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PEEL EXTRACT ASSOCIATED OXIDATIVE GREEN DAKIN SYNTHESIS OF SOME PHENOLS USING AQUEOUS BANANA EXTRACT CATALYST

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The green Dakin reactions can be performed by employing gallic acid as an oxidizing agent. Implementation of gallic acid helps to avoid the usage of catalyst, ligand and any toxic or hazardous oxidizing agent. Gallic acid accelerates the conversion of the atmospheric oxygen into hydrogen peroxide, which helps in the oxidation of aldehydes *in situ*. Mango peel, potato peel, pomegranate pomace, grape pomace extract contains the rich source of gallic acid that performs the oxidations in a natural feedstock. The best results were obtained by mango peel as well as potato peel extract giving excellent yields with minimum time at room temperature. The 'aqueous extract of banana' (AEB), in the said conversion plays a dual role of catalyst and a base. The reported work can be considered as environment-friendly Dakin oxidation, as it is carried out in a neat AEB at room temperature under aerobic conditions with low reaction time and better yield.

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INTRODUCTION

Nowadays, green chemistry or development of sustainable processes in chemical synthesis plays a vital role to eradicate the hazardous organic solvents or any other toxic metal-based chemical reagents[1]. Specifically, agricultural waste is gaining attention due to its reusability and employability. In the case of fruits and vegetables, usually, a high amount of antioxidant compounds is found in peels, kernels or seeds, namely in parts that are removed during processing and become wastes[2]. In order to achieve higher sustainability, metal free methodologies for oxygen activation are highly desirable, particularly if such methods are based on non-toxic compounds from renewable sources at room temperature[3]. The pomegranate fruits are rich in polyphenolic compounds including punicalagin isomers, ellagic acid derivatives and anthocyanins (delphinidin, cyanidin and pelargonidin 3-glucosides and 3,5-diglucosides)[4]. Chlorogenic acid (CGA) is the main content of potato peel which is a part of phenolic acids along with gallic acid (GAC), caffeic acid (CFA) and protocatechuic acid which are present in low amounts[5]. Gallic acid is found in tea and grape seeds[6]. Grapes contain a large amount of polyphenols which include the phenolic acids, flavonoids, anthocyanins and proanthocyanidins[7]. Gallic acid is known to have anti-inflammatory, antimutagenic, anticancer and antioxidant activity. It also seems to have antifungal, antiviral and antibacterial properties. According to literature, gallic acid is cytotoxic typically to the cancerous cells devoid of harm to the healthy cells. In cases of internal hemorrhage, gallic acid acts as an excellent astringent[8]. The quantification of individual phenolic acids, stilbenes, flavonoids including anthocyanins, was done for the comparison of the novel process with conventional pomace extraction[9]. Phenolic compounds are secondary metabolites, ubiquitous in plants and plant-derived foods and beverages. They show a large diversity of structures, including rather simple molecules (e.g., vanillin, gallic acid, caffeic acid), and polyphenols such as stilbenes, flavonoids, and polymers derived from these various groups[10]. Thus, the use of an abundant and underutilized bio-waste, such as grape pomace, in sustainable oxidations with air has also been explored herein.

In the continuation of our previous work[11-23], it was confirmed that until now none of the methods had used such a mild and green catalyst and solvents for Dakin oxidation. The designed method is suitable for the conversion of substituted benzaldehydes to its consequent substituted phenols. Owing to the advantages of green chemistry, this method would be an eco-friendly, economical and a valuable tool for the oxidative synthesis of the compounds through Dakin oxidation. Hence it was decided by us to modify and continue our research in the present work.

MATERIALS AND METHOD

All chemicals, unless otherwise specified, were purchased from commercial sources and were used without further purification. The main chemicals were purchased from Sigma Aldrich and Avra labs. The development of reactions was monitored by thin layer chromatography (TLC) analysis on Merck pre-coated silica gel 60 F254 aluminum sheets, visualized by UV light. Melting points were recorded on SRS Optimelt. Melting points are uncorrected. The ^{1}H NMR spectra were recorded on a 400 MHz Varian NMR spectrometer. The ^{13}C were recorded on a 100 MHz Varian NMR spectrometer. Mass spectra were taken with Micromass-QUATTRO-II of WATER mass spectrometer.

