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Archives of Applied Science Research, 2010, 2 (3): 74-80

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ISSN 0975-508X
CODEN (USA) AASRC9

Acacia concinna pods: as a green catalyst for highly efficient synthesis of Acylation of amines

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Abstract

A general, simple, efficient, cost-effective and green procedure for acylation of amines has been developed by treatment with acetic anhydride is efficiently catalyzed by using intact plant material (aqueous extract of pods of Acacia concinna fruit). Reactions proceed with very good to excellent yields at room temperature.

Keywords: *Acacia concinna*, Shikakai, acylation, amines.

INTRODUCTION

Environmental and economical considerations prompt an argent need to redesign the important chemical process using suitable catalyst and achieve better yields [1]. The choice of the particular catalyst is a matter of chemical institution. Several types of substances such as acids, bases, clays, enzymes, ionic liquids and supercritical solvents have been employed to catalyze reactions. This is due to problems associated with prevailing catalysts like hazardous nature, high cost, tedious work up, difficult to handle, requirement of large quantities of organic solvents during and after the reaction and above all, their detrimental effects on environment. In an attempt to overcome some of the deficiencies of catalysts used in organic synthesis, we looked to nature for help. Nature abounds in number and variety of plants, many of which contain chemical constituents that are pharmacologically and biologically important [2]. Intact plant systems represent a unique class of potential biocatalysts for the reactions of exogenous organic substrates [3]. The synthetic transformations using these materials are more efficient and generate less waste than the conventional chemical reagents and solvents. Recognizing their inherent green aspects, number of synthetic reactions such as asymmetric reduction of aliphatic, aromatic and azidoketones [4], synthesis of organochalcogeno-α-methyl benzyl alcohols [5], oxidation of recemic 1-phenyl ethanol [6] and hydrolysis of recemic mixture of chiral esters [7], aliphatic and aromatic aldehydes and ketones was reduced using coconut juice (*Cocos nucifera*), [8] have been effaciously achieved using intact plant materials as biocatalysts.

The acylation of functional groups, especially amino groups is one of the most basic and frequently used transformations in organic synthesis as it provides a useful and efficient protection protocol in a multistep synthetic process [9]. The most efficient base catalysts are 4-(dimethylamino) pyridine (DMAP) [10a], phosphines, [10b], [10c] $ZrO(OTf)_2$ [10d], Iodine [10e] and the powerful acid catalysts employed include Me_3SiOTf [11a]. $Sc(OTf)_3$ [11b], $In(OTf)_3$ [11c], $Bi(OTf)_3$ [11d] and yttria-zirconica based Lewis acid [11e]. Some of these reagents and catalysts lead to waste as well as some reactions involving organic solvents, often toxic and polluting, hence unacceptable in the present days. One of the major factors for a green chemical process in solution involves the choice of cheap, safe and non-toxic solvents. Water being abundant in nature is the first choice. Thus, development of an efficient and convenient synthetic methodology, the intact plant materials are soaked in water and it is used as a catalyst is an important area of research. Considering the importance of acylation and environmental factors as well as our interest in green chemical processes, we report in this paper acylation of amines in an aqueous extract of pods of *Acacia concinna* fruit, which fulfils many of the above requirements.

In continuation of our research work devoted to the green chemistry [12-13], we have investigate the pericarp of *Sapindus trifoliatus* fruits were used in the synthesis of imine formation [14], we report herein the synthesis of acylation of amines in the presence of aqueous extract of *Acacia concinna* pods under mild condition within much lesser time.

Thus, a need for a practical, efficient and greener alternative for this important transformation prompted us to disclose here a simple procedure for acylation catalyzed by aqueous extract of pods of *Acacia concinna* fruit. (**Scheme 1**).

