

# Green and Efficient Synthesis of Benzothiazole Derivatives Catalyzed by Tamarind Juice in Aqueous Media

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**Abstract:** *A sustainable and convenient method to synthesize the benzothiazole derivatives involves a one-pot reaction of 2-aminothiophenol with diverse aromatic aldehydes using tamarind (*Tamarindus indica L.*) juice. Reactions carried out under mild reaction conditions yielded desired products in moderate to good yields in short reaction times. Tamarind juice is inexpensive, readily available, an environmentally benign, metal-free catalyst. The procedure is also simple, unambiguous in identifying the product, low amount of catalyst required, and avoids toxic chemicals and column chromatography. It confirms the tamarind juice is an effective green catalyst for biologically relevant benzothiazole derivatives.*

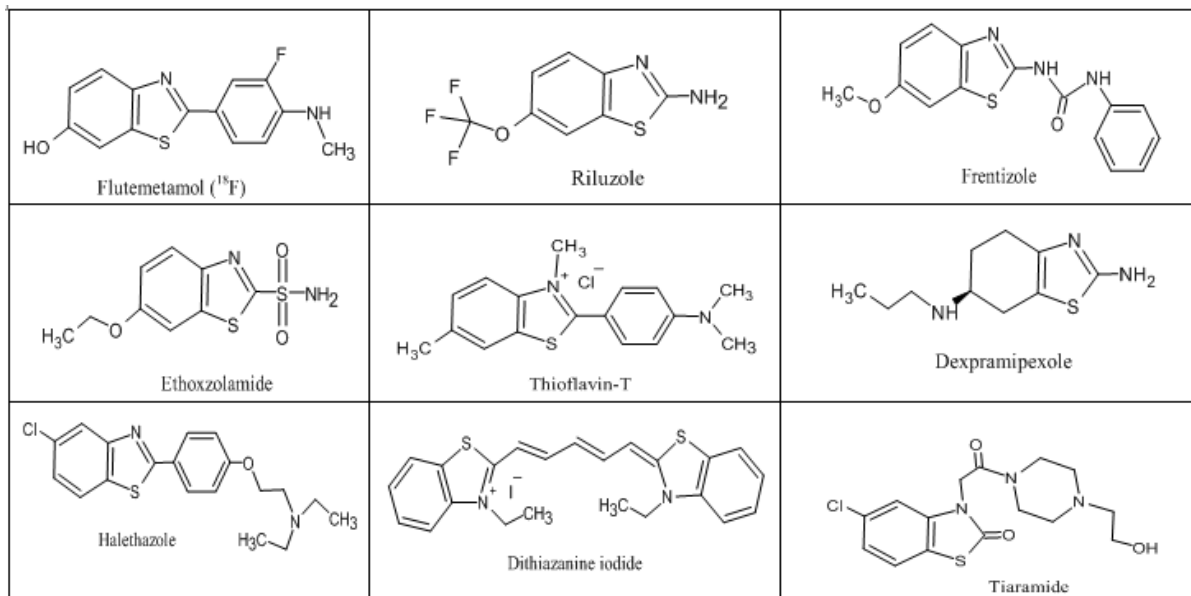
**Keywords:** Tamarind Juice, Biocatalyst, Benzothiazole, Heterocyclic chemistry, One-pot Synthesis

## INTRODUCTION

Benzothiazole belongs to the heterocyclic ring system having a fused structure of sulfur and nitrogen rings and present in many biologically active compounds. Benzothiazoles and their derivatives have gained significant attention in recent years owing to their wide range of pharmaceutical and biological activities. Some biological activities of benzothiazole derivatives that have been reported include anthelmintic activity, antitumor activity, anticancer activity, antitubercular activity, antibacterial activity, antioxidant activity, antidiabetic activity, antiviral activity, anti-inflammatory activity, antiglutamate activity, anticonvulsant activity, antimicrobial activity, neuroprotective activity, and aldose reductase inhibition activity. In addition, some benzothiazole derivatives act as vulcanizing agents, growth regulators, and antioxidants [1-14].

