysts also supports sustainable resource utilization and fits well with the principles of a circular economy [23].

The leaves of *Aegle marmelos* (Bael) are rich in diverse bioactive phytochemicals that mainly belong to alkaloids, coumarins, flavonoids, and terpenoids, which contribute to the plant's widespread use in traditional medicine. Among the alkaloids reported from the leaves are aegeline, marmeline, aegelenine, fragrine, and skimmianine, along with phenylethyl cinnamide derivatives such as anhydromarmeline, aegelinosides A, and aegelinosides B. The leaves also contain important coumarins including marmesin, marmelosin, imperatorin, umbelliferone, and scopoletin. Flavonoids such as rutin and several flavone glycosides are present as major constituents. In addition, the essential oil obtained from the leaves is composed mainly of monoterpenes and sesquiterpenes, with key components such as alpha-phellandrene, p-cymene, δ-carene, limonene, cineol, and lupeol. Besides these compounds, the leaves are also known to contain tannins, saponins, glycosides, and phytosterols including α- and β-sitosterol, which further enhance their biological significance and medicinal value [24–26].

In continuation of our ongoing efforts [27–34] to develop greener synthetic routes for value-added products, the present study reports, for the first time, the application of LEAM (leaf extract of *Aegle marmelos*) as a natural and environmentally benign catalyst for the Knoevenagel condensation carried out at room temperature without the use of additional solvents. This strategy is intended to integrate sustainability with practical simplicity and economic feasibility. The method demonstrates efficient catalytic activity under mild conditions, produces only minimal amounts of naturally degradable waste, shows good compatibility with a range of aldehydes and active methylene compounds, and allows straightforward work-up with potential for scale-up. By utilizing an easily available plant-based extract, this work presents a new approach toward sustainable organic synthesis and supports the broader objectives of green chemistry and renewable catalytic systems.

2. Experimental Section

2.1 General Information

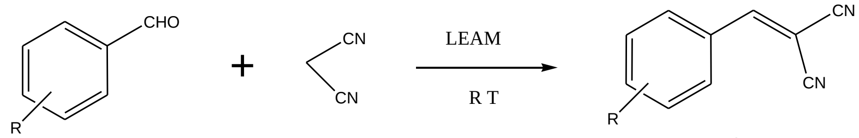
All chemicals were purchased from commercial sources and used without further purification. Melting points were recorded in open capillaries and are uncorrected. Reaction progress was monitored by thin-layer chromatography (TLC) using silica gel plates.

2.2 Preparation of LEAM

Fresh green leaves of *Aegle marmelos* were thoroughly washed with clean water and then ground in a mechanical mixer–grinder using a small quantity of water to obtain a uniform mixture. The resulting slurry was subjected to simple filtration to separate the solid plant residues, yielding a clear green extract. This filtrate was stored in a closed container at room temperature for one month. After this period, the leaf extract (LEAM) was used directly as both the catalyst and the reaction medium for the study. The pH of the freshly prepared extract was found to be 7.2, indicating that it is essentially neutral in nature.

2.3 General Procedure for Knoevenagel Condensation

Aromatic aldehydes (10 mmol), malononitrile (10 mmol), and LEAM (10 mL, pH 7.2) were placed in a round-bottom flask and the mixture was stirred at room temperature (25 °C). Once the reaction was complete, the reaction mixture was poured into ice-cold water to precipitate the product. The resulting solid was collected by filtration and thoroughly washed with water. The crude material obtained was then purified by recrystallization using absolute ethanol.



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3. Results and Discussion

3.1 Optimization Studies

The reaction conditions were systematically optimized by studying the influence of the age of LEAM, the amount of LEAM used, and the reaction temperature. The results showed that the most favorable conditions were achieved using LEAM aged for one month (30 days), with 10 mL of the extract, while stirring the reaction mixture at room temperature for approximately 10 minutes. Extending the aging period of the extract, increasing the catalyst quantity, or prolonging the reaction time did not produce any noticeable improvement in the yield. As shown in Table 1, the yield gradually increased with the age of the extract and reached a maximum of 75% when 30-day-old LEAM was employed, while further aging to 37 days did not enhance the yield, and no reaction occurred in the absence of LEAM. According to Table 2, increasing the volume of LEAM from 1 mL to 10 mL led to a steady improvement in yield, with the best result obtained at 10 mL, whereas using 15 mL provided only a slight change, indicating that 10 mL is sufficient for effective catalysis; again, no reaction was observed without LEAM. The effect of temperature, summarized in Table 3, indicated that performing the reaction at room temperature produced yields that were comparable to or better than those obtained at elevated temperatures. Although higher temperatures slightly reduced or only marginally improved the yield while shortening the reaction time, room temperature was ultimately considered the most suitable condition for this reaction.

Table 1: Optimization for appropriate age of LEAM [a]

Entry	Age of LEAM (days)	Yields (%)[b]
1	fresh	25
2	1	30
3	7	45
4	14	60
5	**30**	**75**
6	37	75
7	-	nd[c]

[a]Reaction conditions: p-anisaldehyde (5 mmol), malononitrile (5 mmol), at RT for 10 min. [b]Isolated yields. [c]Reaction without LEAM.

Table 2: Optimization for appropriate amount of LEAM [a]

Entry	LEAM (ml)	Yields (%)[b]
1	1	56
2	2	64
3	3	67
4	5	68
5	**10**	**74**
6	15	75
7	-	nd[c]

[a]Reaction conditions: p-anisaldehyde (5 mmol), malononitrile (5 mmol), at RT for 10 min. [b]Isolated yields. [c]Reaction without LEAM.

Table 3: Optimization for appropriate reaction conditions[a]

Entry	Reaction temperature with stirring (°C)	Yields (%)[b]
1	**RT**	**60**
2	65	56
3	75	61
4	80	65

[a]Reaction conditions: p-anisaldehyde (5 mmol), malononitrile (5 mmol) in LEAM. Reaction time10 min. [b]Isolated yields.

3.2 Scope of the work

The methodology was successfully applied to various aromatic aldehydes bearing electron-donating and electron-withdrawing substituents. The results are summarized in Table 4.

Table 4. Knoevenagel Condensation of Aromatic Aldehydes with Malononitrile

Sr. No	R	Product	M. P. (°C)	% Yield
1	H	**3a**	81-82	89
2	4-OCH_3	**3b**	111-112	80
3	2-OH	**3c**	99-100	70
4	4-Br	**3d**	165-166	95
5	4-Cl	**3e**	160-161	91
6	3-Cl	**3f**	88-90	82
7	4-CH_3	**3g**	129-130	73
8	4-NO_2	**3h**	159-160	84
9	4-F	**3i**	123-124	76
10	4$N(CH_3)_2$	**3j**	183-184	85

4. Conclusions

A new and environmentally friendly approach for the Knoevenagel condensation has been established by employing LEAM as a natural catalyst. The reaction proceeds smoothly under mild conditions at room temperature and affords high yields in the range of 70–95% along with good product purity. The method is simple to handle, cost-effective, and shows promise for large-scale or industrial use. Overall, this study highlights the usefulness of plant-derived extracts as sustainable substitutes for traditional synthetic catalysts in organic synthesis.

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