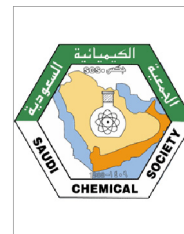




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SPECIAL ISSUE: ENVIRONMENTAL CHEMISTRY

Environment-friendly green chemistry approaches for an efficient synthesis of 1-amidoalkyl-2-naphthols catalyzed by tannic acid

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KEYWORDS

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Abstract A new, facile, cost-effective and environment-friendly protocol is reported for the synthesis of 1-amidoalkyl-2-naphthols exploring tannic acid as a novel, cheap and biodegradable catalyst. β -naphthol is condensed with substituted aromatic aldehydes and various amides using catalytic amount of tannic acid in the absence of solvent under thermal (hot plate and oil bath) and microwave irradiation techniques. This green protocol offers many advantages such as short reaction time, use of environment-friendly and cheap catalyst and good to excellent yields.

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1. Introduction

Our environment, which is endowed by nature, needs to be protected from ever-increasing chemical pollution. Large scale production of pesticides, pharmaceuticals and petrochemicals responsible for causing chemical pollution leads to the development of the concept of “green chemistry”. Among the various techniques of green chemistry, microwave-assisted one pot multi-component reaction under solvent-free condition emerges as a powerful approach for the synthesis of biologically active molecules in a very fast, efficient and time saving

manner without the isolation of any intermediates resulting in atom economy and high selectivity (Anastas and Warner, 1998).

1-Amidoalkyl-2-naphthols have gained remarkable attention in the field of synthetic organic chemistry as a necessary building block for the synthesis of many vital compounds. It is noteworthy that 1-amidomethyl-2-naphthols by amide hydrolysis can be converted to important biologically active 1-aminomethyl-2-naphthol derivatives having hypotensive and bradycardiac activity (Szatmari and Fulop, 2004; Shen et al., 1999). Amidoalkyl-naphthols are also the precursor for the 1,3-oxazine nucleus which are present in numerous natural products, bioactive molecules and potent drugs used in treatment of AIDS and Parkinson's diseases (Ren et al., 2011; Vrouenraets et al., 2007; Joyce et al., 2003).

1-Amidoalkyl-2-naphthols can be prepared by multicomponent condensation of aldehydes, 2-naphthols and acetonitrile or different amides in the presence of Lewis or Bronsted acids such as *p*-TSA (Khodaei et al., 2006), montmorillonite K10

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(Kantevari et al., 2007), $\text{Ce}(\text{SO}_4)_2$ (Selvam and Perumal, 2006), Iodine (Das et al., 2007), NaHSO_4 (Shaterian and Yarahmadi, 2008), $\text{Sr}(\text{OTf})_2$ (Su et al., 2008), $\text{K}_5\text{CoW}_{12}\text{O}_{40}\cdot 3\text{H}_2\text{O}$ (Nagarapu et al., 2007), sulfamic acid (Nagawade and Shinde, 2007; Patil et al., 2007a,b), molybdophosphoric acid (Jiang et al., 2008), cation-exchange resins (Patil et al., 2007a,b), silica sulfuric acid (Srihari et al., 2007), $\text{HClO}_4\text{-SiO}_2$ (Shaterian et al., 2008a), $\text{Fe}(\text{HSO}_4)_3$ (Shaterian et al., 2008b), Amberlite IR-120 (Forouzani and Ghasemnejad-Bosra, 2011), Boric acid (Shahrisa et al., 2012; Karimi-Jaberi and Fakhraei, 2012), anhydrous zinc chloride (Malik et al., 2012), $\text{Mg}(\text{ClO}_4)_2$ (Amrollahi et al., 2013), sulfanilic acid (Singh et al., 2014), PNBA (Li et al., 2014), AgI nanoparticles (Davoodnia et al., 2014), PBS nanoparticles (Borhade et al., 2014), polyphosphate esters (Moghanian and Ebrahimi, 2014) and carbon based solid acids (Davoodnia et al., 2014). However, majority of them suffer from several limitations such as high temperature, long reaction time, use of expensive reagents, low yields of products, high catalyst loading, corrosive reagents, strongly acidic conditions and further purification of products. Therefore development and introduction of convenient and efficient methods for the preparation of 1-amidoalkyl-2-naphthols is of practical importance and is still in demand.

Tannic acid, a naturally occurring plant polyphenol, is composed of a central glucose molecule derivatized at its hydroxyl groups with one or more galloyl residues (Fig. 1). The antioxidant activity of phenolic compounds is mainly attributed to their redox properties, which allow them to act as reducing agents, hydrogen donors and quenchers of singlet oxygen (Gulcin et al., 2010).