Some of the most prominent benzothiazole-based derivatives utilized in pharmaceutical and medicinal applications are summarized below along with their chemical structures.





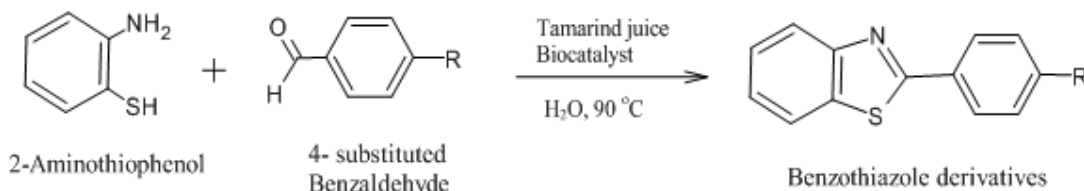
The compounds mentioned above highlight the considerable importance of the benzothiazole core in medicinal chemistry because of its extensive biological and pharmacological properties. The benefits noted earlier have sparked considerable interest in designing new benzothiazole derivatives and establishing an efficient synthetic route for their production. Numerous catalysts have been reported in the literature for the synthesis of benzothiazole derivatives, including, PS-I(OAc)<sub>2</sub> [15], Laccase [16], SnP<sub>2</sub>O<sub>7</sub> [17], TsOH [18], Cu-Pd catalysts [19], RuCl<sub>3</sub> [20], P<sub>4</sub>S<sub>10</sub> [21], Ru(bpy)<sub>3</sub>(PF<sub>6</sub>) [22], Dess\_martin periodinate (DMP) [23], PBu<sub>3</sub> [24], NaHSO<sub>4</sub>-SiO<sub>2</sub> [25], and n-Tetrabutyl ammonium iodide (TBAI) [26] etc. The growing demand for the synthesis of compounds with the benzothiazole ring compels researchers to explore novel methods for creating these heterocycles. However, many conventional methods employ hazardous chemicals, expensive catalysts, or environmentally unfavorable conditions, creating a need for greener, cost-effective, and sustainable synthetic methodologies.

There has been an increased awareness about environmental pollution and natural resource exhaustion that has led to the development of sustainable and environmentally benign synthetic techniques. Green Chemistry emphasizes the adoption of efficient and safer chemical process that involves minimum use and generation of toxic materials. Using renewable and biodegradable chemicals in place of harmful solvents and corrosive catalysts becomes necessary in this regard. In this scenario, biocatalysts available in nature and aqueous reaction media become highly valuable assets in organic synthetic processes. Recently, fruit extracts have attracted great attention as green catalysts owing to their low cost, easy availability, environmental friendliness, and efficiency as a catalyst. Fruit juices like lemon juice, pineapple juice, coconut juice, and tamarind have proved useful as catalysts for Biginelli condensation, Knoevenagel-Michael addition, and heterocycle formation. A significant number of organic reactions utilizing fruit juice have been documented in the literature. Tamarind (*Tamarindus indica* L.), belonging to the Fabaceae family, is considered an excellent natural catalyst in organic reactions. It consists of high levels of organic acids, mostly tartaric acid with traces of citric, malic, and ascorbic acids. This makes the aqueous extract of tamarind acidic (pH ≈ 3). Other ingredients of tamarind fruit are carbohydrates, flavonoids, polyphenols, vitamins, and minerals [26-36]. The acidic nature of tamarind extract allows it to function as an acid catalyst for the formation of benzothiazole.

Herein, We report the synthesis of six benzothiazole derivatives conducted under eco-friendly conditions. This process employs tamarind fruit extract as a sustainable biocatalyst for the condensation of 2-aminothiophenol and aromatic aldehydes in an aqueous medium, thereby eliminating the need for hazardous organic solvents and toxic chemical catalysts.