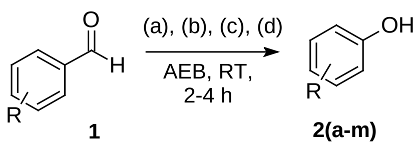
Table 1. Mango peel extract (MPE), grape pomace extract (GPE), pomegranate extract (PE) and potato peel extract (PPE) catalyzed reactions

Entry	Phenols	Time, min				Yield, %				Melting point (°C)
		MPE	GPE	PE	PPE	MPE	GPE	PE	PPE	
2a	PhOH	80	90	80	70	85	58	74	81	40-41
2b	$4\text{-}HOC_6H_4OH$	180	170	150	150	93	85.2	90.1	93	172-174
2c	$2,4\text{-}Cl_2C_6H_3OH$	210	210	195	195	91	91.5	89.1	92	45-47
2d	$2,4\text{-}(MeO)_2C_6H_3OH$	225	215	200	200	72	42	70.2	72	85-86
2e	$3\text{-}O_2NC_6H_4OH$	270	280	240	240	83	63.3	78.4	84	94-95
2f	$4\text{-}O_2NC_6H_4OH$	270	280	270	240	91	71	71	87	110-112
2g	$3\text{-}HOC_6H_4OH$	225	225	215	180	82	54.2	84.5	84	100-101
2h	$3\text{-}MeOC_6H_4OH$	230	230	225	190	94	53.2	69.1	93	201-202
2i	$2\text{-}ClC_6H_4OH$	250	245	230	210	95	69	78	88	163-164
2j	$2,3\text{-}Cl_2C_6H_3OH$	240	250	245	210	91	72.4	82.5	93	56-58
2k	$2\text{-}BrC_6H_4OH$	240	265	210	210	95	89	91.2	93	211-212
2l	$4\text{-}MeC_6H_4OH$	240	270	250	225	88	58	60.2	86	180-182
2m	$4\text{-}MeOC_6H_4OH$	235	260	240	180	91	65.8	79.8	90	51-52

Preparation of aqueous extract of banana

Banana peels were taken and boiled in distilled water for 30 min at 90 °C. The peels were crushed and filtered using a muslin cloth. The filtrated was dried and stored.

The extract was tested for tannins and polyphenol content. It was treated with 5% $FeCl_3$, which resulted in a blue color solution for polyphenol test and with 10 % lead acetate which gave white precipitate for confirmation of the presence of tannins. The tests were negative when the extract was treated with acetone before filtration.



Scheme 1. Reagents and conditions: (a) mango peel extract **(b)** grape pomace extract **(c)** pomegranate pomace extract **(d)** potato peel extract

Preparation of mango peel extract

Dried mango peel powder (var. Kesar) and water in ratio 1:10 was taken and boiled using oil bath at 180 °C for 120 min and dried.

Preparation of grape pomace extract

Dried Grape pomace was taken from the vineyard and extracted with ethanol:water:HCl (7:2.9:0.1) ratio for 3 days and then filtered. The filtrate was used as a source of Gallic acid.

Preparation of pomegranate pomace extract

Pomegranate pomace was dried at 70 °C. Methanolic extraction using Soxhlet (4 cycles) was done of dried pomace powder. The extract was concentrated under vacuum.

Preparation of potato peel extract

Potato peel extract was carried out in two ways:

1) 10 g of dried ground peels were extracted using magnetic stirrer with 200 mL methanol at room temperature overnight. It was then filtered and the residue was re-extracted under the same conditions, the combined filtrate was evaporated at 40 °C. The concentrate was centrifuged for 10 min and stored in the refrigerator.

2) 1 g of dried potato peel was dipped in 20 mL of solvent (methanol) and sonicated for about 15 min then filtered and centrifuged. The extract obtained by the method of sonication gave better results.

