A green synthesis of amino Schiff bases using mango water as a natural catalyst under hand grinding technique

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Received 28 June 2018; accepted (revised) 11 March 2019

The application of edible fruit juice in organic synthesis has attracted the interest of chemists, particularly from the view of green chemistry. A series of amino Schiff bases have been prepared in good to excellent yield from the condensation of 1,2-diaminobenzenes with various aromatic aldehydes in presence of mango water as a natural acid catalyst under hand grinding technique. The reaction is green and economically viable. The product is purified by simple filtration followed by crystallisation with ethanol and drying processes.

Keywords: Green synthesis, amino Schiff bases, natural catalyst, mango water, grinding

The idea of green chemistry^{1,2} and its applications^{3,4} in synthetic organic chemistry have emerged as major solutions for the development of clean and more benign chemical routes. Different methodologies and processes have been developed for this purpose. In recent years, environmentally benign organic research has received considerable attention and a good number of organic transformations have been reported using fruit juice as catalysts⁵.

Mango (*Mangifera indica*) (Figure 1) is grown extensively in South Asia from where it has been distributed worldwide to become one of the most cultivated edible fruits in the tropics. The green mango fruit is sour in taste. The acid part is one of the main ingredients of green mango fruit. It is characterized by the presence of malic acid 12.66% and tartaric acid 7.04% (Ref 6). Thus an aqueous extract of green mango fruit (mango water) is acidic due to presence of edible organic acids and hence it may be work as an acid catalyst for condensation of 1,2-diaminobenzenes and aromatic aldehydes.

Schiff bases represent a class of medicinally important compounds which have wide variety of biological and pharmacological activities such as anticancer⁷, antidepressant⁸, antibacterial⁹. antimicrobial¹⁰, insecticidal¹¹ and anti-inflammatory¹² activity. Schiff base complex of small organic molecules with metal cation has found broad applications in the field of interactions with biogenic macromolecules such DNA, RNA. as and



Figure 1 — Photograph of green mango and mango water

peptides^{13,14}. The current literature shows that there has been a growing interest towards green synthesis of these compounds due to numerous applications in various fields of chemistry. Although various research groups have developed different methods for synthesis of Schiff bases. Many of the reported methods require long reaction times, use of expensive and toxic catalysts and organic solvents^{15,16}. In such consequences we have developed a new method for the synthesis of amino Schiff bases by the condensation of 1,2-diaminobenzenes with various aromatic aldehydes using mango water as catalysts under grinding with short times and high yields. The product can be isolated simply by filtration followed by crystallisation with ethanol and drying processes.

Results and Discussion

In continuation of our research work using edible fruit juice¹⁷⁻²² in organic synthesis here we are pleased to report that a mixture of 1,2-diaminobenzenes (1), aromatic aldehyde (2) (1:1 ratio) in presence of mango water (2 mL) under grinding using mortarpestle furnished amino Schiff bases (3) in good to excellent yields (85-95%, Scheme I).

The reaction was optimized by varying amount of catalyst. We chose the reaction between 3,4-diaminotoluene (1a) and 4-methoxybenzaldehyde (2a) as the model reaction. From the Table I (entry 3), it was found that the best result was obtained by using 2 mL of mango water under grinding protocol

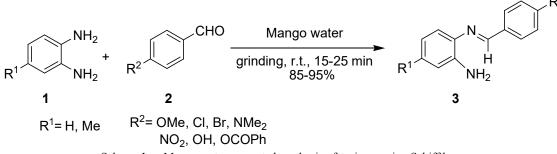
(conversion rate 98% of product 3a) over the conventional RT stirring method (conversion rate 40% only of product 3a) in short reaction time.

Using this methodology these reactions were completed in shorter reaction times (15-25 min) with good to excellent yields (85-95%) of various amino Schiff bases (3a-I, Figure 2). A wide range of aromatic aldehydes were subjected with 0phenylenediamine and 3.4-diaminotoluene to prove the general applicability of our present procedure which is summarized in Table II. Both ophenylenediamine and 3,4-diaminotoluene showed similar activity towards the reactions. The presence of electron donating or electron withdrawing group in the aromatic ring of the aldehydes did not affect the rate of conversion under the present experimental conditions.

Amino Schiff bases (**3a-l**) showed strong characteristics IR absorption bands at a range 3498-3345 cm⁻¹ for NH₂ group as a doublet signal and 1591-1599 cm⁻¹ for C=N bond respectively. In the ¹H NMR spectra of **3a-l**, the NH₂ hydrogen resonated as a broad singlet at a range of 4.18-4.32 ppm. The – CH=N- hydrogen resonated as a singlet at 8.44-8.63 ppm. ¹³C NMR chemical shift for compounds **3a** was observed in their expected region.