## II. EXPERIMENTAL



**Figure-1** Reaction scheme of synthesis of Benzothiazole derivatives

### Materials and Methods

Sigma-Aldrich, E. Merck (India), SDFC Ltd., and Loba Chemie provided all the necessary chemicals, which were used exactly as specified. The melting point ranges of newly synthesized compounds were determined by open glass capillary tubes. Thin layer chromatography (TLC) on aluminum plates coated with a layer of silica gel, provided by Merck, was used to assess the purity of prepared compounds and the progress of all reactions. An iodine chamber was used to visualize the spots. Using KBr pellets, the Shimadzu FTIR model 4800S spectrophotometer captured the infrared spectra in the 4000-400  $\text{cm}^{-1}$  region.  $^1\text{H-NMR}$  spectrum was recorded in  $\text{CDCl}_3$  on Bruker AV-300 (300 MHz) using TMS as an internal standard.

### Preparation of Tamarind fruit juice (Biocatalyst)

Fresh tamarind fruit (*Tamarindus indica*) were obtained from the local market. The seeds and outer shell were removed by hand and tamarind pulp (about 10 g) were obtained. The tamarind pulp was extracted by adding distilled water (about 50mL) and the mixture was kept for 5-6 h to obtain water-soluble components of tamarind fruit. The solution was heated for 2 h under stir conditions to obtain a homogeneous extract. The solution was allowed to cool at room temperature and was filtered twice to remove insolubles. This solution was centrifuged using microcentrifuge to obtain a clear aqueous extract. The aqueous extract thus obtained was observed to have  $\text{pH} \approx 3.0$  because it was containing organic acid which is tartaric acid naturally along with citric acid and malic acid. This freshly prepared tamarind extract was stored at 3-5  $^\circ\text{C}$  and was used as green biocatalyst for synthesis of benzothiazole derivatives [37, 38].

### General Procedure for the Synthesis of 2-(Phenyl)-1,3-benzothiazole and its derivatives

A mixture of 4-substituted benzaldehydes (0.001 mol) and 2-aminothiophenol (0.001 mol) in a minimum amount of water was stirred in the presence of 3 mL of tamarind juice ( $\text{pH} \approx 3.0$ ) for a few minutes at room temperature and then stirred at 90 $^\circ\text{C}$  for an appropriate time as mentioned in Table 2. The progress of the reaction was monitored by thin layer chromatography (TLC) technique. Crushed ice was used to quench the reaction mixture once the reaction was finished. After filtering off the resulting solid and repeatedly washing it with a minimum amount of ice-cold water, the crude product was allowed to air dry. Finally, the crude product was recrystallized with ethanol to give a pure product and dried in a vacuum desiccator over anhydrous  $\text{CaCl}_2$ . The melting points of all synthesized compounds are also reported and identified. The synthesized compound, [2-(4-chlorophenyl)benzothiazole], was fully characterized on the basis of its FTIR and  $^1\text{H-NMR}$  spectral techniques.

## III. RESULTS AND DISCUSSION

The reaction between 4-chlorobenzaldehyde and 2-aminothiophenol has been selected to optimize the synthesis of benzothiazole derivatives using environmentally-friendly and sustainable tamarind juice as a biocatalyst (Scheme 1). Reaction parameters such as temperature, amount of catalyst and type of solvent have been studied systematically and summarized in Table 1.

Initially, temperature effect on the synthesis of benzothiazole was studied by adding 3.0 mL of tamarind juice dissolved in water into the mixture (Table 1, Entries 9-13). Under normal temperature conditions and after 240 min of reaction



time, only small amounts of product have been formed since the ring closure required sufficient heating. Heating the solution up to 50°C resulted in increase of reaction efficiency and formation of the desired product in 42% during 120 min of reaction time. A further increase of temperature up to 70°C improved the yield up to 76% in shorter time of 75 min. The highest efficiency of the reaction has been obtained with temperature of 90°C when it was finished in 55 min and gave a yield of 89%. Higher temperature (100°C) did not affect positively the reaction results as the product yield remained unchanged at 88%. Consequently, 90°C was chosen as the ideal reaction temperature.

