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Lemon Juice: An Environmentally Benign Catalyst for Synthesis of Benzothiazoles and Benzoxazole Derivatives in Aqueous Medium

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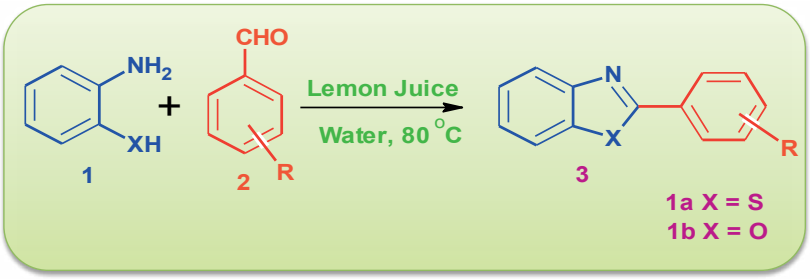
ABSTRACT

Lemon juice as a natural and eco-friendly catalyst has been utilized for the synthesis of benzothiazole and benzoxazole derivatives by the reaction of 2-aminothiophenol or 2-aminophenol with a variety of aryl aldehydes in good-excellent yields. The beneficial features of this new synthetic approach include short reaction time, a clean reaction profile with mild reaction condition and an easy work up procedure.



Graphical Abstract

Keywords: Natural catalyst, Aryl aldehydes, Benzothiazole, Benzoxazole

INTRODUCTION

The traditional reaction conditions increases the environmental pollution posed by utility of toxic, volatile organic solvents. Thus these organic processes generate lot of waste and have rigorous impact on living systems. Hence cleaner green reaction conditions with environmentally acceptable and renewable raw materials which offer environmental and economic advantages over traditional synthetic processes are necessary.

Uses of natural catalyst, environmentally benign solvent under mild reaction condition are the fundamental aspects of green chemistry. Natural catalysts represent a unique class of biocatalysts which are eco-friendly, inexpensive, non-hazardous; biodegradable has large number of application in the organic transformations [1-5].

Benzazoles such as benzathiazole, benzoxazole are privileged structural motifs having potential applications in the pharmacological and biological activities in medicinal chemistry [6-10]. Benzothiazoles are biologically active compounds which is used as valuable intermediates in various organic syntheses [11] and found in variety of natural products showing diverse medicinal applications [12-17]. Further, benzoxazoles exhibits photophysical and photochemical properties and shows chromophoric effect by enhancing the emission quantum yield through decrease in the non-radioactive decay rate constant on the fluorescence of conjugated compound [18]. Some of the typical reported methods for the synthesis of benzothiazoles and benzoxazoles include the reaction of 2-aminothiophenol or 2-aminophenol with variety of aryl aldehydes [19-30]. However, present methods exhibits certain drawbacks such as tedious catalyst preparation, expensive reagents, prolonged reaction times, use of toxic solvent, lower yields, and complicated workup procedures. Therefore, synthesis of benzazole derivatives using natural catalyst, eco-benign solvent under mild reaction condition is highly desirable. Herein, we chose water as a reaction media for condensation

of 2-aminothiophenol or 2-aminophenol with variety of aryl aldehydes using natural catalyst, because water is considerably safe, eco-friendly, non-toxic, and inexpensive compared to other organic solvents.

Citrus limonium, *Citrus aurantium*, and *Citrus indica* are important species of the citrus family, locally known as Limbu or Nimbu in India. The juice obtained from lemon is sour in taste used to control the high blood pressure, arthritis and rheumatism, asthma and to prevent kidney stone it is also well known plant species for antioxidant activity as well as for anti-carcinogenic activity. Acidity caused due to presence of citric and ascorbic acids (vitamin C) to lemon juice are responsible to works as an acid catalyst in organic transformation.

In continuation our research work for the development of sustainable methodologies for the synthesis of bio-active heterocyclic scaffolds [31-32], herein we report the synthesis of benzothiazoles and benzoxazoles by employing lemon juice as a natural, bio-degradable catalyst under mild reaction condition.

MATERIALS AND METHODS

All chemicals were purchased from local sources (Spectrochem and Thomas Bakers) and were of used without further purification. All reactions were carried out under air atmosphere in dried glassware. Melting points were measured by an open capillary method under open atmosphere. The products were in good agreements with those of known compounds by their spectral data. The FT-IR spectra were measured on Bruker ALPHA FT-IR spectrometer. The NMR spectra were recorded on a Bruker AC (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR) spectrometer using $CDCl_3$ as the solvent and TMS as an internal standard. The δ -values are expressed in parts per million (ppm).

