



Research Article

# Acetylation of alcohols, phenols and amines using waste plant extract

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## Abstract

The acetylation of alcohols, phenols and amines using water extract of waste plant extract of rice straw ash and seed husk of *Vigna mungo* ash at room temperature is reported here. The easy availability of plants, high yields, mild reaction conditions, cost effectiveness of the catalyst proved to be an excellent and green protocol for the acetylation reaction.

**Keywords** Acetylation · Green · Waste materials · *Vigna mungo* · Rice straw · Gram scale synthesis

## 1 Introduction

Acetylation reactions have been an important transformation [1] in organic synthesis. These reactions have been used as protective group reactions in agricultural and pharmaceutical industries [2–4]. The transformation has been usually carried out with acetic acid or acetic anhydride in presence of acidic or basic conditions. Amines with carboxylic acid derivatives such as lachrymatory acetyl chloride, acids or esters undergo N-acetylation reactions.

Several methods have been cited in literature for acetylation reaction of alcohols, phenols and amines using different acid or base (Table 1), but they have one or more disadvantages such as the use of harsh reaction conditions, longer reaction time, use of expensive catalyst etc.

Recently reported methods includes the use of metal triflates such as Ce(OTf)<sub>3</sub> [11], Sc(OTf)<sub>3</sub> [12], Cu(OTf)<sub>2</sub> [13], indium triflate [14], Gadolinium triflate [15], Al(OTf)<sub>3</sub> [16]; metal halides such as TaCl<sub>5</sub> [17], InCl<sub>3</sub> [18], and ZrOCl<sub>2</sub>·8H<sub>2</sub>O [19]; and solid acid catalysts such as heteropoly acids [20], Mg(NTf<sub>2</sub>)<sub>2</sub> [21], aluminum-supported MoO<sub>3</sub> [22], BiFeO<sub>3</sub> [23], cation-exchanged montmorillonite K-10 clay [24], phosphomolybdic acid [25], sulfamic acid [26], NaHSO<sub>4</sub>.

SiO<sub>2</sub> [27], polystyrene-bound heterogeneous cobalt(II) salen [28], and [TMBSA][HSO<sub>4</sub>] ionic liquid [29] for acetylation reactions. The preparation of these catalyst normally require harsh reaction conditions, use of toxic chemicals and poor yields are normally obtained.

All these harsh reaction conditions can likely be overcome by using eco-friendly green catalyst for the acetylation reactions. Green chemistry aims at the use of biodegradable, eco-friendly catalyst and the use of plant extracts as catalyst and solvent enhance this application. Plants as green solvents and catalyst offers shorter reaction time, use of non-toxic solvent making an overall extraction process more environment friendly [30]. Thus, owing to the principles of Green Chemistry [31] researchers nowadays are focusing their interest on the use of agricultural waste residues in chemical reactions. These waste plant extract are normally basic in nature, and as cited in literature acetylation reactions is efficiently performed in the presence of base as catalyst. Thus, citing to all the advantages of the plant extracts and considering the increasing pressure from environmentalist we tried to use the waste plant extract of *Vigna mungo* and rice straw as a catalyst in the acetylation reaction.

**Electronic supplementary material** The online version of this article (<https://doi.org/10.1007/s42452-020-03353-2>) contains supplementary material, which is available to authorized users.

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**Table 1** Few Acetylation reactions using different acids/bases

Entry	Substrates	Reaction condition, Time	Acid/Base	Catalyst	Refs.
1	Alcohol, Phenols	Ac <sub>2</sub> O, Ethyl acetate, 48 h	NaHCO <sub>3</sub> (2 eq)	–	[5]
2	Alcohols	Ac <sub>2</sub> O, CH <sub>2</sub> Cl <sub>2</sub> , 3 h	DMAP	Tributylphosphine	[6]
3	Alcohols	Ac <sub>2</sub> O, 10 h	N,N-dimethyl-4-pyridinamine	–	[7]
4	Amines	Toluene, 110 °C, 22 h	Carboxylic acids	ZrCp <sub>2</sub> Cl <sub>2</sub>	[8]
5	Amines	Toluene/fluorobenzene, 22 h	–	Aminoboronic Acids	[9]
6	Amines	EtOAc, 70 °C, 24 h	Pivalic or acetic acid	–	[10]

In many countries, rice straw is an abundant lignocellulose by-product from rice (*Oryza sativa*) production in farming. Similarly, during milling of black gram (*Vigna mungo*) into dhal, husk (seed coat) is a waste by-product that constitutes about 9% of the grain. These large quantities of agricultural residues are reserved only in a minor amount for animal feed, paper industry, household fuel etc. A huge quantity is wasted and burnt or disposed as it is no use.

