SYNTHESIS OF BIOLOGICAL COMPOUNDS 2-NITRO-1-PHENYLETHANOL AND THEIR DERIVATIVE BY HENRY REACTION USING KINNOW PEEL ASH: POSSIBLE PATHWAY FOR CARBOMETHYLATION

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Abstract

Kinnow mandarian is well known for its nutrition and health – promotions values. They have wide range applications such as pharmaceutical, industrial, cosmetics, biological activities (antioxidant, antitumor, antimicrobial etc.), and Carboxymethylation. However, their waste is major problem in present day. Therefore, we utilize this waste as a catalyst in henry reaction and give β-nitroalcohols with 80% yield, which are useful synthons in organic synthesis and also important for biological properties. A simple method is described for synthesis of hennry product.

Keywords: Kinnow peel ash, Fruit waste, Recyclable catalyst, Henry reaction, Green chemistry.

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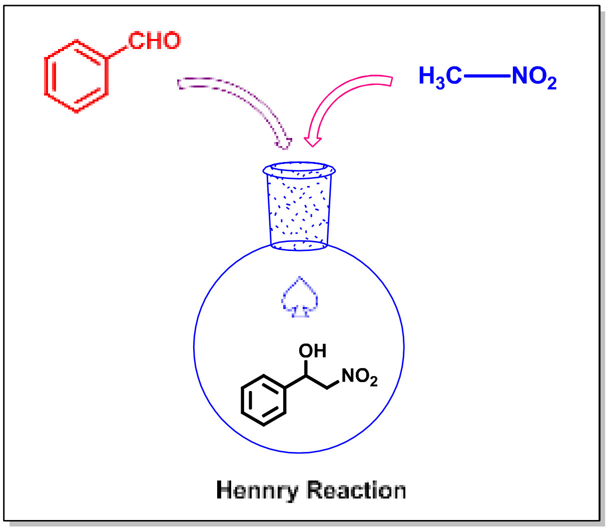


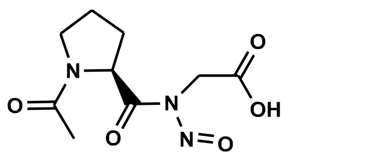
1. Introduction

Kinnow mandarin is a member of the Rutaceae family. Kinnow is used to make commercial products such as fresh juice, dehydrated citrus products. The Kinnow peel contains a variety of bioactive compounds and essential oils, including polyphenols, carotenoids, pectin, naringin, and antioxidants[1], which have been used in antibacterial, ant allergic, anticancer, and antidiabetic effects, and that's why it's also used as nutritional and health supplements[2-6]. Thus the important properties of citrus peel have encouraged the researchers to explore the scope of this waste product is important for pharmaceutical and therapeutic applications such as enzymes, ethanol, microbial biomass, volatile flavoring compounds, organic acids, and antioxidants[7-9]. It has been reported that the Kinnow peel, which accounts for 30-40% of the fruit, is rich in bioactive chemicals[10]. After the juice extraction about 50–60% of the leftover fruit pieces discarded as citrus waste[11] such as the peel, seeds, membrane, and pulp. Millions of tunnes of waste from agricultural and chemical sectors are created every day globally[12-13]. None methods are fully disposes the fruit waste. If waste does not get managed, it may become a major problem[14]. This trash still contains significant amounts of bioactive chemicals that pollute the environment The release of unpleasant odor throughout composting would cause poor air quality[15], global warming, and the possible discharge of toxic compounds like dioxin from open burning may cause some acute health effects like headache, fatigue, diarrhea, and insomnia to human being. Use of biomass waste to create catalysts and catalyst-supports[16]. There are an increasing number of reports of the preparation of heterogeneous catalysts from waste materials. Although, there are several green methods as well as less toxic materials were reported for catalysis and synthetic organic chemistry. But, the wide exposure of waste food material in the field of catalysis and synthesis, still remaining so to expose the wide application of Kinnow mandarin in the field of catalysis, we have planned the catalytic Henry reaction by Kinnow mandarin.

One of the most significant synthetic tools for C–C bond synthesis is the Henry reaction, commonly known as the nitro-aldol reaction. It is the effective reaction to prepare β- nitro-secondary alcohols by using nitro-alkanes and aldehydes or ketones[17-18]. In more complex synthetic chemistry, the Henry reaction will help the joining of two molecular fragments, under moderate conditions ,with the formation of two asymmetric centers at the new carbon–carbon juncture[19]. In catalytic nitro aldol reactions, many typical and widely used catalysts with many different sets of conditions have been reported.