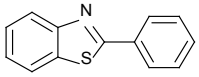
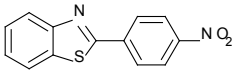
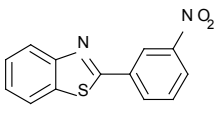
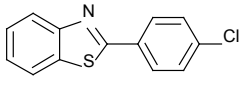
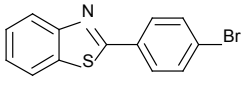
Preparation of lemon juice

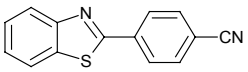
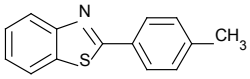
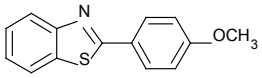
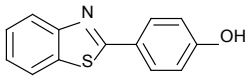
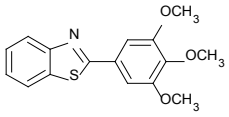
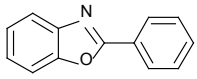
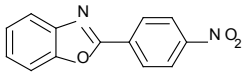
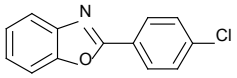
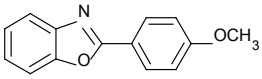
Fresh lemon was purchased from the local market. The pieces were made using a knife and pressed in a fruit juicer to obtain the juice. Then the juice was filtered through filter paper to remove solid material and clear portion of juice was used as a catalyst. The pH of the extracted lemon juice was found to be 2.3.

General procedure for the synthesis of benzazoles

In typical procedure, 2-aminothiophenol or 2-aminophenol (1 mmol), aryl aldehyde (1 mmol), and lemon juice: water mixture (1:1 v/v) (4 mL) was added in the reaction vessel. The reaction mixture was stirred at 80°C temperature for a specified time (**Table 1**). After reaction completion as analyzed by TLC, the reaction mixture was quenched with cold water and stirred continuously until free flowing solid was obtained. The resulting solid was filtered, air dried and recrystallization from ethanol to get pure product. The identity of the compound [2-(4-chlorophenyl) benzothiazole] was ascertained on the basis of ^{1}H NMR and ^{13}C NMR spectroscopy as shown in **Figures 1 and 2**. The physical and spectral data are in agreement with the literature data.

Table 1: Lemon juice catalyzed synthesis of benzothiazole and benzoxazole[a].

Entry	Amine	Aldehyde	Product (3)	Lemon juice		Pineapple juice		Orange juice	
				Time (min)	Yield[b] (%)	Time (min)	Yield[b] (%)	Time (min)	Yield[b] (%)
1	1a	H		45	91	50	90	50	88
2	1a	4-NO_2		50	90	55	88	55	87
3	1a	3-NO_2		51	88	56	87	58	86
4	1a	4-Cl		52	88	55	86	60	84
5	1a	4-Br		60	87	64	85	65	83

6	1a	4-CN		50	60	55	88	55	86
7	1a	4-CH_3		65	88	70	87	75	86
8	1a	4-OCH_3		70	87	74	80	80	83
9	1a	4-OH		72	88	75	84	85	82
10	1a	3,4,5-OCH_3		90	84	95	85	99	80
11	1b	H		120	82	125	81	130	80
12	1b	4-NO_2		75	90	90	86	90	84
13	1b	4-Cl		80	89	85	85	90	81
14	1b	4-OCH_3		100	88	105	83	105	80

[a]Reaction conditions: Aryl aldehydes (1 mmol), 2-aminothiophenol/2-aminophenol (1 mmol), lemon juice: water (4 mL, 1:1, v/v) at 80°C. [b]Isolated yields after purification