The main demerit of using strong acid for catalyzing amidoalkyl-naphthol synthesis results in some disadvantages. Because of the use of acidic catalysts in most of the reported methods, application of aldehydes bearing basic groups or acid-sensitive aldehydes in the reaction is not possible. Polyphenolic nature of tannic acid may be explored for their catalytic efficiency. Its weak acidity (pK_a around 6) is due to

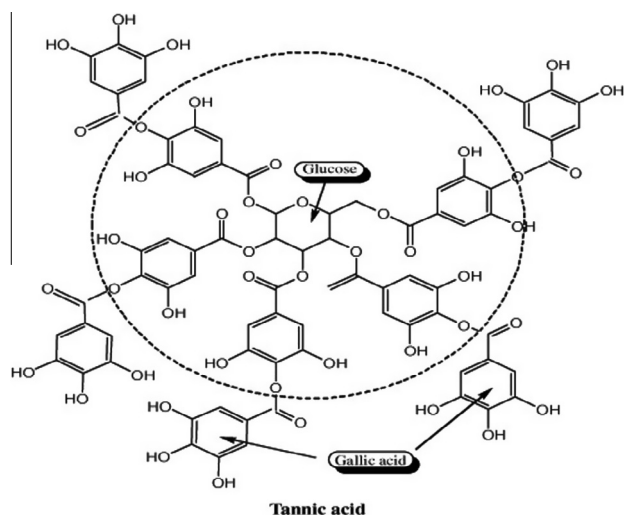


Figure 1 Chemical structure of tannic acid, a deca-galloyl glucose consisting of a center glucose molecule esterified at all five hydroxyl moieties with two gallic acid molecules. The shaded circle highlights pentagalloylglucose and the core structure of tannic acid (Reproduced from Gulcin et al., 2010).

the numerous phenol groups in the structure. Because of their controlled reducing property and optimum hydrogen donor's capability, it may be used as a mild catalyst where strong Bronsted acids are found detrimental. We have earlier explored the catalytic ability of tannic acid for the synthesis of 1,5-benzodiazepines with promising results (Sandhar et al., 2012). Tannic acid was found to be non-toxic, cheap and efficient catalyst for that particular reaction. Herein, we have investigated the potential of tannic acid as a catalyst for the synthesis of 1-amidoalkyl-2-naphthol derivatives *via* one-pot multi-component condensation reactions without solvent by various green chemistry methods (Method A, B and C) (Scheme 1).

2. Result and discussion

In continuation of our work for the green synthesis of amidoalkyl-naphthols using novel environment-friendly catalysts (Singh et al., 2014, Li et al., 2014; Duvedi and Singh, 2012), we in this article, are reporting the use of tannic acid as a highly efficient non-toxic catalyst which has not been explored much for its catalytic activity (Shitole et al., 2013).

Firstly, in order to determine the amount of catalyst required for carrying out this reaction, model reaction was performed for the synthesis of N-[phenyl-(2-hydroxynaphthalene-1-yl)-methyl]-acetamide. For this, 2-naphthol, benzaldehyde and acetamide in the ratio 1:1:1.2 mmol are treated with different quantities of tannic acid under solvent-free conditions by three methods (Method A: microwave, B: Oil bath and C: Hot plate). It was found that the use of just 0.03 mmol (3 mol%) of tannic acid is sufficient to push the reaction forward (Table 1). The fewer amounts gave an even lower yield and the more amounts could not cause the obvious increase in the yield of the product. A comparative study of the required concentration of catalyst, method and time of completion of reaction was made as shown in Table 1. The synthetic approach is outlined in Scheme 1.

To show the generality of this method, the optimized system was used for the synthesis of other amidoalkyl-naphthol derivatives. The results are summarized in Table 2. Various functionalities present in the aryl aldehydes, such as methyl, chloro, dimethyl amino, nitro, and methoxy with urea/acetamides/benzamides groups were well tolerated under these conditions (Table 2). However, the reactions of aliphatic aldehydes would fail to give the desired products. In all these cases, the corresponding 1-amidoalkyl-2-naphthols were obtained in good to excellent yields without the formation of any side products such as dibenzoxanthenes, which are normally observed under the influence of strong acids.

A mechanistic rationale portraying the probable sequence of events is given in Scheme 2. It is assumed that tannic acid due to its reducing and hydrogen donor's capability may activate the oxygen of the carbonyl group in the initial step and ultimately enhances the electrophilicity of the aldehyde and leads to reduction in reaction time. Further, the activated aldehyde attacks and condenses with 2-naphthol to give ortho-quinone methides (*o*-QMs). The same *o*-QMs, generated in-situ, may undergo a nucleophilic conjugate addition with acetamide to form 1-amidoalkyl-2-naphthol derivatives. Electron-withdrawing groups on benzaldehydes in the *o*-QMs increase the rate of the 1,4-nucleophilic addition reaction because the alkene LUMO is at lower energy in the presence of electron-

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