Rice straw mainly contain lignocelluloses as the main component which is a compact structure of cellulose (28–36%) and hemicelluloses (23–28%) in close association with lignin (12–16%) [32]. Black gram lentil (*Vigna mungo* L.) is a rich source of fibre, protein, several vitamins and essential minerals such as calcium and iron [33]. Prasada Rao *et al.* found that the husk of *Vigna mungo* had the highest dietary fibre content (78.5%) [34] and carotenoids. Similar to total polyphenol content, anthocyanin content was also found to be the highest in husk fraction (87 mg/100 g). Due to the burning or disposal of these agricultural residues, the valuable components in them are wasted and it causes pollution in the atmosphere which is a threat to the environment [35].

This paper thus reports the application of waste plant extract of *Vigna mungo* and rice straw as an excellent catalyst for the acetylation of various alcohols, phenols and amines. The easy availability of these waste residues and eco-friendly nature also added as an advantage for its utilization as a green catalyst. The high catalytic activity may be due to the basic nature of the waste plant extract and the presence of various fibres, proteins, polyphenols, lignins, cellulose and vitamins in these extracts enhance them to proceed as an efficient catalyst.

## 2 Experimental

### 2.1 Preparation of catalyst

*Vigna mungo* (black gram) and rice straw were collected from the nearby area of Dibrugarh University, Dibrugarh, Assam, India. They were air dried and the husk of *Vigna*

*mungo* was removed, and the rice straw was separated. It was then washed with deionized water and air dried. 4 g of both dry *Vigna mungo* husk and rice straw were taken separately and burnt to ashes in a furnace and 3.5 g of ash was obtained. This was then warmed at 50 °C in 100 mL deionised water separately for 15 min where almost all the ashes got dissolved, and filtered with whatmann No. 1 filter paper. The filtrate obtained is thus named as Water Extract of *Vigna mungo* seed husk (WEVMS) and Water extract of rice straw ashes (WERSA) (Fig. 1). Both the extracts were then used as a catalyst for the acetylation reaction of various alcohols, phenols and amines.

## 3 General procedure for acetylation reaction

To a mixture of substrate (0.537 mmol) and acetic anhydride (1 eq), 70 µL of the WERSA/ 40 µL of WEVMS was added and stirred at room temperature for appropriate time. The progress of the reaction was monitored by TLC. The product was extracted with ethyl acetate, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated. The reaction completed in in very short time without the formation of any side products (Scheme 1). The characterization of the products was done by <sup>1</sup>H NMR and <sup>13</sup>C NMR. The reaction was initially carried out using aniline and acetic anhydride as a model reaction by using WERSA/WEVMS as a catalyst.

## 4 Result and discussion

Literature cited the presence of twelve different types of flavonoids [36] i.e. two leucoanthocyanins, two glycoflavones, three anthocyanins and five flavonol glycosides in the seed coats of *Vigna mungo*. In another study the seed coat was found to contain the saponins of soyasaponins I, II and V [37].

The EDX analysis of the both dry *Vigna mungo* seed husk and rice straw ashes were performed and are shown in Fig. 2. The report reveals a very high distribution of the oxides of K, Si, Ca in *Vigna mungo* seed husk; and the



