iMedPub Journals www.imedpub.com

DOI: 10.21767/2471-9889.100029

Trends in Green Chemistry ISSN 2471-9889 2020

Vol.6 No.1:01

Onion Waste Catalyzed Synthesis of Flavones Derived from Chalcones to Unveil the Pathway of Green Catalysis

Abstract

Efficient, facile, and alternate synthesis of biologically potential flavones is reported. The 2-hydroxychalcones derived from condensation between acetophenones and salicylaldehyde in presence of Silica.SO3H underwent oxidative cyclization in the presence of onion waste extract with iodine, generating useful flavones under solvent-free conditions. The solid catalyst has been characterized by SEM, TEM and X-ray diffraction method. Reported compounds synthesized in good yields and their mechanisms of formation are explained.



Keywords: Green synthesis; Silica.SO3H; Chalcones; Onion waste; Flavones

Received: February 10, 2020, Accepted: April 01, 2020, Published: April 08, 2020

Suman Sangwan*, Rajvir Singh, Susheel Gulati and Suprita

Department of Chemistry, CCSHAU Hisar, Haryana, India

*Corresponding author: Suman Sangwan

sangwansuman99@gmail.com

Department of Chemistry, CCSHAU Hisar, Haryana, India

Tel: 91-9728345466

Citation: Sangwan S, Singh R, Gulati S Suprita (2020) Onion Waste Catalyzed Synthesis of Flavones Derived from Chalcones to Unveil the Pathway of Green Catalysis. Trends Green Chem Vol.6 No.1: 01.

Introduction

Our environment needs to be saves from increasing amount of wastes and by-products. Therefore synthetic chemists must have to develop new protocol for organic synthesis which plays an important role in green catalysis. Hence, the one pot multicomponent synthesis of biologically active heterocyclic compounds is very charmful pursuit in organic synthesis. Flavones are known for having a broad range of biological activities such as anticancer [1], antioxidant [2], anti-inflammatory [3], antidiabetic [4] and anti- ostioporotic [5]. Generally flavones are synthesized by Wittig reaction [6], Auwer's method [7] and Allan-Robinson Strategy [8]. Synthetic pathways are crucial for nature and livelihoods. Although demands for highly active chemicals is anticipated to increase significantly in the future, the ensuing environmental change will intensify competition for resources demanding that these production systems must increase both productivity and potency of chemical compounds. Henceforth, we thought that the use of green catalysts is directly related to clean and green synthesis of bioactive heterocycles like chalcones and flavones. The current study was conducted on green catalysis because the 'Green' synthesis in recent past has attracted huge attention in chemical synthesis sector due to its inherent advantages and applications. The advantages of the present

method are normal reaction temperature, easy isolation of the product, higher yield, recyclability of the catalyst, and reactions without use of hazardous, volatile organic solvent. The green catalyst was recycled efficiently without any loss of activity.

Materials and Methods

Most of the chemicals used during the research work were of laboratory grade. All commercial reagents and solvents were obtained from SRL (Sisco Research Laboratory) and CDH (Central Drug House) and used without purification. The characterization of synthesized biocatalyst was done on JSM-6100 Scanning Electron Microscope SEM, Transmission Electron Microscope TEM and X-Ray diffraction methods. Melting points were determined in open capillaries on a Ganson electric melting point apparatus and are uncorrected. Infrared spectra of the synthesized compounds and intermediates were recorded in KBr pellets on Perkin Elmer FT-IR-R 2X spectrophotometer and frequency is expressed in cm⁻¹. The 1HNMR spectra were recorded in CDCl, or DMSO-D6 using tetra methyl silane (TMS) as internal reference on "Brucker Ac 400 F"(400 MHz) nuclear magnetic resonance spectrometer. The chemical shifts values are expressed in delta (ppm), while J value in Hz and are compatable with the assigned structures.

Synthesis of silica.SO3H

A solution of 1 mL concentrated sulphuric acid in 15 mL acetone was added to a dispersion of 50 gm silica gel in 100 mL beaker and stirred at room temperature for 1 hour. The solvent was removed under reduced pressure. A yellow brown powder was obtained and that can store in a desiccator for a long period of time without any appreciable loss of activity (**Figure 1a**) [9].