The limitations of Henry reaction is formation of side product, toxicity, catalyst recoverability and reusability, low yield, high reaction time and high cost. Green chemistry plays important role in synthetic chemistry because it provides good results without using any hazardous chemicals and and specific reaction conditions. There are so many literature reported on green chemistry such as biomass production from cyanobacteria[20], cytotoxicity of nanoparticles used in cosmetic industries[21], Mixed matrix membranes extracted from oil palm empty fruit bunches[22], production of bioinsecticide from pong-pong fruit seeds[23], green synthesis of silver nanoparticles[24], and production of biogas from olive pomace[25], fruit waste[26] etc.

In order to overcome these challenges we have planned to prepare the design heterogeneous catalyst by using citric waste. Therefore, reactions catalyzed by development of new heterogeneous metal-free catalysts could lead to green and productive methodologies for a variety of chemical transformations of interest to the chemicals and other industries. Carboxymethylation can be synthesized by Hennry reaction, where a carboxymethyl moiety is covalently bonded to an oxygen or nitrogen atom at various positions of nucleobases. DNA carboxymethylation is mainly induced upon exposure to endogenous and exogenous sources of N-nitroso compounds (NOCs) (Figure 1), and it was hypothesized as a potential etiological factor for gastrointestinal carcinogenesis. NOCs are characterized by a nitroso group (N¼O) being bonded to a nitrogen atom and are capable of inducing a diverse array of DNA adducts[27].



N-(N-acetyl-L-prolyl)-N-nitrosoglycine (APNG)

Figure 1: APNG is example of NOCs that is carboxymethylating agents.

2. Experimental Methodology

2.1 Materials

Waste fruit peels of Kinnow mandarin is selected and used as a catalyst. The fruit peels are collected from local fruit stalls in Jaipur, Rajasthan. For characterization of compounds, Bruker Fourier transform infrared spectroscopy (FT-IR), and Thin layer chromatography (TLC) are used. All chemicals and solvents are used without further purification: Nitromethane, benzaldehyde, ethyl acetate and Hexane.

2.2 Preparation of Kinnow peel Ash

Kinnow peel are washed with di-ionized water to remove the dirt particle and clean them well. The waste is dried in an oven for 24 h at 100 ℃ to remove the moisture content. The dried peel waste is converted into powder form. After that to obtain the Kinnow peel ash, put the powder into the furnace for 6 h at 650 ℃ temperature and then the ash is store for the further experiment.

2.3 Preparation of 2-nitro-1-phenylethanol and their derivatives

The mixture of benzaldehyde (1mmol), nitromethane (1mmol) and Kinnow peel ash (20 mg) used as catalyst is stirred for 3 hours on the magnetic stirrer at room temperature. The TLC plates were used to confirm the reaction. After that, confirm the reaction separate the catalyst and compound by filter paper. 80 % yield is obtained. By following this method, we have done reactions between derivatives of benzaldehyde and nitromethane.

2.4 Optimization table for catalytical performance

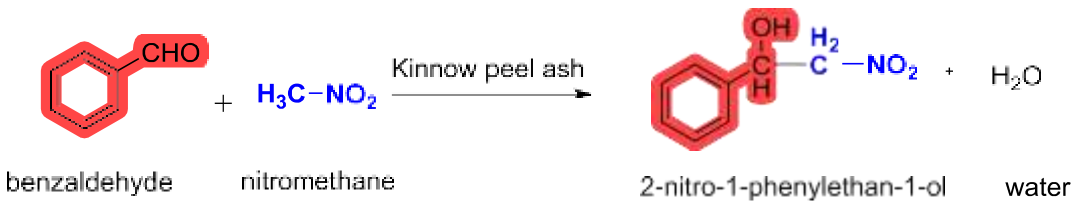
Kinnow peel ash is used for hennry reaction. To check the best performance of the catalyst for hennry reaction, the effect of catalyst loading and solvent effects are observed. From table no. 1, its is very clear that best reaction condition is 20 mg without solvent and obtained 80% yield.