Fig. 1 Preparation of the catalyst

Scheme 1 General scheme for acetylation reaction

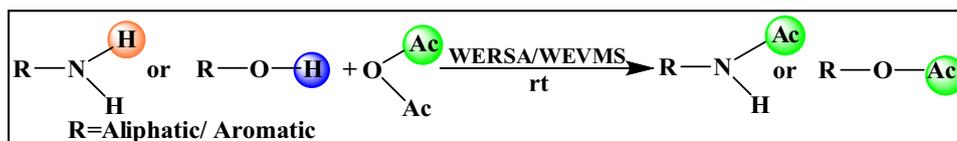
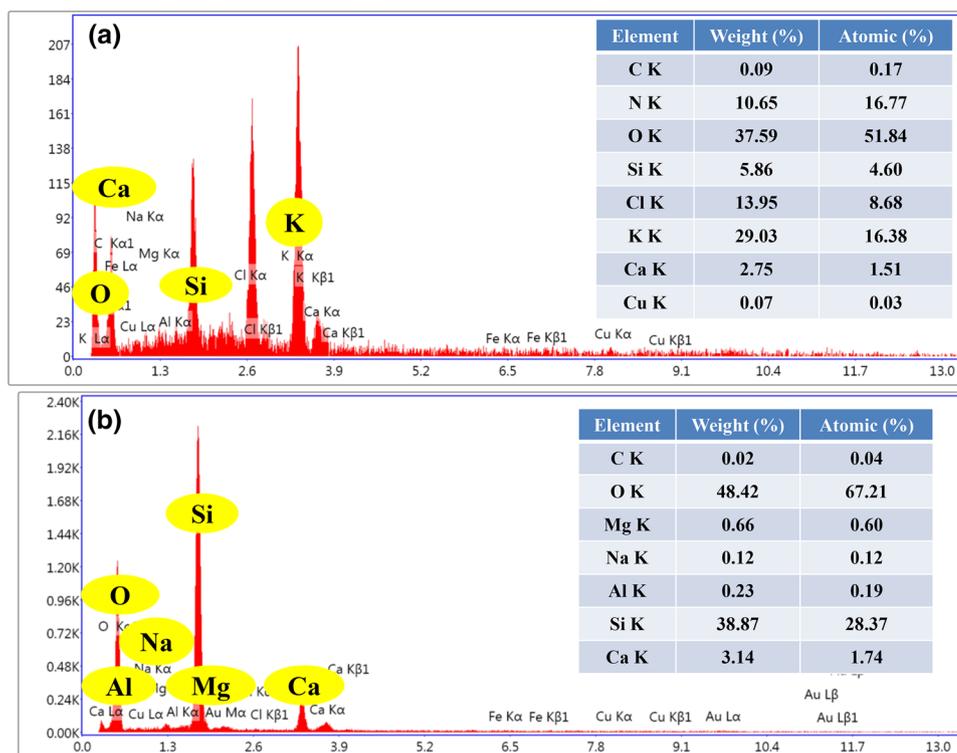


Fig. 2 a EDX spectrum of the dry ashes of *Vigna mungo* seed husk, b EDX spectrum of the dry ashes of Rice Straw





**Scheme 2** Model reaction used for optimization

presence of Na, Mg, Al, Si, Ca in rice straw ashes. The pH measurement of both the extract was tested using Digital pH meter model 111/101 and found to be 8.84 in WEVMS and 9.61 in WERSA. This proved the basic nature of the WEVMS and WERSA.

The effectiveness of the WEVMS/WERSA was then explored in the acetylation reactions of various alcohols, phenols and amines. We initially, optimized our reaction condition by performing the acetylation of aniline as the model substrate (Scheme 2). The effects of different amounts of the WEVMS/WERSA were monitored for different intervals of time (Table 2). The best result was obtained when 40  $\mu\text{L}$  of WEVMS (Table 2, entry 5), and 70  $\mu\text{L}$  of WERSA (Table 2, entry 6), were used respectively. However, without the use of extract the reaction did not proceed up to 240 min. Thus this seems to be the fastest, economic and green protocol for the acetylation reaction. On increasing the amount of WEVMS to 50  $\mu\text{L}$  no change in the yield of the product was obtained.

The reaction was also explored by the influence of different bases on the model reaction of aniline and acetic anhydride (Table 3). As the pH of both WERSA and WEVMS was found to be basic, so we prepared some base solutions in the same pH range of 9.2 for optimization. Surprisingly, it was found that the addition of our catalyst led to the immediate formation of the product, while the bases required more time.

