



# Fruit Juice: A Natural, Green and Biocatalyst System in Organic Synthesis

Rammohan Pal\*

Department of Chemistry, Acharya Jagadish Chandra Bose College, 1/1B, A. J. C. Bose Road, Kolkata 700 020, India

\*Corresponding author (Email: pal\_rammohan@yahoo.com)

**Abstract** -The role of naturally available fruit juice in organic synthesis has attracted the interest of chemists, particularly from the view of green chemistry. This review summarizes the versatile synthetic applications of fruit juice as a biocatalyst in different chemical transformations. Fruit juice of lemon, pineapple, tamarind, *Acacia concinna*, *Sapindum trifolium*, and coconut is extensively used in organic synthesis. Lemon juice catalyzed reactions including Knoevenagel condensation, three-component synthesis of dihydropyrimidinones, triazoles, synthesis of schiff bases, and bis-, tris- and tetraindoles are reported. Pineapple juice and tamarind juice has been used for the synthesis of dihydropyrimidinones and bis-, tris- and tetraindoles respectively. Anilides and aldamines were also synthesized by *Acacia concinna* fruit juice and *Sapindum trifolium* fruit juice respectively. Coconut juice was used as a biocatalyst for reduction of carbonyl compounds and hydrolysis of esters, amides and anilides. Application of fruit juice as a natural and biocatalyst allows mild and highly selective transformation and synthesis in a facile and environmentally friendly manner. Moreover, fruits are inexpensive and easily available in the market, and its juice can be extracted easily which can be used as catalyst in the organic transformations.

**Keywords** - Fruit Juice, Environmentally Friendly, Economic, Biocatalyst, Organic Synthesis

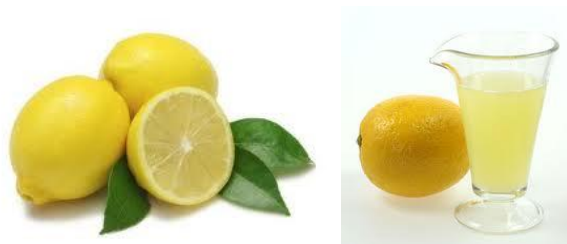
## 1. Introduction

In recent years, organic research is mainly focused on the development of greener and eco-friendly processes which involve in the use of alternative reaction media to replace toxic and expensive catalysts or volatile and hazardous solvents like benzene, toluene and methanol, commonly used in organic synthesis. Nowadays, many organic transformations have been carried out in water [1-3]. It is unique solvent because it is readily available, inexpensive, nontoxic, safer, and environmentally benign. The applications of an aqueous extract of different fruit juice have witnessed a rapid development. This growing interest in fruit juice is mainly because of its biocatalysts, environmentally benign character, nonhazardous and cost effectiveness. In literature, number of organic reactions are reported in which natural catalysts like clay [4-6], phosphates [7, 8], gold [8], animal bone [9] are employed. In recent years, chemical reactions using plant cell cultures and part of plants as biocatalysts have received great attention [10-12]. This crescent interest is due to the wide biotechnological potential of the enzymatic reactions. The biocatalytical transformations using edible plants [13], plant root [14, 15], plant tubers [16] and plant leave [17] extract can be applied in many organic reactions. Fruit juice is also naturally occurring which was used as a biocatalysts in organic synthesis. Fruit juice is now being routinely used in organic

synthesis as homogeneous catalysts for various selective transformations of simple and complex molecules. The purpose of the present review is to summarize the utility of different fruit juice with emphasis on recent synthetic applications; Literature coverage is through till 2013.

## 2. Fruit Juice of Lemon

The lemon is a small evergreen tree and the tree's ellipsoidal yellow fruits. *Citrus limonium*, *Citrus indica*, *Citrus aurantium* are some important species of citrus family. The lemon is indigenous to the north-west regions of India. It is now widely grown in all tropical and subtropical countries. In India it is also cultivated in home gardens. Lemon juice [18] obtained from lemon is sour in taste. The use of lemon juice, pulp and zest in our day-to-day life can not be understated. Lemon juice is used to make lemonade, soft drinks, and cocktails. It is used for deodorize the garbage, freshen the room and fridge. The juice is used to control the high blood pressure, arthritis and rheumatism, asthma, prevent kidney stone etc.



**Fig.1.** Photography of Fruit and Lemon Juice of *Citrus Limon*

### 2.1. Composition of Lemon Juice

The main ingredients of the extract of *Citrus limonium* species of lemon are moisture (85%), carbohydrates (11.2%), citric acid (5-7%), protein (1%), ascorbic acid or vitamin-C (0.5%), fat (0.9%), minerals (0.3%), fibres (1.6%) and some other organic acids [18]. The juice is soluble in water. Due to presence of citric acid and ascorbic acid, lemon juice is acidic (pH= 2-3) in nature, and thus it works as acid catalyst in organic reactions.

### 2.2. General Procedure for Extraction of Lemon Juice

Fresh lemon was cut by using knife and then pieces were pressed in a fruit juicer to get the juice extract. Then the juice was filtered through cotton/muslin cloth and then through filter paper to remove solid material and to get clear juice which as used as a catalyst.

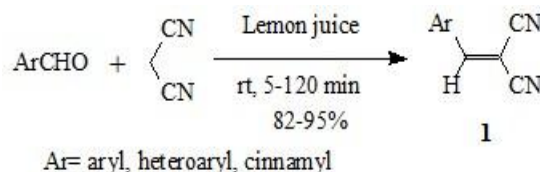
### 2.3. Applications of Lemon Juice in Organic Synthesis

Most people are familiar with the traditional uses for lemon juice such as culinary, medicinal and industrial purposes. Nowadays the lemon juice has played an important role in organic synthesis. Lemon juice was reported to catalyze Knoevenagel condensation reaction to synthesise arylidene-malononitriles which shows antibacterial and antifungal activity [19]. Dihydropyrimidinones are interesting intriguing therapeutic and pharmacological properties [20, 21]. 1, 2, 4-Triazole derivatives are found to be associated with various biological activities such as anticonvulsant [22], antifungal [23], anticancer [24] and antibacterial [25]. Schiff bases exhibit significant biological activities like antitumor [26], anti-inflammatory agents [27], antituberculosis [28] and anti-

microbial [29] activities. Bis-, and tris (indolyl) methanes are used to prevent bladder cancer growth, mammary tumor growth and also shows numerous activities [30a]. Tetraindolyl derivatives [30b] are used in the treatment of fibromyalgia, chronic fatigue and irritable bowel syndrome. These important compounds have efficiently been synthesised using naturally occurring biocatalyst, lemon juice.