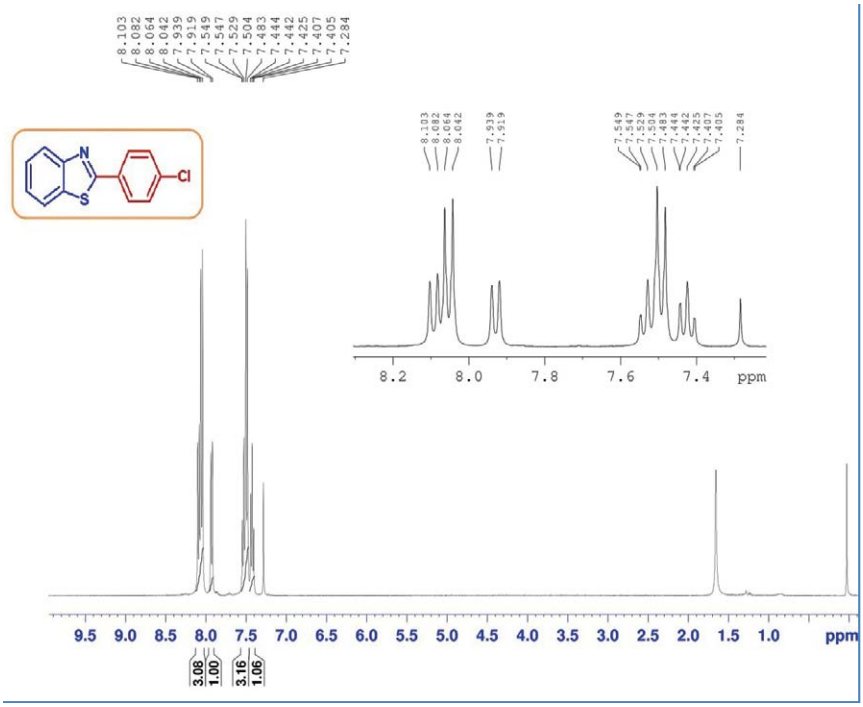


Figure 1: [1]H-NMR spectra of 2-(4-chlorophenyl) benzothiazole.

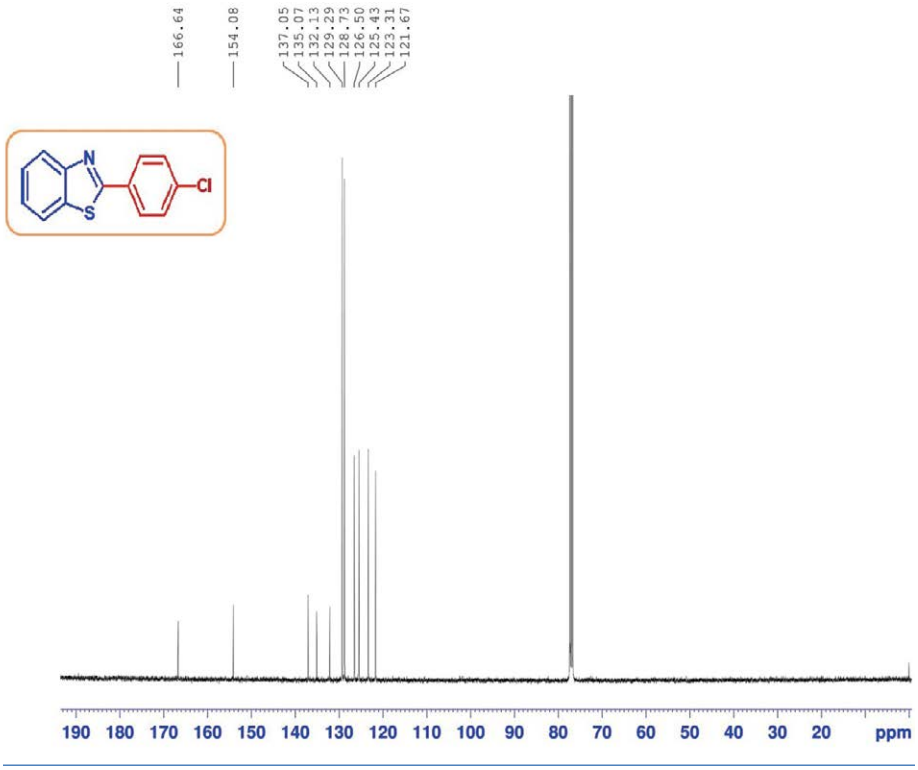


Figure 2: ^{13}C NMR spectra of 2-(4-Chlorophenyl) benzothiazole.

Selected spectral data

2-(phenyl) benzothiazole (Table 1, entry 1)

Off-white solid, MP: 111-113°C (34); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.10-8.13 (m, 3H), 7.92-7.94 (d, 1H, *J*=8 *Hz*), 7.50-7.54 (m, 4H), 7.39-7.43 (m, 1H)); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 121.6, 123.2, 125.2, 126.2, 127.5, 129, 130.9, 133.6, 135, 154.1, 168; IR (KBr) (cm^{-1}): 3056, 1622,1448, 755, 623.

2-(4-nitorphenyl) benzothiazole (Table 1, entry 2)

Yellow Solid, MP: 229-331°C (34); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.09-8.14 (m, 2H), 7.93-7.95 (d, 2H, J=7.6 Hz), 7.66-7.93 (m, 1H), 7.18-7.28 (m, 2H), 7.03-7.15 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 121.6, 123.8, 124.3, 125.8, 126.2, 127.1, 128, 129.7, 132.8, 141.2, 147.7, 149.5, 157; IR (KBr) (cm^{-1}): 3044, 1627, 1557, 1360, 822, 756.