We further optimized our reaction using different amounts of acetic anhydride (Table 4) on the model reaction. It was observed that by using 0.5 equivalent of  $\text{Ac}_2\text{O}$  (Table 4, entry 5) nearly 60% product yield was found, this might be because of the longer reaction time for the

**Table 2** Effects of the amount of WEVMS in the acetylation on the model reaction<sup>a</sup>

Entry	WEVMS			WERSA		
	Amount ( $\mu\text{L}$ )	Time (min)	Yield (%) <sup>b</sup>	Amount ( $\mu\text{L}$ )	Time (min)	Yield (%) <sup>b</sup>
1 <sup>c</sup>	0	240	No product	0	240	No product
2	10	60	Trace	20	60	80
3	20	60	80	40	60	90
4	30	10	90	50	15	98
5	40	< 1	98	60	10	98
6	50	< 1	98	70	< 1	98

<sup>a</sup>Reaction Conditions: Aniline (0.537 mmol),  $\text{Ac}_2\text{O}$  (1 eq), room temperature

<sup>b</sup>Isolated yields

<sup>c</sup>Reactions carried out without Extract

**Table 3** Effects of the amount of different bases in the acetylation on the model reaction

Entry	Base	Amount ( $\mu\text{L}$ )	Time (min)
1 <sup>a</sup>	KOH	400	25
2 <sup>a</sup>	NaOH	40	15
3 <sup>a</sup>	$\text{K}_2\text{CO}_3$	400	45
4	WERSA	70	< 1 min
5	WEVMS	40	< 1 min

Reaction Conditions: Aniline (0.537 mmol),  $\text{Ac}_2\text{O}$  (1 eq), room temperature

<sup>a</sup>Base: 0.000016 M

**Table 4** Optimization of acetic anhydride on the model reaction

Entry	$\text{Ac}_2\text{O}$ (Equiv.)	Time (min)	Yield <sup>a</sup> (%)
1	0	240	No product
2	0.2	60	Trace
3	0.3	40	30
4	0.4	40	45
5	0.5	20	60
6	1	< 1 min	98
7	1.1	40 s	98
8	1.2	1 min	96
9	2.0	5 min	96

Reaction Conditions: Aniline (0.537 mmol) at room temperature

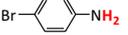
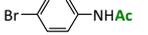
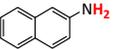
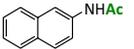
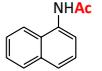
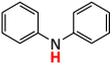
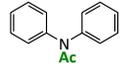
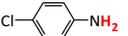
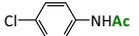
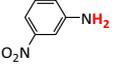
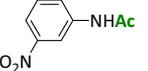
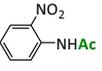
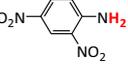
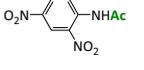
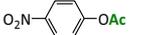
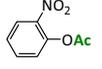
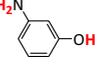
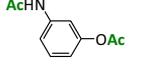
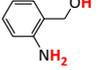
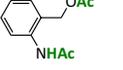
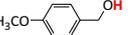
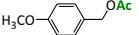
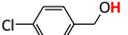
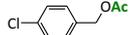
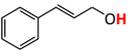
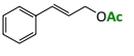
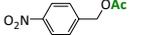
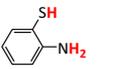
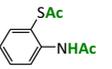
<sup>a</sup>Isolated Yields

product formation. The reaction progressed immediately after the addition of the extract by using 1 equivalent of acetic anhydride (Table 4, entry 6).

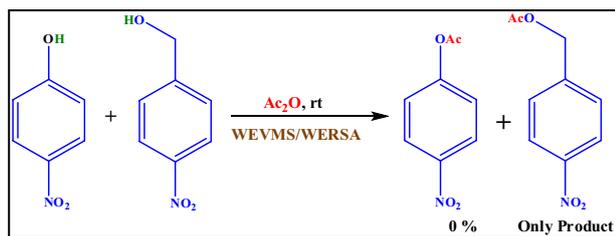
#### 4.1 Acetylation of different substrates using extracts

The above optimization condition was explored using 20 different substrates of alcohols, phenols and amines

**Table 5** Substrate scope variation of the acetylation reaction with Ac<sub>2</sub>O under solvent free conditions in the presence of Extract<sup>a</sup>