#### 2.3.1. Knoevenagel Condensation Reaction

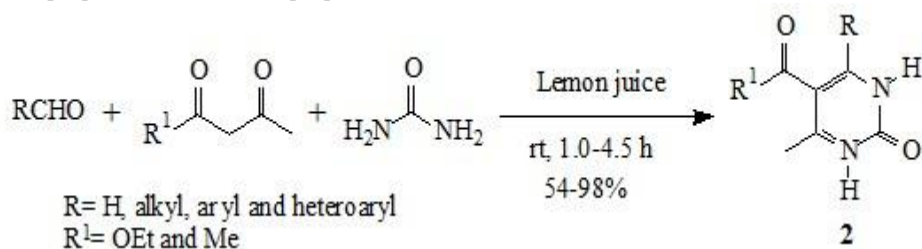
The Knoevenagel condensation [31] of aldehydes with active methylene compounds is an important method used for the synthesis of pharmaceutically important organic compounds. Deshmukh and his co-workers [18] showed that lemon juice can act as an efficient homogeneous acid catalyst for the Knoevenagel condensation reaction under solvent-free conditions. Thus, when various aldehydes and malononitrile were mixed with lemon juice and the mixture were stirred at room temperature for 5-120 min afforded the condensation product **1** in good yields (Scheme 1). The new approach for Knoevenagel condensation by lemon juice is nonpolluting and does not employ any toxic material, quantifying it is a green method.



**Scheme 1.** Lemon juice catalyzed Knoevenagel condensation

#### 2.3.2. Synthesis of Dihydropyrimidinone

Patil *et al.* reported an efficient one-pot, three component Biginelli type synthesis of dihydropyrimidinone (**2**) under solvent-free conditions from aldehydes, 1,3-dicarbonyl compounds and urea at room temperature using extract of lemon juice (*Citrus limonium* species) as natural catalyst (Scheme 2) [32]. Compared with the other methods for multicomponent synthesis of 3, 4-dihydropyrimidinones this new procedure using lemon juice offers better yields, non-polluting and green approach to this biocyclocondensation reaction.

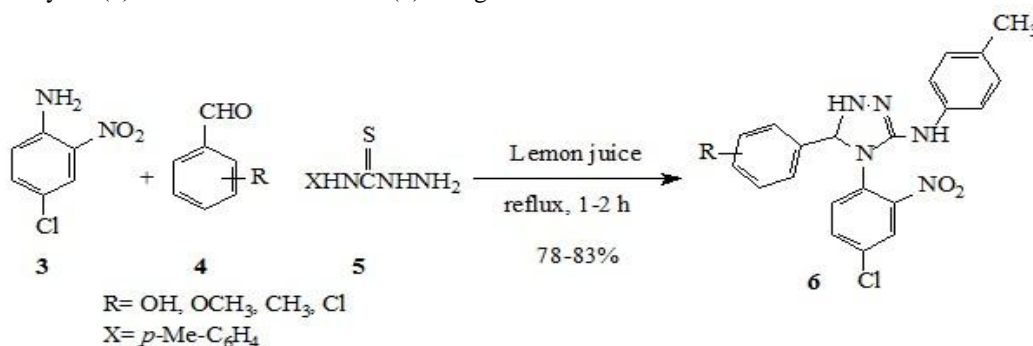


**Scheme 2.** Three-component synthesis of dihydropyrimidinones catalyzed by lemon juice

### 2.3.3. Synthesis of Triazoles

A three component one-pot clean biocyclocondensation reaction was reported by Sachdeva et al. using biocatalyst lemon juice of *Citrus limonium* species of lemon. Thus, substituted-2H-1,2,3-triazole phenol derivatives (**6**) were synthesized by Sachdeva et al. using lemon juice in aqueous ethanol in reflux by the reaction of 4-chloro-2-nitro aniline (**3**) and aromatic aldehydes (**4**) with thiosemicarbazide (**5**) in high

yield (Scheme 3) [33]. Citric acid (5-7%) present in lemon juice (pH= 2-3) works as acid catalyst for the synthesis of triazole derivatives. The use of water as a green solvent and the use of lemon juice as a natural catalyst offer a convenient, non-toxic, and inexpensive reaction medium for the environment-economic synthesis of triazole derivatives. Synthesized compounds **6** were found to be excellent fluorescent materials and potent fungicidal agents.

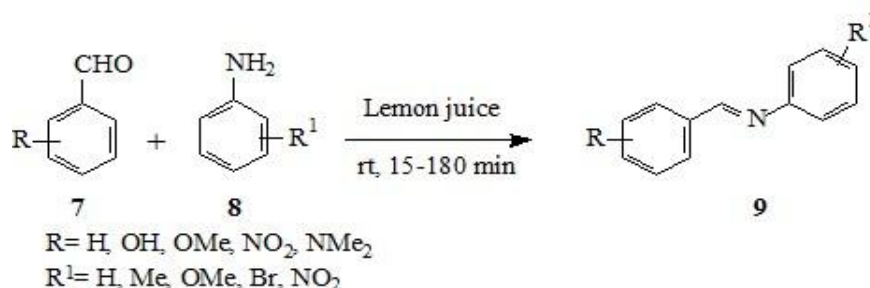


**Scheme 3.** Three-component synthesis of triazole derivatives catalyzed by lemon juice

### 2.3.4. Synthesis of Schiff Base

Lemon juice is a powerful and selective natural acid catalyst for condensation reaction. Patil and his coworker have reported a mild and selective imine **9** formation of aryl aldehyde (**7**) and aromatic primary amine (**8**) using lemon juice (*Citrus limonium* species) at room temperature in 25-300 min in good to excellent yields (42-100%) (Scheme 4) [34]. It was found

that electron withdrawing groups attached to aromatic aldehydes and electron donating groups attached to aromatic amines facilitates the reaction. However no result was obtained when condensation is carried without employing lemon juice. The role of lemon juice is catalyzing the reaction was demonstrated by the lack of schiffs base formation when the reaction is carried out in absence of catalyst.