2-(4-chlorophenyl) benzothiazole (Table 1, entry 4)

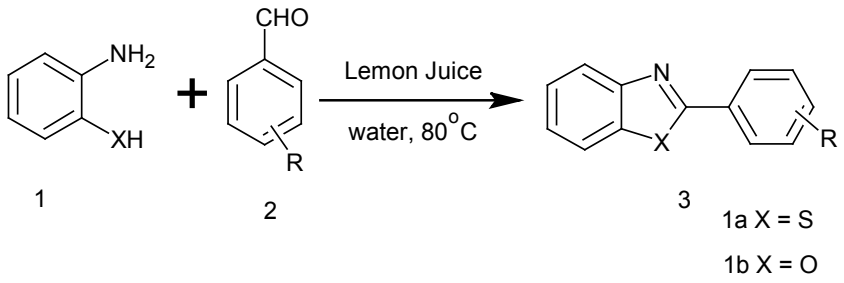
White Solid, MP: 107-109°C (34); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.04-8.10 (m, 3H), 7.92-7.93 (d, 1H, J=8 Hz) 7.48-7.54 (m, 3H), 7.40-7.44 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 121.6, 123.3, 125.4, 126.5, 128.7, 129.2, 132.1, 135, 137, 154, 166.6; IR (KBr) (cm^{-1}): 3056, 1630,1445, 850, 733.

2-(4-nitrophenyl) benzoxazole (Table 1, entry 12)

Yellow Solid, MP: 263-265°C (34); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.23-8.28 (m, 2H), 7.45-7.52 (m, 2H), 7.33-7.42 (d, 2H, J=8.4 Hz), 7.22-7.31 (d, 2H, J=7.4 Hz), 7.33-7. 84 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 122.6, 124.8, 124.5, 126.8, 128.4, 130.7, 132.4, 142.2, 148.7, 158.4; IR (KBr) (cm^{-1}): 3048, 1621, 1556, 1533, 1352.

RESULTS AND DISCUSSION

Initially, in order to optimize various reaction conditions for the synthesis of benzothiazole we conducted the model reaction between 2-aminothiophenol (1 mmol), 4-nitrobenzaldehyde (1 mmol) and lemon juice:water (4 mL, 1:1, v/v) **Scheme 1**.



Scheme 1: Synthesis of benzazoles using lemon juice as a natural catalyst.

Initially, to study the effect of catalyst loading the model reaction was carried out at ambient temperature by increasing amount of lemon juice from 1 to 3 mL, but moderate product was obtained with prolonged reaction time (**Table 2**, entries 1-5). Continuing our effort by paying attention on yield, surprisingly the considerable influence on the yield (81%) obtained when the model reaction was carried out at 80°C in presence of 2 ml lemon juice (**Table 2**, entry 6). Further in order to check the effect of the solvent on the yield of the product, the above reaction was performed in different solvents like methanol, ethanol, and water at temperature 80°C. In all cases 81-90% yield of desired product was obtained (**Table 2**, entry 7-9). We also optimized the catalyst-solvent proportion on conducting the model reaction by changing lemon juice: water ratio (**Table 2**, entry 9-11). The result showed that 2:2 (lemon juice: water) proportions suitable for smooth conversion of reactant to corresponding product with respect to time and yield.

Table 2: Effect of catalytic amount of catalyst and temperature on time and yield of the model reaction[a].

Entry	Amount of lemon juice (mL)	Solvent	Temperature (°C)	Time (min)	Yield[b] (%)
1	1.0	-	RT	120	Trace
2	1.5	-	RT	120	20
3	2.0	-	RT	120	35
4	2.5	-	RT	120	35
5	3.0	-	RT	120	35
6	2.0	-	80	50	80
7	2.0	Methanol	80	70	81
8	2.0	Ethanol	80	65	83
9	2.0	Water	80	50	90
10	2.5	Water	80	50	90
11	3.0	Water	80	50	89

[a]Reaction conditions: 4-nitrobenzaldehydes (1 mmol), 2-aminothiophenol (1 mmol), lemon juice:water (4 mL, 1:1, v/v) at 80°C. [b]Isolated yield after purification

With these optimized condition in hand, we extended this protocol for the synthesis of benzothiazoles and benzoxazole derivatives by using various natural catalyst such as pineapple juice, and orange juice. It was observed that, both pineapple and orange juice efficiently undergo this transformation giving satisfactory yield of anticipated product. The pH analysis of all above natural catalyst is summarized in **Table 3**. As juices are acidic in nature it was used as acid catalyst for this protocol. Among all, the pH of lemon juice was found to be lowest as 2.3. Therefore, the yield of benzothiazoles and benzoxazole derivatives by using lemon juice was quite high as compared to pineapple juice and orange juice (**Table 1**).