TEM images of Silica.SO3H (Figure 1b-1e) reveals the pore configuration of silica was not collapsed during sulphuric acid adsorption. Figure 1b showed Silica.SO3H particles at 100 nm. Figure 1c and 1d presented the particles at 50 nm and Figure 1e showed the particles at 20 nm. Following TEM images at low and high magnification showed the clusters of primary particles with an irregular geometry and a spherical shape along with a wide size distribution. Every particle was interconnected and adhered with each other.



Figure 1a Untreated and treated Silica Gel.



(1b)

(1c)



Figure 1b-e TEM images of Silica.SO3H at high and low magnifications.

SEM scans a focused electron beam over a surface to create an image. The electrons in the beam interact with the sample, producing various signals that can be used to obtain information about the surface topography and composition. **Figure 1f** shows SEM images shows the morphology of untreated Silica gel. From the images **Figure 1g and 1h** we can see that catalyst was in smooth form. At low magnification, Silica.SO3H shows irregular shaped particles. But at high magnification Silica.SO3H shows needle shaped micro-particles at 20 μ m. SEM image shows uniform particles at 20-50 μ m and confirms the adsorption of sulphuric acid on silica surface.

XRD analysis of the catalyst was done with the help of X-ray diffractometer with a Cu (K α) radiation source (K α = 1.5406) for determining the phase of Silica. The XRD scans were recorded from 10°-80° 2 Θ with minimum step size omega: 0.001. Phase analysis was performed by comparing the d-values and intensity ratios of the main fundamental peaks with data available in the data book published by the Joint Committee of Powder Diffraction Standards (1974). At low temperature silica is crystalline but more crystallization occurs when temperature raises. **Figure 1i** clearly shows crystalline form of untreated silica (d-spacing 3.4830 Å) but **Figure 1j** shows crystalline form (d-spacing 2.9939 Å) of Silica. SO3H. The difference in d-spacing confirms crystalline to more crystalline transformation.

Synthesis of onion waste.I2

Two parts of ground solid waste (apical trimming and outer dry layers were dispersed in 15 mL of buffer solution and centrifuged



Figure 1f SEM Images of Untreated Silica.



2020

Vol.6 No.1:01





at 3000 rpm, treated with 0.5 gm lodine and then filtered and this filtrate was used as biocatalyst [10].

Chemistry of onion waste with iodine

Chemistry of Onion waste with iodine is shown in the figures (Figure 2a-2c) and the structure is given below.



General procedure for synthesis of flavones compounds

A mixture of the selected aldehyde (0.1 mmol), acetophenone (0.1 mmol), and Silica.SO3H (0.05) were added and stirred at room temperature. The progress of the reaction was monitored by TLC. The product was dried and recrystallized from ethylacetate to obtain the pure product. Then cyclization of these synthesized chalcones have done by catalyst (Onion waste 12) to give 2-(4-hydroxyphenyl)-4H-chromen-4-ones (18). The reaction was found to complete within 40 min to give product in quantitative yield (**Table 1**, entry 1). Various derivatives of flavones and their yield formed are shown in **Table 1** under (**Scheme 1**), also the



Figure 2a Onion Waste.



Figure 2b Onion waste in water.



Figure 2c Filtrate after treatment of iodine.

Vol.6 No.1:01



 Table 1 Physical and Chemical data.

speciality of the catalyst in comparison of others are shown in **Table 2**.

Results and Discussion

A mixture of salicylaldehyde (1) (2.44 g; 20 mmole) and 4-hydroxyacetophenone (2) (2.72 g; 20 mmole) in presence of Silica.SO3H (0.05 gm) was taken in flask. The reaction mixture was stirred at room temperature. Progress of the reaction was monitored with the help of TLC. After completion of the reaction, the reaction mixture was cooled and then recrystallized from ethylacetate to furnish (10) as intermediate compound in quantitave yield and then cyclization of these synthesized chalcones have done by catalyst (Onion waste I2) to give substituted flavones (18) (Table 1, Entry 1). Inspired by this result concentration of catalyst was optimized through the above reaction by using different concentrations of Silica.SO3H at 65°C (Table 3, Entry 1-7), reusability was evaluated without loss of activity ((Table 4) and 1.0, 1.5, 2.0, 2.5, 3.0, 3.5 ml (Table 2, Entry 1-6) of onion waste extract at room temperature for 40 min to give the desired products (18). The reaction procedure was performed in absence of catalyst at the same conditions, a low yield is obtained which shows the value of the prescribed catalyst.