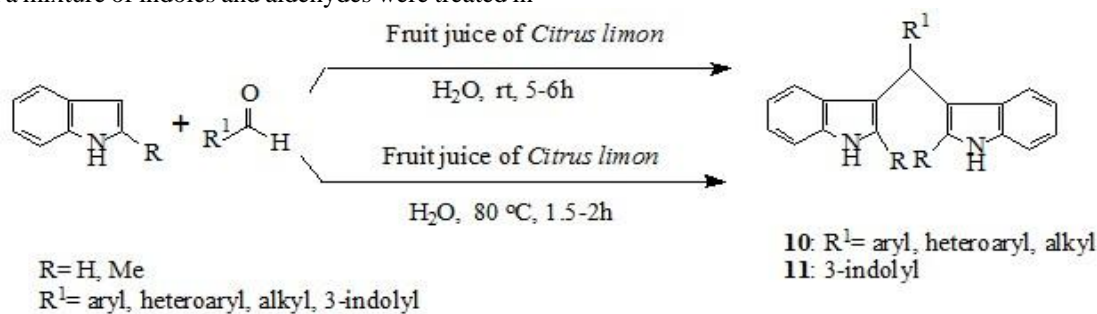


**Scheme 4.** Lemon juice catalyzed synthesis of Schiff bases

### 2.3.5. Synthesis of Bis-, Tris- and Tetraindoles

Pal and coworkers [35] observed that lemon juice can be utilized for the biocondensation of indoles and aldehydes for the synthesis of bis-, and tris (indolyl) methanes (Scheme 5). Thus, when a mixture of indoles and aldehydes were treated in

fruit juice of *Citrus limon*-water mixture at pH 3 in stirring at room temperature for 5-6 h or refluxed at 80 °C for 1.5-2.0 h afforded compounds **10** and **11** in excellent yields without column chromatographic separation.



**Scheme 5.** Lemon juice catalyzed synthesis of bis- and tris (indolyl) methanes

This method proved to be chemoselective as only aldehydes reacts with indoles while ketones did not give corresponding products. The use of lemon juice as biocatalyst and water as solvent in this reaction makes the method is inexpensive and green as complete elimination of toxic solvent, catalysts, and inorganic support.

Microwave-assisted [36] efficient, rapid and eco-friendly synthesis of bis-, tris (indolyl) methanes (**10** and **11** respectively) and di-bis (indolyl) methanes (**14**) by the reaction of indoles and aldehydes in presences of lemon juice (*Citrus limon*) as biocatalysts under solvent-free conditions was re-

ported by Pal. Various substituted aromatic, heteroaromatic and aliphatic aldehydes smoothly reacts with indoles to give corresponding products **10**, **11** in excellent yields. Terephthalaldehydes (**12**) containing two aldehyde functional groups react with indoles in 1:2 ratio gave p-bis-indolylmethane benzaldehyde (**13**) and in 1:4 ratio gave p-di (bis-indolylmethane) benzene (**14**) in good yield (Figure 2).

The same biocondensation reaction was demonstrated by Pal in his another paper using aqueous ethanol as solvent under ultrasound irradiation [37] in high yield within 15-25 min.

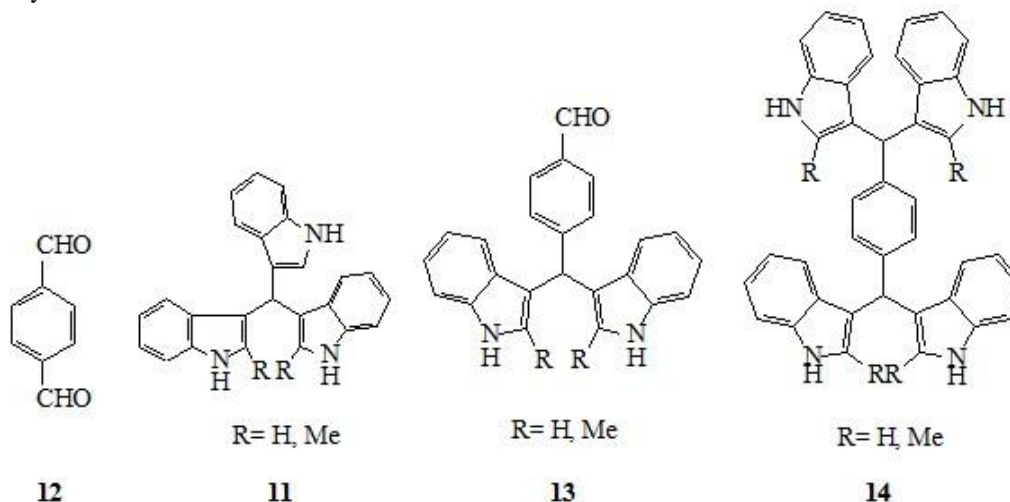


Figure 2. Structure of Terephthalaldehydes (**12**) and Lemon Juice Catalyzed Synthesized Compounds (**11**, **13** and **14**)

### 3. Fruit Juice of Pineapple

Pineapple (*Ananas comosus*) is sometimes called the King of Fruit [38]. Pineapple is grown extensively in Hawaii, Philippines, Caribbean area, Malaysia, Australia, Thailand, Mexico, Kenya and South Africa. Pineapple has long been one of the most popular of the non-citrus tropical and subtropical fruits, largely because of its attractive flavour and sugar-acid balance [39].



Fig.3. Fruit and Pineapple Juice of *Ananas Comosus*

#### 3.1. Composition of Pineapple Juice

The main ingredient of 100 g pineapple contain water (85.3 – 87.0 g), protein (0.4 – 0.7 g), fat (0.2 – 0.3 g), total carbohy-

drate (11.6 – 13.7 g), fiber (0.4 – 0.5 g), ash (0.3 – 0.4 g), calcium (17 – 18 mg), phosphorous (8 – 12 mg), iron (0.5mg), sodium (1 – 2 mg) and potassium (125 – 146 mg). It contains 12 – 15% sugars of which two-third in the form of sucrose and rest are glucose and fructose and 0.6 – 1.2% acid of which 87% is citric and 13% is malic acid [40,41]. The composition of the juice varies with geographical, cultural and seasonal harvesting and processing.

#### 3.2. General Procedure for Extraction of Pineapple juice

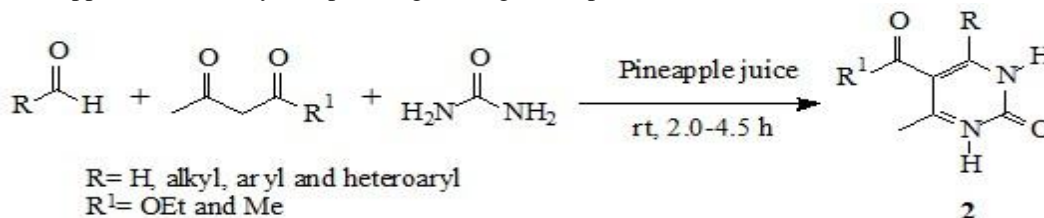
The crown and stem portion of the fresh pineapple (*Ananas comosus*) were removed and the skin was peeled using knife. Then the fruit was sliced and the fruit slices pressed in a fruit juicer for one or two minutes to get the semisolid mass which was then filtered through to get liquid pineapple juice. The extract of the pineapple is acidic having pH 3.7 and the acidity percentage is 53.5% and hence it will be worked as acid catalyst in organic reactions.