S. No	Substrate	Product	Time (min)	Yield <sup>b</sup> %
1			<1	98
2			5	98
3			5	95
4			5	95
5			5	96
6			5	97
7			10	95
8			20	95
9			60	90
10			50	75
11			50	75
12			45	80 <sup>c</sup>
13			30	75 <sup>c</sup>
14			60	90
15			30	95
16			30	90
17			30	92
18			60	95
19			30	93
20			30	80 <sup>c</sup>

<sup>a</sup>Reaction conditions: alcohols/phenols/anilines (0.537 mmol), WERSA(70  $\mu$ L)/ WEVMS (40  $\mu$ L), acetic anhydride (1 eq)<sup>b</sup>Isolated Yield<sup>c</sup>Ref. [38, 39]



**Scheme 3** Chemoselectivity in presence of extract

(Table 5). Excellent yields have been obtained with the aniline derivatives compared to alcohols and phenols. The chemoselectivity was however not observed with two different functional groups such as  $-NH_2$ ,  $-OH$  and  $-SH$  (entries 12, 13, 20) [38, 39]. We were surprised to find that by using 1 eq of  $Ac_2O$  for 0.537 mmol of the substrate (entries 12, 13, 20) diacetylated products were obtained with isolated yields, however the reaction required longer reaction time compared to the acetylated products. This might be because the acetic acid formed in the reaction as a by-product would act as acetylating agent for the diacetylation.

The chemoselectivity was evaluated using a mixture of substituted benzyl alcohol and phenol. An equimolar mixture of 4-nitro benzyl alcohol and 4-nitro phenol was reacted with acetic anhydride in presence of extract as catalyst. The result of this reaction revealed that it proceeded with absolute chemoselectivity towards 4-nitro

benzyl alcohol (Scheme 3). The absolute chemoselectivity of benzyl alcohol might be because acetylation of substituted phenols required longer reaction time compared to benzyl alcohols as shown in Table 5.

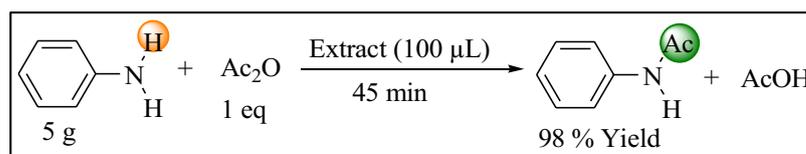
The multi-gram scale synthesis of aniline was also performed to demonstrate the practicality of this approach (Scheme 4). The reaction proceeded smoothly with only 100  $\mu L$  of the extract and 98% of the product was obtained.

We further compared the efficiency of the WEVMS/WERSA as catalyst with previously reported catalyst for the acetylation reaction of aniline and acetic anhydride as the model substrate (Table 6). The previously reported catalyst suffered one or more disadvantages compared to our green and ecofriendly superior catalyst.

## 5 Conclusion

The present work describes an environmentally-friendly, economic, excellent protocol for the acetylation reaction using waste material of plants for the first time showing immediate formation of product for the acetylation of aniline. Subsequently, high yields in short reaction times were achieved for various alcohols, phenols and amines without the need of an expensive catalyst. Moreover the chemoselectivity of the catalyst has also enhanced its application. The easy availability of the catalyst, cost effectiveness, less reaction time, high yield products, mild reaction

**Scheme 4** Multi-gram scale synthesis of N-phenylacetamide



**Table 6** Comparison efficiency of WEVMS/WERSA with some reported catalysts for the acetylation reactions of aniline

Entry	Reaction conditions	Time	Amount of catalyst	Yield (%)	Refs.
1	CDI DMAc	1 h	2 mol equiv	85	[40]
2	Zinc Acetate (Microwave)	20 min	0.045 mmol	91	[41]
3	RHA/TiO <sub>2</sub>	9 h	20 mol	93	[42]
4	Fe <sub>3</sub> O <sub>4</sub> @PDA-SO <sub>3</sub> H	30 min	2 mol	96	[43]
5	Zeolite H-FER	2 h	150 mg	99	[44]
6	WEVMS/WERSA	< 1 min	40 $\mu L$ /70 $\mu L$	98	This Work

conditions proved to be a green and excellent protocol for the acetylation reaction.

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### Compliance with ethical standards

**Conflict of interest** On behalf of all authors, the corresponding author states that there is no conflict of interest.

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