Upon determining the optimal temperature, the effect of catalyst loading was assessed at 90°C in water medium (Table 1, entries 1-4, 12 and 14). The reaction rate is rather slow in the presence of 1.0 mL of tamarind juice, producing the yield of just 19% after 120 minutes. With gradual increase of the volume of catalyst up to 3.0 mL, the yield gradually improved from 36% to 89%. In turn, the time needed for the completion of the reaction decreased significantly. Exceeding the amount of the catalyst beyond 3.0 mL did not cause any changes in the yield, meaning that the number of catalytic sites at 3.0 mL is enough.

The influence of solvent was then studied on the optimized catalytic conditions. Out of the solvent media considered, the best results were obtained with water medium, providing the greatest yield (89%) in the shortest period of time (Table 1, Entry 12). Ethanol and methanol were somewhat less efficient, yielding 84% and 82% (Table 1, Entries 5-6), while acetonitrile turned out to be unsuitable since it provided the yield of just 26% (Table 1, Entry 7). Without solvent, the yield was observed as 79% (Table 1, Entry 8). The improved efficiency noted in the case of water can be related to the proper distribution of the tamarind extract in aqueous medium and the efficient catalysis offered by the organic acids naturally present in the fruit juices.

Accordingly, based on these studies, it was found that 3.0 mL of tamarind juice with water at 90°C was the best condition and was thus used to prepare different benzothiazoles. At this condition, various aromatic aldehydes containing electron-donating or electron-withdrawing group reacted well with 2-aminothiophenol, resulting in the respective benzothiazole compounds. It indicates that the optimal condition is achieved during the progress of the reaction. Analysis of the melting point, FT-IR, and NMR spectrum of the end product, 2-(4-chlorophenyl) benzothiazole, showed that the results corresponded to those reported in the literature sources [39, 40]. It proves the synthesis of 2-(4-chlorophenyl) benzothiazole and effectiveness of the tamarind juice as a biocatalyst.

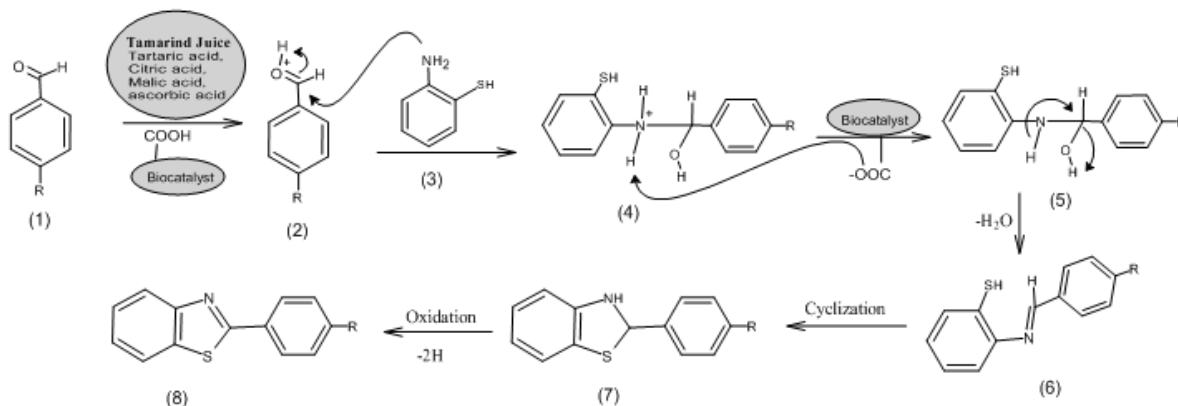
**Table-1 Effect of catalytic amount of catalyst, solvent and temperature on time and yield of the model reaction.**

Entry	Tamarind Juice (mL)	Solvent	Temperature (°C)	Time (min.)	Yield (%)
1	1.0	Water	90	120	19
2	1.5	Water	90	90	36
3	2.0	Water	90	80	51
4	2.5	Water	90	65	68
5	3.0	Ethanol	reflux	70	84
6	3.0	Methanol	reflux	75	82
7	3.0	Acetonitrile	reflux	180	26
8	3.0	---	90	60	79
9	3.0	Water	Room temperature	240	Trace
10	3.0	Water	50	120	42
11	3.0	Water	70	75	76
12	3.0	Water	90	55	89
13	3.0	Water	100	55	88
14	3.5	Water	90	55	89