Table 3: pH of different natural catalyst.

Entry	Natural catalyst	pH
1	Lemon juice	2.3
2	Pineapple juice	3.5
3	Orange juice	3.7

Next, we turned our efforts towards the scope and generality of protocol for the synthesis of benzothiazole and benzoxazole derivatives by reacting 2-aminothiophenol or 2-aminophenol with diverse array of aryl aldehydes and the results are depicted in **Table 1**. It was observed that, aromatic aldehydes bearing electron donating as well electron

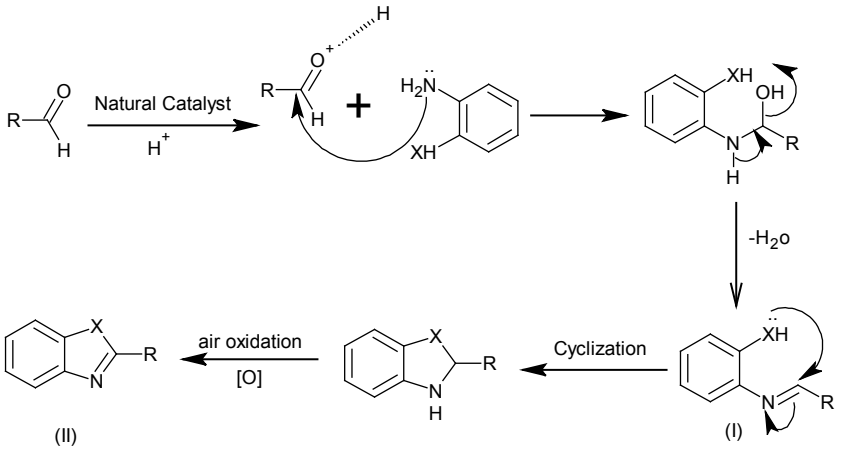
withdrawing groups reacted efficiently with 2-aminothiophenol and 2-aminophenol giving corresponding product in good to excellent yields. It was noticed that the aldehydes with electron donating groups required longer reaction time than the aldehydes with electron withdrawing groups.

We then compared results obtained by above protocol with the reported catalysts for synthesis of benzothiazoles and benzoxazole derivatives (**Table 4**). It was observed that the present protocol is best fitted with the previous results in terms of reaction time and product yields.

Table 4: Comparison of efficiency of natural catalyst with reported catalyst [33-37].

Entry	Catalyst	Reaction condition	Benzothiazole derivatives		Benzoxazole derivatives		Ref.
			Time (min)	Yield (%)	Time (min)	Yield (%)	
1	Lemon Juice (2 ml)	Water/80°C	50	90	75	90	Present work
2	CdSNS(5 mg)	visible light, ethanol/RT	20	95	-	-	33
3	Catalyst-free	Water/110°C	180	96	-	-	22
4	Nano-ZnO (10 mol %)	EtOH/reflux	95	72	90	70	34
5	Nano-alumina (10 mol %)	EtOH/reflux	95	78	95	78	34
6	Nano-ZMS-5 (10 mol %)	EtOH/reflux	90	80	80	82	34
7	Nano-crystalline SZ (10 mol %)	EtOH/reflux	75	91	75	84	34
8	$NaHSO_3$ (200 mol %)	DMA/120°C	30	80	-	-	35
9	Fe(III)–Schiff base/SBA-15 (0.01 gm)	Water/reflux	180	89	180	87	36
10	P_2O_5 (10 mol %)	RT/MeOH	420	78	-	-	37

The possible mechanism for the synthesis of benzazole is depicted in **Scheme 2**. It is believed that carbonyl group is activated by acidity of natural catalyst for nucleophilic attack that led to the formation of intermediate (I). The intermediate I undergo intra-molecular cyclization, followed by air oxidation, leading to the formation of the desired product (II).



Scheme 2: Plausible mechanism for synthesis of benzazoles derivatives using natural catalyst.

CONCLUSION

In conclusion, we have developed simple and green protocol for synthesis of benzothiazoles and benzoxazole derivatives comprising the reaction of various aryl aldehydes with aminobenzenes in good to excellent yield using natural catalyst. This method offers several advantages such as mild reaction condition high yield, short reaction time, and simple experimental and workup procedure.

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