#### 3.3. Application of Pineapple Juice in Organic Synthesis: Preparation of Dihydropyrimidinone

Patil and his groups [42] synthesized a series of dihydropyrimidinone (DHPMs) derivatives **2** in presence of pineapple juice as a natural catalyst in good to excellent yields using a three component reaction sequence. Thus, an equimolar quantities of an aldehydes, ethyl acetoacetate and urea is stirred in presence of pineapple juice at room temperature for



2-5.5 h produced **2** (Scheme 6). Due to acidic nature (pH 3.7) pineapple juice acts as a catalyst in the formation of DHPMs. This solvent-free approach is totally nonpolluting having



**Scheme 6.** Pineapple juice catalyzed synthesis of dihydropyrimidinones

## 4. Fruit Juice of Tamarind

Tamarind (*Tamarind indica*) is a leguminous tree in the family Fabaceae indigenous to tropical Africa. The tamarind tree produces edible, pod-like fruit which are used extensively in cuisines around the world. It has long been one of the most popular non-citrus tropical and sub-tropical fruit, largely because of its attractive flavor and refreshing sugar-acid balance. The fruit juice is also used as traditional medicine and metal polishes.



**Fig.4.** Photography of Fruit and Tamarind Juice of *Tamarindus Indica*

### 4.1. Composition of Tamarind Fruit Juice

The main ingredient of 100 g of pulp of tamarind fruit [43] contain water (15-30%), protein (2-9%), fat (0.5-3%), total carbohydrate (56-82%), edible fiber (2.2-18.3%), ash (2.1-3.3%), calcium (81-466mg), phosphorous (86-190 mg), iron (1.3-10.9 mg), sodium (23-28 mg), potassium (62-570 mg). It also contains 41-58% sugar of which 25-45% is in the form of reducing sugars and 16% is in the form of non-reducing sugars and tartaric acid is (8-18%) and ascorbic acid is (3-9 mg). The composition of the tamarind fruit juice varies with geographical, cultural and seasonal harvesting and processing. An aqueous extract of tamarind fruit juice is acidic having pH 3 and acidity percentage is 50.3% and hence it will be worked as an acid catalyst in acid catalyzed reactions.

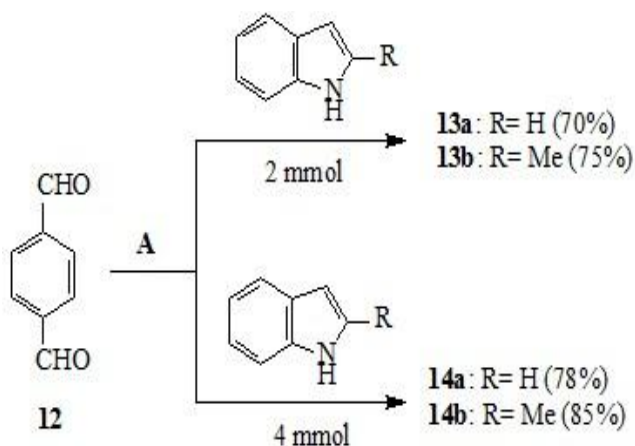
several advantages such as shorter reaction time, mild reaction conditions, simple work-up and reduces environmental impact.

### 4.2. General Procedure for Extraction of Tamarindus Indica Fruit Juice

The upper shell and inner grain of unripe tamarind fruit were removed with the help of a knife. The hard green material (pulp, 10 g) was boiled with water (50 mL), cooled and it was centrifuged. The clear portion of the aqueous extract (pH 3) of tamarind fruit was used as catalyst for the reaction.

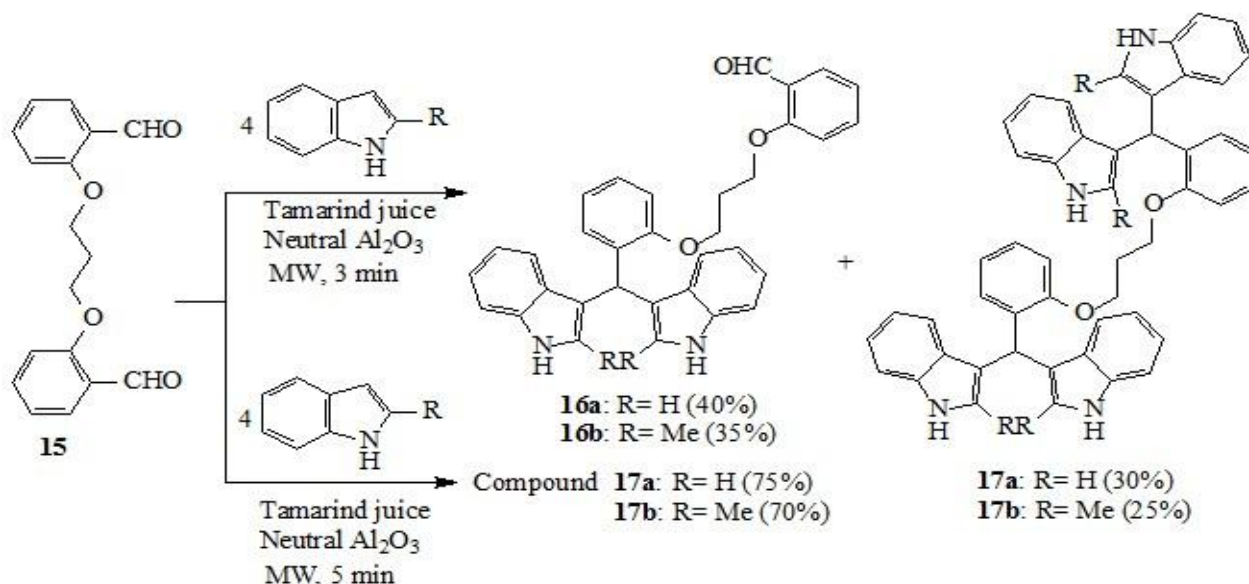
### 4.3. Application of Tamarind Juice in Organic Synthesis: Preparation of Bis-, Tris- and Tetraindoles

Tamarind (*Tamarindus indica*) fruit juice has been applied as a biocatalyst for the first time for rapid synthesis of bis-, tris(indolyl)methanes and tetraindolyl compounds by Pal [44] in excellent yields by electrophonic substitution reaction of indoles with aldehydes using microwave irradiation under solvent-free conditions.