General procedure for the synthesis of compound 2(a-m):-

To the mixture of aldehyde (0.1g) and AEB (3 mL), a catalyst amount of natural feedstock extract was added. A reaction mixture was stirred to at room temperature & progress was monitored by TLC. After completion of the reaction (2-4 h), the reaction mixture was extracted with ethyl acetate and water (3×15 mL) and aqueous layer quenched with saturated aqueous sodium bicarbonate solution (15 mL). The solvent was evaporated to dryness to afford the product. The product was further purified by column chromatography.

RESULTS AND DISCUSSION

Our investigation initiated by the literature survey was found that Dakin oxidation of benzaldehyde to phenols was carried using H_2O_2 and aqueous extract of banana (AEB) as a neat reaction media at room temperature. Our initial efforts focused on identifying new catalyst showing oxidative properties to replace the toxic effect of H_2O_2. Hence this novel protocol represents an efficient and an interesting substitute to the initial H_2O_2 bearing method of Dakin oxidation. We first studied the impact of various extracts containing gallic acid (mango peel extract, potato peel extract, pomegranate peel extract, grape pomace extract), which are discussed earlier concerning the subject of this reaction.

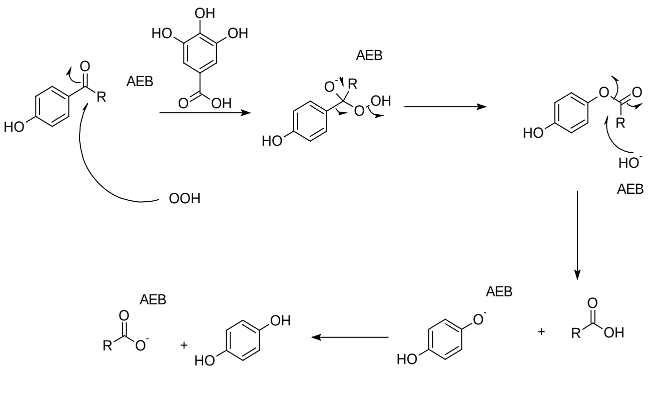


Figure 1. Plausible reaction mechanism

We found that the best results were given by mango peel as well as potato peel extract giving excellent yields with minimum time at room temperature (Table 1). A range of commercially available substituted benzaldehydes was screened to investigate the scope of this method (Table 1). Out of the 13 benzaldehydes chosen, the compounds **2b**, **2c**, **2h**, **2i**, **2j**, **2k** and **2m** gave excellent yields using mango peel and potato peel extracts respectively with comparable reaction times. Though the rate of completion of the reaction was slower using AEB conditions than that of H_2O_2, it was identified as a greener approach concerning the reaction yield. Also, the raw material required for the preparation of extracts is cheap and easy to procure with the simple method of extraction. Therefore, the method is economical as it uses water majorly as the solvent.

From the literature [2,] it is confirmed that gallic acid helps in the conversion of atmospheric O_2 to hydrogen peroxide *in situ*. Here AEB acts as a base which helps in the abstraction of a proton from H_2O_2, which further helps in the oxidation of benzaldehydes. The nucleophilic addition takes the place of a hydroperoxide anion to the carbonyl carbon to give a tetrahedral intermediate. A phenyl ester formation takes place through hydroxide elimination with the help of[1-2] aryl migration. Afterward, the hydrolysis of phenyl ester takes place to form a second tetrahedral intermediate with the elimination of phenoxide to form a carboxylic acid. Finally, the AEB extracts the acidic hydrogen from carboxylic acid to form the corresponding phenol.

CONCLUSION

In conclusion, we have developed an aerobic and green catalytic system for Dakin Oxidation. In this manuscript, we investigated the applicability of green catalyst using natural feedstock of AEB in Dakin Oxidation for a wide range of organic compounds. Our method has a minimum environmental impact, is flexible and economical for various catalytic reactions. Reactions were done with potato peel extract (ultrasonic extraction) and mango peel extract gave better results. The catalytic system represents the most effective green catalyst for Dakin Oxidation at room temperature. We believe that this catalytic protocol has significant importance in industry as well as laboratory due to all its advantages.

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