Experimental Section

All reactions were carried out in dried glassware. Reagents were purchased from Spectrochem/



Scheme I — Mango water promoted synthesis of various amino Schiff bases

Table I — Model reaction of 3,4-diaminotoluene (1.0 mmol) with 4-methoxybenzaldehyde (1.0 mmol) using mango water as catalyst ^a									
Entry	Amount of mango water ^b (mL)	Reaction time (min)	Conversion rate at RT (%)	Grinding method conversion rate (%)					
1	0	40	0	trace					
2	1	40	10	30					
3	2	25	40	98					
4	2	40	45	90					
5	5	40	42	85					
^a % of conversion of the reaction was measured by TLC with respect to aldehyde									
^b p H of the mango water was 3.0									

Loba/SRL and were used without further purification. Melting points were determined on a Kofler block and are uncorrected. Reactions were performed in a mortar and pestle made of ceramic. ¹H and ¹³C NMR spectra were recorded as solutions in CDCl₃ on a Bruker AV-300 spectrometer using TMS as an internal standard operating at 300 MHz for ¹H, 75 MHz for ¹³C. Infrared spectra were recorded on a Bruker Tensor 27 IR spectrometer (KBr pellets).

Analytical samples were dried in vacuo at RT. Thin layer chromatography was carried out on silica gel G for TLC obtained from SRL Pvt. Ltd.

Preparation of mango water

The green mango fruits of Mangifera indica were purchased from the local market. The upper shell of the green mango fruit and its inner grain were removed. The hard material (10 g) was boiled with

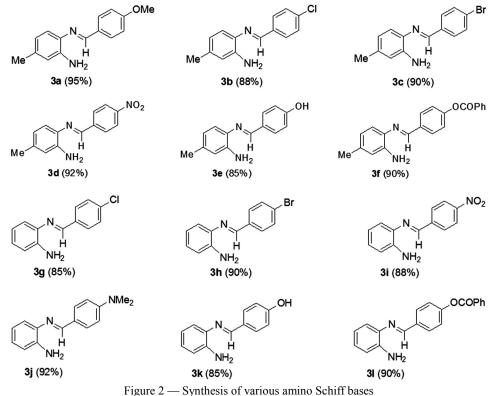


		Table II	- Synthesis of amino Schiff bas	ses ^a using mango	water ^b	
Compd	\mathbf{R}^1	R^2	Reaction time (min)	Yield ^c	m.p. (°C)	
				(%)	Obsd.	Lit. (Ref.)
3 a	Me	OMe	25	95	80-82	-
3b	Me	Cl	20	88	132-34	-
3c	Me	Br	20	90	110-12	-
3d	Me	NO_2	15	92	128-30	-
3e	Me	OH	20	85	150-52	-
3f	Me	OCOPh	22	90	122-24	-
3g	Н	Cl	20	85	284	284-86 (23)
3h	Н	Br	25	90	240-42	242-44 (23)
3i	Н	NO ₂	15	88	300-302	298-300 (23)
3ј	Н	NMe ₂	25	92	134	132-34 (23)
3k	Н	OH	25	85	270-72	270-72 (23)
31	Н	OCOPh	20	90	116-18	118-20 (23)

^a All the products were characterized by IR, ¹H and one of them by ¹³C spectral data.

^b Mango water taken 2 mL in each reaction.

^c Isolated yields based upon starting aldehyde.

water (50 mL), cooled and it was filtered with the help of cotton. The filtrate was further centrifuged using micro centrifuge (REMI RM-12C). The clear portion of the aqueous extract (pH 3) of the mango fruits called mango water was used as catalyst for condensation reactions.

General procedure for synthesis of amino Schiff bases

A mixture of compound 1 (1 mmol), compound 2 (1 mmol) and mango water (2 mL) were taken in a mortar and it was ground by pestle in open air at RT for the time period mentioned in the Table II. The progress of the reaction was monitored by TLC over silica gel. When the reaction was found to be complete, 10 mL of water was added to it. The solid product 3 was collected by simple filtration and washed with hot water. The crude products 3a-1 were purified by recrystallization from ethanol.

The structures of compounds **3a-f** were characterized by IR, ¹H NMR and one of them by ¹³C NMR spectral data and compounds **3g-l** were characterized by comparing their melting points with reported data and TLC with their authentic samples, characterized previously in our laboratory²³.