A: Tamarind juice, Neutral Al<sub>2</sub>O<sub>3</sub>, MW, 2 min

**Scheme 7.** Reaction of lemon juice with terephthalaldehyde and indoles under solvent-free conditions



**Scheme 8.** Preparation of bis (indolyl) methane benzaldehyde and di-bis (indolyl) methane derivatives

Aromatic as well as aliphatic monoaldehydes and 3-formyl indole afforded bis- and tris (indolyl) methanes (**10** and **11**) respectively with indoles in presence of tamarind juice under microwave irradiation. Dialdehyde, such as terephthalaldehyde (**12**) when reacted with indoles in 1:2 ratios gave p-bis (indolyl) methane benzaldehydes (**13**) and in 1:4 ratios afforded p-di (bis-indolylmethane) benzene (**14**) in good yields within 2 min under the similar reaction conditions (Scheme 7).

The condensation of 4 equivalents of indoles with 1 equivalent of 2, 2'-di (formylphenoxy) propane (**15**) gave compounds **16** and **17** in 3 min under the similar reaction conditions (Scheme 8). It was also found that on increasing the reaction time to 5 min, only compounds **17** was obtained in good yield. The catalytic role of tamarind fruit extract in the above process was clearly evident from the observation that in its absence a little reaction took place. Neutral alumina was acted as solid support only.

## 5. Fruit Juice of *Acacia Concinna*

*Acacia concinna* fruit is a member of Leguminosae, sub-family Mimosaceae. *Acacia concinna* is a medicinal plant that grows in tropical rainforests of southern Asia, and its fruits are used for washing hair, for promoting hair growth, as an expectorant, emetic and purgative [45]. Aqueous extracts of this fruit has been in use as detergent since a long time in India. Various properties of *Acacia concinna* fruit are due to the presence of saponins [46] in it. Saponins have surfactant properties similar to dodecylbenzene sulfonates [47].



**Fig.5.** Photography of *Acacia Concinna* Fruit and Juice

### 5.1. Composition of *Acacia Concinna* Fruit Juice

The pods of *Acacia concinna* have been found to contain the saponin of acaciic acid, a trihydroxymonocarboxylic acid belonging to the tetracyclic triterpene group [48]. The aqueous extract of these pods of fruits shows acidic (pH 2.1) which is due to presence of acaciic acid with molecular formula C<sub>30</sub>H<sub>48</sub>O<sub>5</sub>.

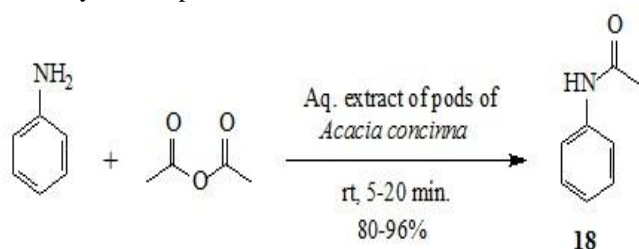
### 5.2. General Procedure for Extraction of *Acacia Concinna* Fruit Juice

100 g dry pods of *Acacia concinna* fruit was soaked in 1000 ml distilled water for 12 h. The material was then filtered through Whatman filter paper and filtrate was used as a catalyst. The aqueous extract of the juice is acidic in nature (pH 2.1) due to presence of acaciic acid which prompted chemists to use as catalyst in organic synthesis.

### 5.3. Application of *Acacia Concinna* Fruit Juice in Organic Synthesis: Preparation of Acetanilides

A facile, efficient, cost-effective and green protocol was reported by Mote *et al.* [49] for the synthesis of acetanilides **18** in good to excellent yields by reaction of aromatic primary amines and acetic anhydride, catalyzed by aqueous extract of pods of *acacia concinna* fruit at room temperature (Scheme 9). The acetylation reaction was completed within very short

time (5-20 min) using this juice as natural catalyst and the rate enhancement in aqueous extract of pods of acacia concinna fruit can be attributed due to its surfactant property and acidic nature (pH 2.1). The saponin which are high acidic solubilize the reactant species strongly by hydrogen bond formation in aqueous solution. This increases number of favorable collision between the reactant species. Further encapsulation of hydrophobic end of the product in micellar cages drives the equilibrium towards product side which increase the speed as well as yields of products.



**Scheme 9.** Acylation of amines with  $\text{Ac}_2\text{O}$  catalyzed by Pods of *Acacia concinna* fruit

## 6. Fruit Juice of *Sapindum Trifoliatum*

*Sapindus trifoliatum* is known as soapnut tree or three-leaf soapberry that grows in South India. The shell is of a red color and become darker after they are harvested and dried. Aqueous extract of the pericarp of this fruit have been used as detergent since a long time in India [50]. It is also known to possess various pharmacological activities [51].



**Fig.6.** Photography of Fruit and Juice of *Sapindum Trifoliatum*

### 6.1. Composition of *Sapindum Trifoliatum* Fruit Juice

The pericarp of this fruit is known to contain 10-11.5% of

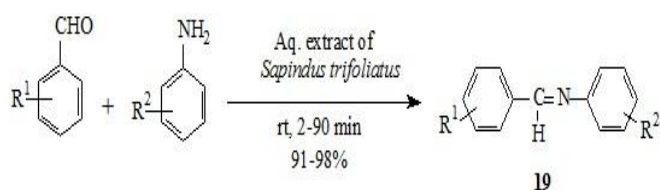
saponins [52]. These saponins have a common structural skeleton containing a pentacyclic triterpenoid part substituted with different carbohydrate side chains [53]. The aqueous extract of the pericarp of *Sapindus trifoliatum* fruits shows an acidic (pH 3.8), which is due to the presence of a  $\text{COOH}$  group in the triterpenoid part. This acidic nature of the aqueous extract prompted organic chemists to use it as a catalyst in acid-catalyzed reactions.

### 6.2. General Method for Extraction of *Sapindum Trifoliatum* Fruit Juice

The dry pericarp of the *Sapindus trifoliatum* fruit (100 g) was soaked in water (400 ml) for 12 h. The material was then macerated with the water in which it was soaked and filtered. The filtrate, *i.e.*, the aqueous extract, was kept below  $5^\circ\text{C}$  and used as catalyst for 15 days.

### 6.3. Applications of *Sapindum Trifoliatum* Fruit Juice in Organic Synthesis: Preparation of Aldamines

Pore and his group [54] were demonstrated the catalytic efficiency of the aqueous extract of the pericarp of *Sapindus trifoliatum* fruits in the chemoselective synthesis towards aldamines (**19**) (Scheme 10). Thus, when a mixture of aromatic aldehydes and aromatic amines were stirred in presence of this fruit extract produced aldamines in good yields whereas aromatic ketone and aromatic amines did not yield ketamines under comparable reaction conditions indicating chemoselective catalysis of the extract. The mild conditions, high yields, and short reaction times not only make this protocol a valuable alternative to the conventional methods, but it also become significant under the roof of environmentally greener and safer processes.