Spectral data of some selected compounds

2-(4-hydroxyphenyl)-4H-chromen-4-ones (18): yellow solid. mp: 101–103°C; 1H NMR (400 Hz, $CDCl_3$): 6.52(s, 1H, C_3 -H); 7.21-7.77(m, Ar-H); 7.81-8.53 (m, Ar-H); IR (KBr) cm⁻¹ 3665 (OH), 3031 (C=CH), 1656 (C=O), 1590 (C=C, aromatic), 1089 (C-O-C).

2-(4-chlorophenyl)-4H-chromen-4-ones: Pale yellow solid. mp: 185-187°C; 1H NMR (400 Hz, CDCl₃): 6.71(s, 1H, C₃-H); 7.22-7.76(m, Ar-H); 7.81-8.56(m, Ar-H); IR(KBr)cm–1: 3668 (OH), 3032 (C=CH), 1654 (C=O), 1594 (C=C, aromatic).

2-(4-methylphenyl)-4H-chromen-4-ones: Pale yellow solid. mp: 124-126°C; 1H NMR (400 Hz, CDCl₃): 2.51(s, 3H, CH₃); 6.72(s, 1H, C₃-H); 7.287.77(m, Ar-H); 7.84-8.56(m, Ar-H); IR (KBr) cm–1: 3661 (OH), 3030 (C=CH), 1666 (C=O), 1590 (C=C, aromatic), 1089 (C-O-C).

Plausible mechanism for synthesis of chalcones in presence of Silica.SO3H and cyclization of synthesized chalcones in presence of onion waste.I2

Chalcones can also be synthesized (**Table 1**) in presence of acidic conditions via aldol condensation reaction. The acid catalyst activates the acetophenone and acid catalyst increases



Table 2 Optimization of catalyst (Silica.SO3H) for synthesis of compound10 at 65°C.

Entry	Amount of Catalyst (gm)	Solvent	Time (hours)	Yield (%)
1	0.01	Methanol	4	28
2	0.01	Dichloromethane	6	15
3	0.01	Solvent free	2	28
4	0.02	Methanol	3.4	70
5	0.02	Solvent free	3	72
6	0.05	Methanol	2.5	80
7	0.05	Solvent free	1.2	83

 Table 3 Optimization of Onion waste.I2 for synthesis of compound 18 at room temperature.

Entry	Amount of Catalyst	Time (min)	Yield
1	1.0 ml	60	60
2	1.5 ml	50	78
3	2.0 ml	40	82
4	2.5 ml	40	85
5	3.0 ml	35	80
6	3.5 ml	35	80

Table 4 Reusability of catalyst (Silica.SO3H).

Reuse Cycle	Fresh	First	Second	Third
Time (hours)	1.2	1.2	1.5	2.5
Yield (%)	83	83	76	72

	•		• •		•	
S.No.	Catalyst	Solvent	Temperature (°C)	Time (hours)	Yield (%)	Reference
1	Na2TeO3	DMSO	80	3	15-20	[12]
2	FeCl3/piperidine	Toluene	130	6	60	[13]
3	Iodine	DMSO	130	1.5	74	[14]
4	[bmim]BF4	-	100	45	67	[15]
5	K2CO3	DMF	80	9	54	[16]
6	Br2	CHCl3	120	2.3	72	[17]
7	[EtNH3]NO3	-	MW	40 sec	88	[18]
8	Onion Waste.I2	water	RT	40	85	Present work

Table 5 Comparison of the results of the present methods for synthesis of flavones with the reported methods.



the activity of aldehyde component by formation of carbonium ion. After that the resonance stabilized activated acetophenone attacks on the carbonium ion of benzaldehyde resulting in a new carbon –carbon bond formation to form a intermediate. Then deprotonation takes place to stabilizion of intermediate. After that protonation and dehydration takes place to form desired product. Cyclization of 2-hydroxychalcone by using onion solid waste.12 as a catalyst is given below. Here iodine provides help in oxidative intramolecular cyclization. In first step isomerization forms highly reactive flavylium ion [11-18]. Further water molecules attack on the more reactive 3-position of flavylium ion to form hydroxyl product. Then hydroxyl product immediately oxidized to form flavones (**Scheme 2**).

Comparison of the results of the present methods for the synthesis of pyrazoles with the reported methods

Table 5 indicates the comparison of the activity of different catalysts by considering the yield of the reaction. We observed that the lemon juice give catalytic activity in terms of product yield, solvent and reaction time compared to other catalysts in the literature such as Na₂TeO₃, K_2CO_3 , FeCl₂, [bmim]BF₄, Br₂ and [EtNH₃]NO₃. Onion waste easily available and inexpensive catalyst, which makes this method green and mild. In additrion, above catalyst is a renewable catalyst which follows one of the green chemistry principle regarding the maximum yield of renewable resources.