**Figure 2** illustrates possible mechanism of synthesis of benzothiazole derivatives mediated by tamarind juice. Initially, the electrophilicity of the carbonyl of the aromatic aldehyde (1) is enhanced by protonation, thus forming a protonated carbonyl compound intermediate (2), which is an electrophile itself. Amino nitrogen of 2-aminothiophenol (3) adds to



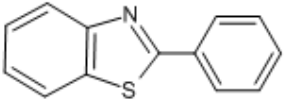
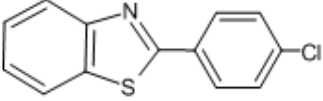
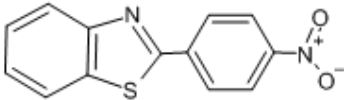
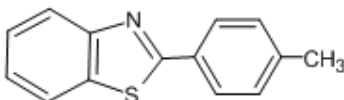
the activated carbonyl carbon at an early stage to give the carbinolamine intermediate (5) and eliminated one molecule of water gives imine intermediate (6). Further, intramolecular nucleophilic addition of the sulfur atom of the thiol group to the imine intermediate resulted in ring closure to produce a 2,3-dihydro benzothiazole intermediate (7), and the target benzothiazole derivative (8) is produced via air oxidation. The tamarind juice helped to promote the reaction efficiently by activating substrate and proton transfer under mild reaction conditions.



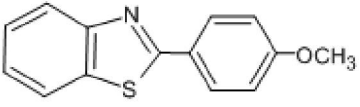
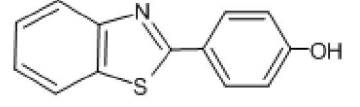
**Figure-2 Possible mechanism for the Synthesis of Benzothiazole derivatives using Tamarind juice**

The different substituted aromatic aldehydes have been converted to the corresponding benzothiazole derivatives using tamarind juice as a biocatalyst under optimized reaction conditions. Reaction occurred smoothly in the timeframe of 42-75 min, affording products in 78-92% yields. The obtained melting points are in good agreement with the literature values, confirming the identity and purity of the synthesized compounds. It showed the general applicability and excellent efficiency of developed and green protocol for benzothiazole synthesis.

**Table-2 Optimization study of Substrate for the Synthesis of benzothiazole Derivatives**

Sr. No.	Aldehyde	Product/Name	Time (min.)	Yield (%)	Melting point ( $^{\circ}$ C)	
					Observed	Lit. value [39]
1	R=H	 2-(phenyl) benzothiazole	48	88	112-114	110-112
2	R = Cl	 2-(4-chlorophenyl) benzothiazole	55	89	104-106	108-110
3	R = NO <sub>2</sub>	 2-(4-nitrophenyl) benzothiazole	42	92	230-232	228-230
4	R = CH <sub>3</sub>	 2-(4-methylphenyl) benzothiazole	67	84	84-86	82-84



5	R = OCH <sub>3</sub>	 2-(4-methoxyphenyl) benzothiazole	70	81	120-122	118-120
6	R = OH	 2-(4-hydroxyphenyl) benzothiazole	75	78	228-230	224-226

#### 2-(4-chlorophenyl)-1,3-benzothiazole

IR: 3072, 3027  $\nu$ (C-H), 1612, 1448  $\nu$ (C=C), 856, 747.

<sup>1</sup>H-NMR  $\delta$  (ppm): 8.12-8.06 (m, 3H), 7.92 (d, 1H, J=8 Hz), 7.58-7.52 (m, 3H), 7.43-7.39 (m, 1H).

#### IV. CONCLUSION

In this report, we are describing the synthesis of benzothiazole derivatives using tamarind juice as a naturally obtained biocatalyst. The tamarind juice proves out to be a very effective biocatalyst in which the product can be synthesized with efficiency. Tamarind juice is cheap and eco-friendly and also facilitates in rapid reaction rates, ease of product separation thus a successful example of green approach in the synthesis of benzothiazole derivatives.

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