Table no: 1 Optimization table for Hennry reaction

Entry	Catalyst loading (mg)	Solvent	Yield %
1	10	Ethanol	50%
2	10	Methanol	55%
3	10	Water	40%
4	10	Neat	60%
5	20	Neat	80%

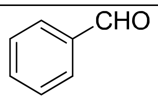
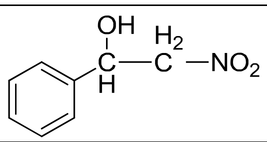
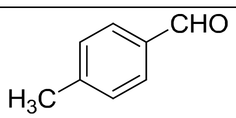
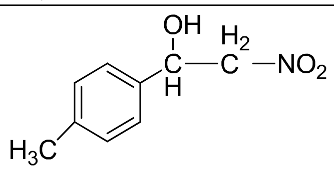
3. Result And Discussion

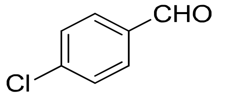
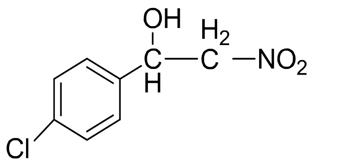
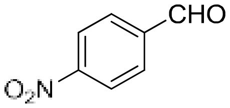
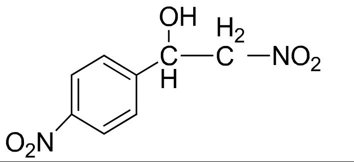
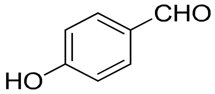
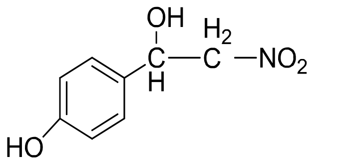
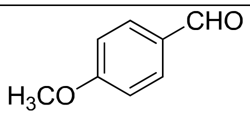
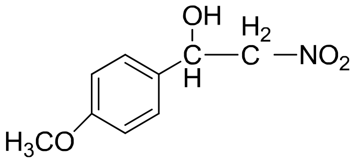
Henry reaction was performed by benzaldehyde and nitromethane (Scheme1). This reaction is catalyzed by the Kinnow peel ash and provide 80% yield of product in neat condition. This reaction also performed by different derivatives of benzaldehyde name as 4-methyl benzaldehyde, 4- hydroxy benzaldehyde, 4-methoxy benzaldehyde, 4-chloro benzaldehyde and 4-nitro benzaldehyde with nitromethane by using 20 mg of catalyst without using solvent. Total six reactions is performed. From table no.2, it conclude that all six reactions is completed in different time with different yield. Benzaldehyde has highest yield, 80% and nitro benzaldehyde has very less yield 55%. The product is characterized by FTIR. Comparison of the fresh Kinnow peel ash and recovered Kinnow peel ash by IR spectrum is done. Both have same peaks.



Scheme1. Henry reaction

Table no.2 Henry reaction by using different derivatives of aniline and benzaldehyde

Entry	Benzaldehyde	Nitromethane	Product	yield	Time (Hours)
1		H_3C-NO_2		80%	3h
2		H_3C-NO_2		80%	5h

3		$H_3C{-}NO_2$		70%	5h
4		$H_3C{-}NO_2$		55%	5h
5		$H_3C{-}NO_2$		60%	5h
6		$H_3C{-}NO_2$		72%	5h

3.1 Fourier transform infrared spectroscopy spectrum of fresh, recovered Kinnow peel powder, and 2-nitro-1-phenylethanol

The Infrared Spectroscopy spectrum of fresh Kinnow peel powder (Figure 1. a) and recovered Kinnow peel powder is compared (Figure 1. b), which shows a broad peak at 3310 cm^{-1} and 3312 cm^{-1} in the high-frequency area attributed to the stretching mode of the O-H bond, which reveals the presence of hydroxyl groups in both Kinnow peel powder. The band observed at 1737 cm^{-1} and 1738 cm^{-1} are assigned to the carboxyl group. The sharp peak found at 1645 cm^{-1} and 1645 cm^{-1} is a resonance peak that can be assigned to the stretching and bending vibration of OH. The peak at 1228 cm^{-1} and 1228 cm^{-1} denotes C-O-C stretching and the peak at 1050 cm^{-1} and 1050 cm^{-1} corresponds to the vibrational mode of the C-O group. The IR peaks of 2-nitro-1-phenylethanol is shown in figure 2.