Conclusion

The present study focused on the importance of biocatalysts in organic synthesis Therefore benefit of green catalysts in organic synthesis is based on benign, safe and cheap biocatalyst. Catalyst based activity is consisting of the appraisal of bio-waste in various organic transformations including the carbon-carbon and carbonoxygen bond formation in various biologically active organic compounds. Hence green chemistry will invade an era of benign design regarding organic synthesis and their mechanisms in near future.

Acknowledgement

We are very thankful to Chaudhary Charan Singh HAU Hisar for providing necessary research facilities and also Sophisticated Analytical Instrumentation Facility, PU Chandigarh for NMR and IR analysis.

Conflict of interest

Authors declare that there is no conflict of interest regarding the publication of this article.

References

- 1 Batra P, Sharma AK (2013) Anti-cancer potential of flavonoids: recent trends and future perspectives. Biotech 3: 439-459.
- Balsubraniyan, KV (2015) Flavonoes as antioxidant. Asian J Chem 8: 399-406.
- 3 Spagnuolo C, Moccia S, Russo GL (2018) Anti-inflammatory effects of flavonoids in neurodegenerative disorders. Eur J Med Chem 153: 105-115.
- 4 Brahmchari G (2011) Bio-flovonoids with promosing anti-diabetic potentials: A crucial survey. Opportunity, Challenge and Scope of Natural products in Medicinal Chemistry 187-212.
- 5 Ye Q, Ma X, Hu C, Lin B, Xu B, et al. (2015) Osteoporotic activity and constituents of Podocarpium podocapum. Phytomedicine 22: 94-102.
- 6 Muthukrishnan M, Patil S, More V, Joshi A (2005) Synthetic approach of flavones. Mendeleev Communications 15: 100.
- 7 Li J, Corey EJ (2005) Name reactions in hetrocyclic chemistry. John Wiley and Sons, New York.
- 8 Barto D, Ollis W (1979) The synthesis and reactions of organic compounds. Comprehensive of organic chemistry.
- 9 Keri RS, Hosamani KM, Reddy HRS (2009) A Solvent-Free synthesis of Coumarins Using Phosphotungstic Acid as Catalyst. 131: 321-327.
- 10 Boumendjel (2004) Aurones: a subclass of flavones with promising biological potential. Current Medicinal Chemistry 10: 2621-2623.

- 11 Fichner C, Remennikov G, Mayr H (2001) Kinetics of the Reactions of Flavylium ions with π -Nucleophiles. Eur J Org Chem 23: 4451-4456.
- 12 Kumar S, Sharma D (2011) Oxidative Cyclisation of 2'-Hydroxychalcones using Sodium Tellurite: Synthesis of Flavones. Orient J Chem 27: 761-763.
- 13 Maiti M, Karmakar R, Bhattacharya RN, Kayal K (2011) A novel one pot route to flavones under dual catalysis, an organo- and a Lewis acid catalyst. Tetrahedron Lett 52: 5610-5612.
- 14 Lokhande PD, Sakate SS, Taksande KN, Navghare B (2005) Dimethylsulfoxide— iodine catalysed deprotection of 2'-allyloxychalcones: synthesis of flavones. Tetrahedron Lett 46: 1573-1574.
- 15 Bhosalea RS, Sarda SR, Girama RP, Rauta DS, Parwea SP, et al. (2009) Ionic liquid: Efficient solvent for synthesis of flavones from dione. J Iran Chem Soc 6: 512-519.
- 16 Jie Z, Yufen Z, Hua F (2012) K2CO3-Catalyzed Synthesis of Chromones and 4- Quinolones through the Cleavage of Aromatic C–O Bonds. Organic Lett 14: 2710-2713.
- 17 Garg S, Ishar MPS, Sarin R, Gandhi RP (1994) Photochemical transformations in 1- (O-Hydroxyaryl)-1,3-diketones Indian J Chem 33B: 1123-1128.
- 18 Sarda SR, Pathan MY, Paike VV, Pachmase PR, Jadhav WN, et al. (2006) A facile synthesis of flavones using recyclable ionic liquid under microwave irradiation. ARKIVOC (Archive for Organic Chemistry) 16: 43-48.