**Scheme 10.** Synthesis of aldamines catalyzed by aqueous extract of *Sapindus trifoliatum*

## 7. Fruit Juice of Coconut

*Cocos nucifera* is a member of the family *Arecaceae* (palm family). Coconut juice is a pleasant and refreshing beverage derived from the fruit of *Cocos nucifera*. Its juice is also called “coconut water”, and is widely consumed as a nourishing soft drink in tropical and subtropical countries as it is flavorful, sweet, and contains antioxidants. Coconut water is the clear liquid inside green young coconuts. In early, development serves as a suspension for the endosperm of the coconut during their nuclear phase of development. As growth continues the endosperm mature into their cellular phase and deposit into the rind of the coconut meat. The juice is used for the treatment of high blood pressure, hypertension



and diarrhea related dehydration.



**Fig.7.** Photography of Fruit and Coconut Juice of *Cocos Nucifera*

### 7.1. Composition of Coconut Juice

The main ingredients [55-57] per 100 g of coconut juice of *Cocos nucifera* are water (94.99 g), carbohydrates (3.71 g), protein (0.72 g or 1.2%), fat (0.2 g), ascorbic acid or vitamin-C (2.4 mg or 3%) as a water soluble antioxidant, pantothenic acid (0.043 mg or 1%), electrolytes; such as potassium (250 mg or 5%), sodium (105 mg); minerals such as magnesium (25 mg or 7%), phosphorous (20 mg or 3%), calcium (24 mg) and iron (0.29 mg or 2%). The juice contains cytokinins which promote plant cell division and growth, showed significant anti-ageing, anti-carcinogenic, and anti-thrombotic effects. Coconut water is composed of many naturally occurring bioactive enzymes such as acid phosphatase, catalase, dehydrogenase, diastase, peroxidase, RNA-polymerase etc. Due to presence of ascorbic acid and pantothenic acid, coconut juice is low acidic in nature.

### 7.2. General Method for Extraction of Coconut Juice

The coconut juice (water) was obtained by perforating the fruit with a metallic sharp object (knife). The coconut juice was filtered using Whatman 47 mm filter paper for the elimination of solid residues. The clear filtrate was used as catalyst in the reaction.

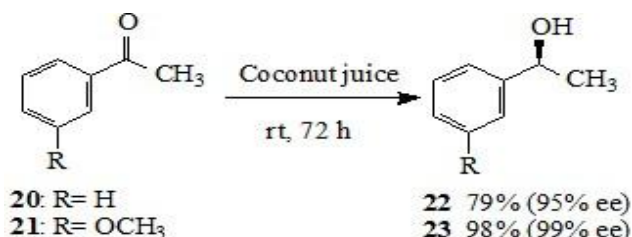
### 7.3. Applications of Coconut Juice in Organic Synthesis

Coconut juice also represents a very important class of biocatalyst in organic synthesis. The use of coconut juice as biocatalyst for selective reduction of aromatic and aliphatic carbonyl compounds and dimerisation of aromatic nitro compounds has been reported. The coconut juice is also effectively hydrolyzed esters, amides and anilides under mild conditions.

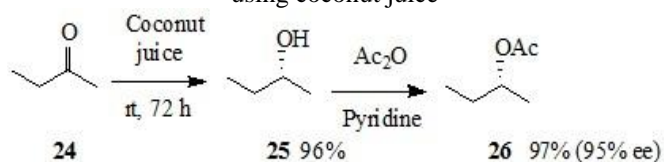
#### 7.3.1. Reduction of Carbonyl Compounds

Fonseca *et al.* [58] developed a simple and green method for the selective bioreduction of aliphatic and aromatic aldehydes and ketones in high yields using coconut juice as nat-

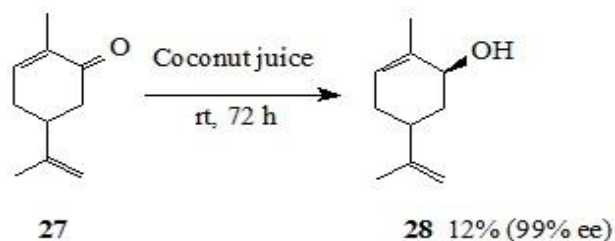
ural catalysts. When various carbonyl compounds such as **20**, **21**, **24** and **27** were added to the freshly prepared coconut juice of *Cocos nucifera* and the mixture were shaken (160 rpm) at room temperature for 72 h, gave corresponding alcohols. Enantioselectivity, induced by coconut juice, was observed in the reduction of the pro-chiral ketones **20**, **21** where the alcohols **22** (79%) and **23** (98%) and the ee ranging from 95% to 99%, respectively.



**Scheme 11.** Enantioselective reduction of aromatic ketone using coconut juice

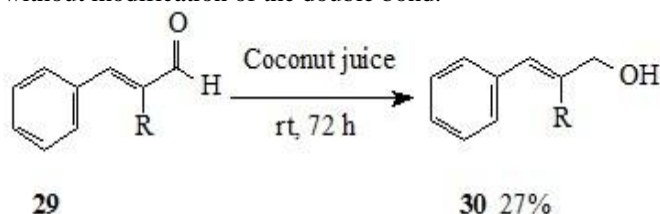


**Scheme 12.** Enantioselective reduction of aliphatic ketone using coconut juice



**Scheme 13.** Chemo- and stereoselective reduction of  $\alpha$ ,  $\beta$ -unsaturated ketone using coconut juice

Aliphatic ketone **24** enantioselectively produced alcohol **25** (96%) and the ee was determined as 95% of its acylated derivatives **26**. Chemoselectivity was also observed for the reduction of  $\alpha$ ,  $\beta$ -unsaturated ketones **x** using coconut juice. The chemoselective reduction of **27** yielded **28** in low yield (12%); however, with high ee (99%) and "S" configuration. A regioselective reaction was observed using coconut juice. The compound **29** was reduced selectively at the carbonyl functional group, yielded only the corresponding alcohol **30** (27%), without modification of the double bond.