MATERIALS AND METHODS

General

All reported yields are based on isolated compounds. Melting points were determined with a Buchi melting point apparatus and are uncorrected. TLC separations were carried out on silica gel plates with UV indicator from Aldrich; visualization was by UV fluorescence or by staining with iodine vapor. ^{1}H NMR spectra were recorded on a Bruker Avon 300 MHz spectrometer using DMSO as solvent. Tetramethylsilane (TMS) was used as an internal standard. Infrared spectra were recorded on a Perkin-Elmer One FTIR spectrometer. The samples were examined as KBr discs ~5 % w/w. All chemicals were purified prior to use**.**

Plant material

Dried *Acacia concinna* fruits were purchased from local market and authenticated from Department of Botany, Shivaji University, Kolhapur - 416004 (India).

Preparation of catalyst
100 gm dry pods of *Acacia concinna* 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 (10%). The activity of catalyst remains unchanged for more than one month when kept below 5 ^{0}C.

General procedure for the acylation of amines.
A mixture of aniline (1 mmol), acetic anhydride (1.05 mmol) and aqueous extract of pods of *Acacia concinna* fruit as a catalyst (10 %, 10ml) was stirred at room tempreture for an appropriate time (Table 2). After completion of the reaction as indicated by TLC (hexane/ethyl acetate 8:2). Reaction mixture was washed by cold water. The reaction mixture was filtered by whatman filter paper, the remaining solid material was washed with cold water. The solid product was recrystallized to give pure product.

RESULTS AND DISCUSSION

To begin with, pods of *Acacia concinna* fruit was chosen for experiment. *Acacia concinna* fruit is commonly known as 'Shikakai' in Hindi is a member of the Leguminosae, sub-family Mimosacaea. It is a common bush. *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 pugitive [15]. Aqueous extract of this fruit has been in use as detergent since a long time in India. Various properties of *Acacia concinna* fruit are due to presence of saponins in it [16]. The structures of different saponins present in the fruit have been recently established [17] and it is found that they have surfactant properties similar to dodecylbenzene sulfonates [18]. The pods of *Acacia concinna* have have been found to contain the saponin of acaciac acid. Acaciac acid was found to be a trihydroxymonocarboxylic acid belonging either to the α-amyrin group or to the tetracyclic triterpene group [19], [20]. The aqueous extract of these pods of fruit shows acidic pH (ca 2.1) which is due to presence of a acaciac acid is a trihydroxy-monocarboxylic acid with molecular formula $C_{30}H_{48}O_5$ corresponding to pentacyclic triterpenes. (**Fig-1**) [21]. These interesting properties of *Acacia concinna* fruit prompted us to use it as catalyst in acylation of amines.

Herein we report a general, rapid, and one-pot convenient procedure for N-acetylation of amines using acetic anhydride under room temperature catalyzed by pods of *Acacia concinna* fruit (**Scheme -1**).

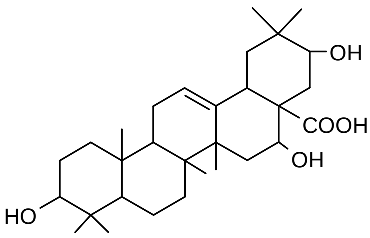
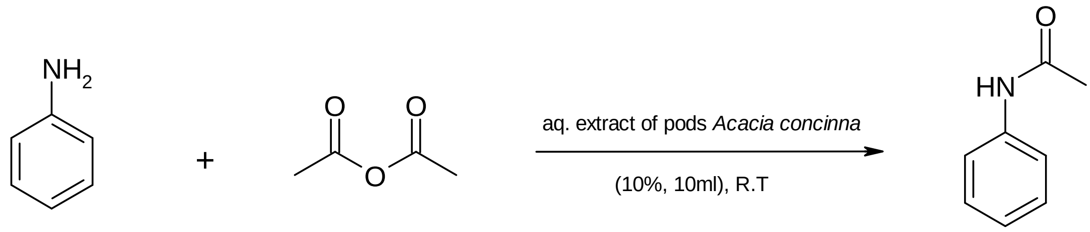


Fig 1: Structure of acaciac acid in the saponin of pods of *Acacia concinna*.