Compound 3a: Yellow crystal. m.p.80-82°C. ¹H NMR (300 MHz, CDCl₃): δ 8.46 (s, 1H, HC=N), 7.85 (d, J = 8.7 Hz, 2H), 6.96 (d, J = 9.0 Hz, 2H), 6.95 (d, J = 8.1 Hz, 1H), 6.60 (s, 1H), 6.55 (s, 1H), 4.18 (br. s, 2H, NH₂), 3.87 (s, 3H, OMe), 2.27 (s, 3H, Me); ¹³C NMR (75 MHz, CDCl₃): δ 161.86, 155.90, 141.97, 137.19, 135.20, 130.15 (two carbons), 129.75, 119.21, 116.75, 115.99, 114.07(two carbons), 55.40 (OMe), 21.22 (Me); IR (KBr): 3469 & 3369 (NH₂), 1594 cm⁻¹ (C=N).

Compound 3b: Whitish grey solid. m.p.132-134 °C. ¹H NMR (300 MHz, CDCl₃): δ 8.49 (s, 1H, HC=N), 7.83 (d, J = 8.1 Hz, 2H), 7.42 (d, J = 8.1 Hz, 2H), 6.99 (d, J = 8.1 Hz, 1H), 6.61 (s, 1H), 6.56 (d, J = 7.8Hz, 1H), 4.21 (br. s, 2H, NH₂), 2.28 (s, 3H, Me); IR (KBr): 3478 & 3376 (NH₂), 1599 cm⁻¹ (C=N).

Compound 3c: Yellow crystal. m.p.110-112°C. ¹H NMR (300 MHz, CDCl₃): δ 8.48 (s, 1H, HC=N), 7.77 (d, J = 7.8 Hz, 2H), 7.58 (d, J = 8.4 Hz, 2H), 6.99 (d, J = 8.4 Hz, 1H), 6.61 (s, 1H), 6.56 (d, J = 7.8Hz, 1H), 4.20 (br. s, 2H, NH₂), 2.28 (s, 3H, Me); IR (KBr): 3392 & 3312 (NH₂), 1591 cm⁻¹ (C=N). **Compound 3d**: Red crystal. m.p.128-130°C. ¹H NMR (300 MHz, CDCl₃): δ 8.63 (s, 1H, HC=N), 8.31 (d, J = 8.7 Hz, 2H), 8.05 (d, J = 8.7 Hz, 2H), 7.07 (d, J = 8.1 Hz, 1H), 6.63 (s, 1H), 6.57 (d, J = 8.1Hz, 1H), 4.32 (br. s, 2H, NH₂), 2.29 (s, 3H, Me); IR (KBr): 3498 & 3392 (NH₂), 1595 cm⁻¹ (C=N).

Compound 3e: Yellow crystal. m.p.150-152°C. ¹H NMR (300 MHz, CDCl₃): δ 8.44 (s, 1H, HC=N), 7.80 (d, J = 8.4 Hz, 2H), 6.95 (d, J = 7.8 Hz, 1H), 6.90 (d, J = 8.4 Hz, 2H), 6.60 (s, 1H), 6.56 (d, J = 8.1Hz, 1H), 4.20 (br. s, 2H, NH₂), 3.51 (br. s, 1H, OH), 2.27 (s, 3H, Me); IR (KBr): 3698 (OH), 3440 & 3345 (NH₂), 1592 cm⁻¹ (C=N).

Compound 3f: Yellow crystal. m.p.122-124°C. ¹H NMR (300 MHz, CDCl₃): δ 8.55 (s, 1H, HC=N), 8.22 (d, *J* = 8.4 Hz, 2H), 7.98 (d, *J* = 8.7 Hz, 2H), 7.66 (t, 1H), 7.53 (t, 2H), 7.33 (d, *J* = 8.7 Hz, 2H), 7.01 (d, *J* = 7.8 Hz, 1H), 6.61 (s, 1H), 6.58 (d, *J* = 8.1 Hz, 1H), 4.23 (br. s, 2H, NH₂), 2.29 (s, 3H, Me); IR (KBr): 3433 & 3350 (NH₂), 1719 (C=O), 1597 cm⁻¹ (C=N).

Conclusions

We developed a convenient, simple, efficient, and eco-friendly green procedure for the synthesis of amino Schiff bases from 1,2-diamino benzenes and various aromatic aldehydes under grinding using mango water, a natural acid catalyst obtained from green mango fruit. This protocol has several advantages like short reaction time, very high yields, simple product purification technique, low cost, safety and satisfactorily addresses environmental concerns. All these advantages make this methodology an alternative platform to the conventional method and also make it significant under the umbrella of environmentally greener processes.

Acknowledgements

The author gratefully acknowledges financial support from the University Grant Commission, New Delhi, Government of India (UGC MRP Grant no. PSW-055/15-16 (ERO) dated: 27.06.17). The author is grateful to Dr. Tapas Sarkar, CSIR-Indian Institute of Chemical Biology, Kolkata for providing the NMR spectral data and to the Principal, A. J. C. Bose College, Kolkata for constant encouragement and providing necessary facilities.

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