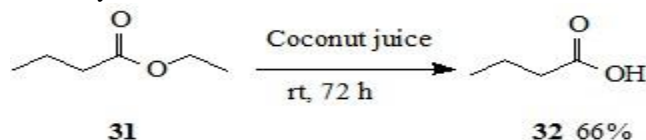


**Scheme 14.** Regioselective reduction of  $\alpha$ ,  $\beta$ -unsaturated aldehyde using coconut juice

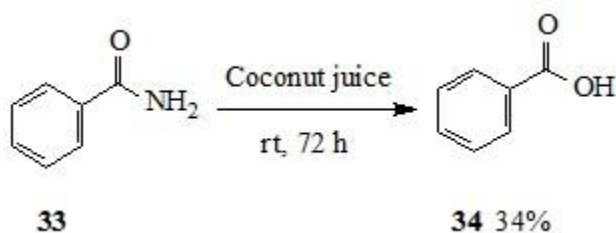


### 7.3.2. Hydrolysis of Ester, Amide and Anilides

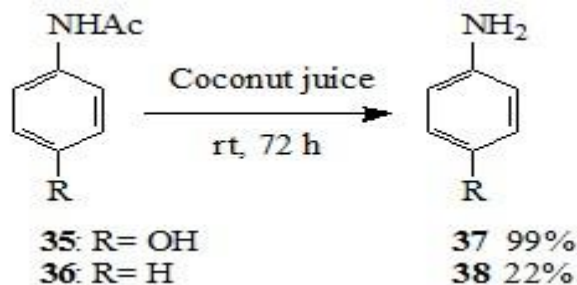
Hydrolysis of ester and amide with water has been accomplished using coconut juice. Fonseca and co-workers [58] reported that coconut juice acts as a biocatalyst for the hydrolysis of **31** and **33**. Bioconversion of ester **31** and amide **33** to the corresponding acids **32** (66%) and **34** (34%) were observed after 3 days under constant stirring at room temperature. The enzymatic anilide hydrolysis of **35** and **36** by coconut juice is quite effective for 4-hydroxyacetanilide yielding **37** (99%). However, hydrolysis proceeds much lower yield with unsubstituted anilide **36**, which producing aniline **38** in only 22%.



**Scheme 15.** Hydrolysis of ester using coconut juice



**Scheme 16.** Hydrolysis of amide using coconut juice



**Scheme 17.** Hydrolysis of anilides using coconut juice

## 8. Conclusions

This review focuses the importance of fruit juice as a natural and biocatalyst in organic transformations. The growing interest of fruit juice in organic synthesis is mainly due to their acidic properties, enzymatic activity, benign environmental character, inexpensive, and commercial availability. The catalytic activity including the application of fruit juice in various organic transformations such as formation of C-C, C-N bonds and breaking of C-O, C-N bonds in different synthetically important organic compounds have been studied. Although many observations have not received by application of fruit juice in synthesis of natural products or complex structured molecules in details, it is believed that in near future the fruit juice chemistry will continue to attract significant research activity. Therefore, the present review would serve the need of organic chemists in searching new applica-

tions of fruit juice for organic synthesis.

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## References

- [1] Li, C. J.; Chan, T. H. "Organic reactions in aqueous media" John Wiley & Sons, New York, 1997.
- [2] Kumar, S.; Grover, I. S.; Sandhu, J. S. *Indian J. Chem. Sect. B* **2009**, *48*, 585.
- [3] Mallik, A. K.; Pal, R.; Guha, C.; Mallik, H. *Green Chem. Lett. Rev.* **2012**, *5*, 321.
- [4] Ramesh, E.; Raghunathan, R. *Synth. Commun.* **2009**, *39*, 613.
- [5] Habibi, D.; Marvi, O. *Arkivoc* **2006**, *xii*, 8.
- [6] Zahouily, M.; Mounir, B.; Charki, H.; Mezdar, A.; Bahlaouan, B.; Ouammou, M. *Arkivoc* **2006**, *xii*, 178.
- [7] Zahouily, M.; Bahlaouan, B.; Rayadh, A.; Sebti, S. *Tetrahedron Lett.* **2004**, *45*, 4135.
- [8] Genin, E.; Toullec, P. Y.; Marie, P.; Antoniotti, S.; Brancour, C.; Genet, J. P.; Michelet, V. *Arkivoc* **2007**, *v*, 67.
- [9] Riadi, Y.; Mamouni, R.; Azzalou, R.; Boulahjar, R.; Abrouki, Y.; Haddad, M. El.; Routier, S.; Guillaumet, G.; Lazar, S. *Tetrahedron Lett.* **2010**, *51*, 6715.
- [10] Giri, A.; Dhinga, V.; Giri, C. C.; Singh, A.; Ward, O. P. Narasu, M. L. *Biotechnol. Adv.* **2001**, *19*, 175.
- [11] Villa, R.; Molinari, F.; Levati, M.; Aragozzini, F. *Biotechnol. Lett.* **1998**, *20*, 1105.
- [12] Bruni, R.; Fantin, G.; Medici, A.; Pedrini, P.; Sacchetti, G. *Tetrahedron Lett.* **2002**, *43*, 3377.
- [13] Andrade, L. H.; Utsunomiya, S.; Omori, A. T.; Porto, A. L. M.; Comasseto, J. V. *J. Mol. Catal. B: Enzyme* **2006**, *38*, 84.
- [14] Comasseto, J. V.; Omori, A. T.; Porto, A. L. M.; Andrade, L. H. *Tetrahedron Lett.* **2004**, *45*, 473.
- [15] Yadav, J. S.; Reddy, T.; Nanda, S.; Rao, A. B. *Tetrahedron: Asymmetry* **2001**, *12*, 3381.
- [16] Mironowicz, A. *Phytochemistry* **1998**, *47*, 1531.
- [17] Silver, G. M.; Fall, R. *Plant Physiol.* **1991**, *97*, 1588.
- [18] Deshmukh, M. B.; Patil, S. S.; Jadhav, S. D.; Pawar, P. B. *Synth. Commun.* **2012**, *42*, 1177.
- [19] Bhuiyan, M. M. H.; Hossain, M. I.; Alam, A.; Mahmud, M. M. *Chem. Jour.* **2012**, *2*, 30.
- [20] Rovnyak, G. C.; Kimall, S. D.; Beyer, B.; Cucinotta, G.; DiMarco, J. D.; Gougoutas, J.; Hedberg, A.; Malley, M.; McCarthy, J. P. *J. Med. Chem.* **1995**, *38*, 119.
- [21] Atwal, K. S.; Rovnyak, G. C.; Schwartz, J.; Moreland, S.; Hedberg, A.; Gougoutas, J. Z.; Malley, M. F.; Floyd, D. M. *J. Med. Chem.* **1990**, *33*, 1510.
- [22] Kane, J. M.; Baron, B. M.; Dudley, M. W.; Sorenson, S. M.; Staeger, M. A.; Miller, F. P. *J. Med. Chem.* **1990**, *33*, 2772.
- [23] Rollas, S.; Kalyoncuoglu, N.; Sur-Altiner, D.; Yegenoglu, Y. *Pharmazie* **1993**, *48*, 308.
- [24] Gilbert, B. E.; Knight, V. *Antimicrob. Agents Chemther.* **1986**, *30*, 201.
- [25] Malbec, F.; Milcent, R.; Vicart, P. Bure, A. M. *J. Heterocyclic Chem.* **1984**, *21*, 1769.
- [26] Kong, D.; Zhang, X.; Zhu, Q.; Xie, J.; Zhou, X. *Zhongguo Yaowu Huaxue Zazhi* **1998**, *8*, 245.
- [27] Hadjipavlou-litina, D. J.; Geronikaki, A. A. *Drug Des. Discov.* **1996**, *15*, 199.
- [28] Solak, N.; Rollas, S. *Arkivoc* **2006**, *xii*, 173.
- [29] Wadher, S. J.; Puranik, M. P.; Karande, N. A.; Yeole, P. G. *Int. J. Pharm. Tech. Res.* **2009**, *1*, 22.