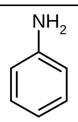
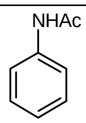
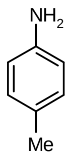
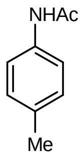
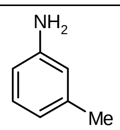
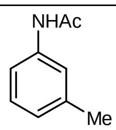
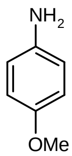
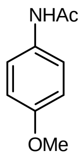
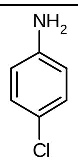
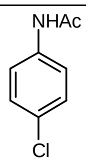
1 2 3

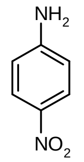
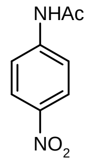
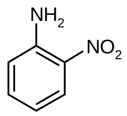
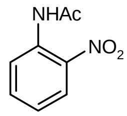
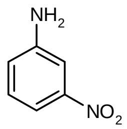
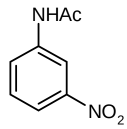
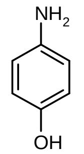
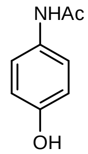
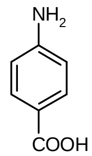
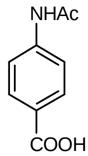
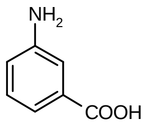
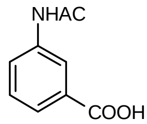
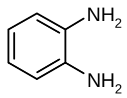
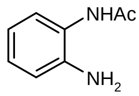
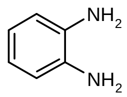
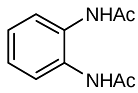
Scheme-1 Acylation of amines with Ac_2O catalyzed by Pods of *Acacia concinna* fruit

Table -1 Effect of concentrationof aqueous extract of *Acacia concinna* pods

Entry	**Conc.of.aq.extract of *Acacia concinna* pods % (*W/V*)**	**Time (min)**	**Yield (%)**
1	2.5	60	80
2	5	50	89
3	10	30	96
4	20	30	96
5	30	30	96

Table-1 Acylation of amines with Ac_2O catalyzed by Pods of *Acacia concinna* fruit

Entry	**Amine**	**Time (min)**	**Product**	**Yield [a,b] (%)**
1		5		96
2		5		94
3		9		80
4		5		92
5		7		94

6		10		90
7		10		90
8		15		88
9		15		89
10		12		90
11		15		89
12		15		90
13		20		88

[a]*Products were compaired with IR and* ^{1}*H NMR data authentic sample.*
[b]*Isolated yield after purification.*

The general efficiency of this reaction is evident from the variety of aromatic amino compounds which react in excellent yields within a very short time; aniline is acylated within 5 min. First, we have tried to optimize the reaction conditions for acetylation of aniline at different concentrations of catalyst **(Table-1).** It gives good results at 10%, 20% and 30% aqueous extract of *Acacia concinna* pods. Therefore, use of 10%, 10ml aqueous extract of pods of *Acacia concinna* fruit with 1 mmol of aniline and 1.05 mmol of acetic anhydride at room temperature gave 96% of acetanilide. Similarly, we have converted in all cases gives relatively good yields under identical reaction conditions (**Table-2**). The reactants were dissolved in a very short time and it was exciting to observe that the reaction occurred immediately on stirring the reaction mixture at room temperature. The reaction was completed within 5min and desired acetanilide was obtained in 96% isolated yield. The rate enhancement in aqueous extract of pods of *Acacia concinna* fruit can be attributed due to its surfactant property and pH. The saponins which are highly acidic solubalize the reactant species strongly by hydrogen bond formation in aqueous medium. This increases number of favorable collisions between the reactant species. Further encapsulation of hydrophobic end of the product in micellar cages drives the equilibrium towards product side which increases the speed as well as yields of products. This remarkable activation in reaction rate, prompted us to explore the potential of this protocol for the synthesis of acylation of amines.

CONCLUSION

In conclusion, we have developed a simple, convenient and efficient synthetic protocol for the acylation of amines using a catalytic amount of pods of *Acacia concinna* fruit extract. Thus pods of *Acacia concinna* fruit extract as a catalyst could be viable, economic and ecofriendly catalyst. Another advantage of this method is excellent yields in shorter reaction time with high purity of the products.

Acknowledgments

We greatfully acknowledge the financial support from the Department of Science Technology and University Grants Commission for FIST and SAP respectively.

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