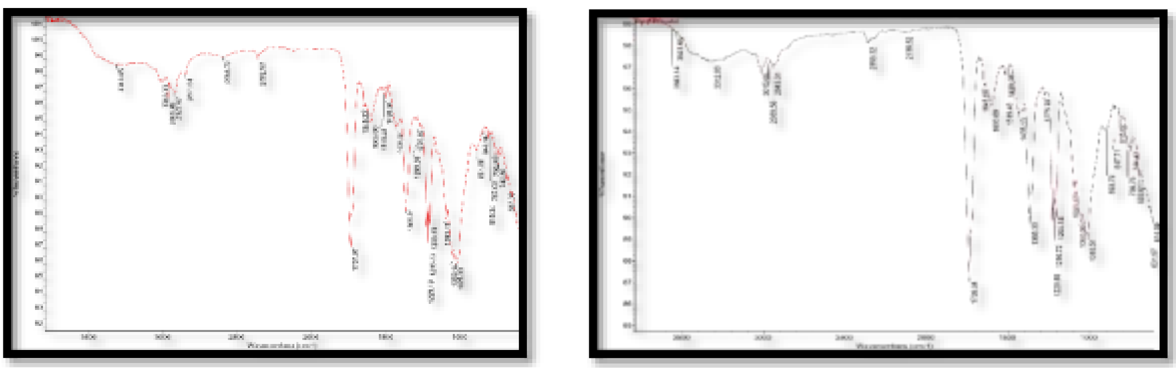


Figure1: (a) IR of Spectrum of Fresh Kinnow peel powder and (b) IR of recycled of Kinnow peel powder

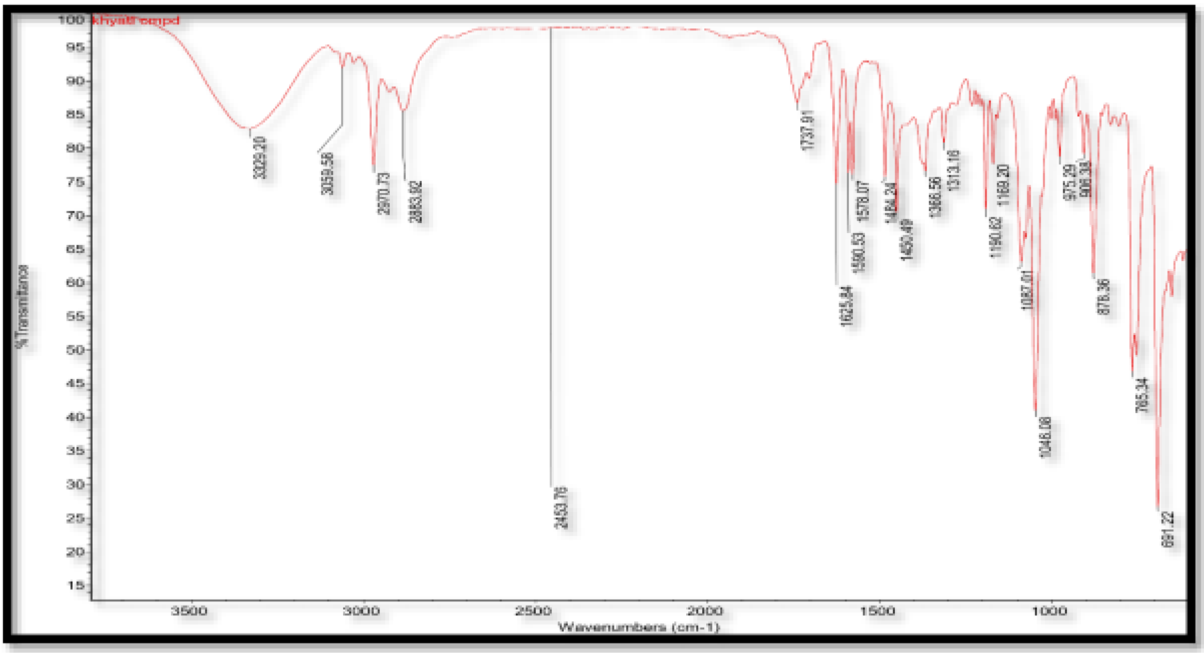


Figure 2: IR Spectrum of 2-nitro-1-phenylethanol

4. Conclusion

We have utilized the citrus waste as a catalyst in Henry reaction to obtained β-nitroalcohols and their derivatives with 80% yield in neat condition by using benzaldehyde and nitromethane, which are useful synthons in organic synthesis. We have described new method to synthesized the herpetology compound without any typical reaction condition.

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