- [30a] Shiri, M.; Zolfigol, M. A.; Kruger, H. G.; Tanbakouchian, Z. *Chem. Rev.* **2010**, *110*, 2250.
- [30b] Bradfield, C. A.; Bjeldanes, L. F. *J. Toxicol. Environ. Health* **2003**, *21*, 311.
- [31] Jones, G. *The Knoevenagel condensation reaction. In Organic reactions*; Wiley: New York, 1967.
- [32] Patil, S.; Jadhav, S. D.; Deshmuk, M. B. *Arch. Appl. Sci. Res.* **2011**, *3*, 203.
- [33] Sachdeva, H.; Saroj, R.; Khaturia, S.; Dwivedi, D. *Org. Chem. Int.* **2013**, ID 659107.
- [34] Patil, S.; Jhadav, S. D.; Patil, U. P. *Arch. Appl. Sci. Res.* **2012**, *4*, 1074.
- [35] Pal, R.; Khasnobis, S.; Sarkar, T. *Chem. Jour.* **2013**, *3*, 7.
- [36] Pal, R. *IOSR J. Appl. Chem.* **2013**, *3*, 1.
- [37] Pal, R. *Int. J. Org. Chem.* **2013**, *3*, 136.
- [38] Arthey, D. "Fruit and Vegetable Product," In: Ranken, M. D.; Kill, R. C.; Baker, C. G. J. Eds., *Food Industries Manual*, Chapman & Hall, London, 1995.
- [39] Bartolome, A. P.; Ruperez, P.; Fuster, C. *Food Chem.* **1995**, *53*, 75.
- [40] Samson, J. A. "Tropical fruits," 2<sup>nd</sup> Edition, Longman Inc., New York, 1986.
- [41] Adhikar, S. K.; Harkare, W. P.; Govindan, K. P.; Chikkappaji, K. C.; Saroja, S.; Nanjundaswamy, A. M. *Indian J. Technol.* **1987**, *25*, 24.
- [42] Patil, S.; Jadhav, S. D.; Mane, S. *Int. J. Org. Chem.* **2011**, *1*, 125.
- [43] El-Siddig, K.; Gunasena, H. P. M.; Prasad, B. A.; Pushpakumara, D. K. N. G.; Ramana, K. V. R.; Vijayanand, P.; Williams, J. T. "Fruits for the future 1- Tamarind, *Tamarindus indica*;" Southampton Centre for Underutilised Crops, UK, 2006.
- [44] Pal, R. *Int. J. Chemtech Appl.* **2013**, *2*, 26.
- [45] Tezuka, Y.; Honda, K.; Banskota, A. H.; Thet, M. M.; Kadota, S. *J. Nat. Prod.* **2000**, *63*, 1658.
- [46] Gafur, M. A.; Obata, T.; Kiuchi, F.; Tsuda, Y. *Chem. Pharm. Bull.* **1997**, *45*, 620.
- [47] Pratap, G.; Bhaskar Rao, V. S. *Fett Wissenschaft Technologie* **1987**, *89*, 205.
- [48] Farook, M. O.; Varshney, I. P.; Naim, Z. *Arch. Pharm.* **1961**, *294*, 133.
- [49] Mote, K.; Pore, S.; Rashinkar, G.; Kambale, S.; Kumbhar, A.; Salunkhe, R. *Arch. Appl. Sci. Res.* **2010**, *2*, 74.
- [50] Rao, K. N. "Wealth of India" Vol. IX, NISCOM (CSIR), New Delhi, 1972 and 1999.
- [51] Arora, S. K.; Srivastava, V.; Addepalli, V.; Natesan, S.; Goel, R.; Eur. Pat. EP 1556062, 2005; Arulmozhi, D. K.; Veerranjanyulu, A.; Bodhankar, S. L.; Arora, S. K. *J. Ethnopharmacol.* **2005**, *97*, 491.
- [52] Nivsarkar, M.; Shrivastava, N.; Patel, M.; Padh, H.; Bapu, C. *Asian J. Androl.* **2002**, *4*, 233.
- [53] Grover, R. K.; Roy, A. D.; Roy, R.; Joshi, S. K.; Srivastava, V.; Arora, S. K. *Magn. Reson. Chem.* **2005**, *43*, 1072.
- [54] Pore, S.; Rashimkar, G.; Mote, K.; Salunkhe, R. *Chem. Biodiver.* **2010**, *7*, 1796.
- [55] Reddy, K. V.; Das, M.; Das, S. K. *J. Food Eng.* **2005**, *69*, 381.
- [56] Farr, S. *Food Manuf.* **1994**, *69*, 29.
- [57] Chumbimuni-Torres, K. Y.; Kubota, L. T. *J. Food Compos. Anal.* **2006**, *19*, 225.
- [58] Fonseca, A. M.; Monte, F. J.; Oliveira, M. C. F.; Mattos, M. C. M.; Cordell, G. A.; Braz-Filho, R.; Lemos, T. L. G. *J. Mol. Catal. B: Enzyme* **2009**, *57*, 78.

### Authors' Biographical Data



**Rammohan Pal** was born in 1978 in Kolkata, India. He obtained his B.Sc. in 1999 and M.Sc. in 2001 in Chemistry from University of Calcutta, India. He worked as a DBT-project fellow at the Biological Department of Chemistry, Indian Association for the Cultivation of Sciences (IACS), Kolkata and as a UGC-JRF at the Natural Product Laboratory, Indian Institute of Chemical Technology (IICT), Hyderabad, India. He carried out his predoctoral research work at the Department of Chemistry, Jadavpur University under the supervision of Prof. Asok Kumar Mallik. He received his Ph.D. degree in 2011 from Jadavpur University on synthesis and reactions of some nitrogen heterocycles. He has published over 26 scientific papers. His current research interests cover the development of synthetic methodology, green chemistry and synthesis of heterocyclic compounds. Presently, he is an Assistant Professor of Organic Chemistry at the Acharya Jagadish Chandra Bose College, Kolkata, India.