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Green and cost effective protocol for the synthesis of 1,8-dioxo-octahydroxanthenes and 1,8-dioxo-decahydroacridines by using sawdust sulphonic acid

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Abstract A heterogeneous solid acid catalyst has been prepared by covalent grafting of chlorosulphonic acid on the surface of sawdust (SD-OSO_3H). The structure of the prepared catalyst was assessed by FT-IR, solid state CP/MAS ^{13}C-NMR spectroscopy, field emission scanning electron microscopy and energy dispersive X-ray. The catalytic performance of the solid acid catalyst has been evaluated in the synthesis of 1,8-dioxo-octahydroxanthenes and 1,8-dioxo-decahydroacridines. High conversion, shorter reaction time, cleaner reaction profile, environmentally benign solvent, simple experimental and work-up procedure, and reusability of catalyst are the striking features of our synthetic route.

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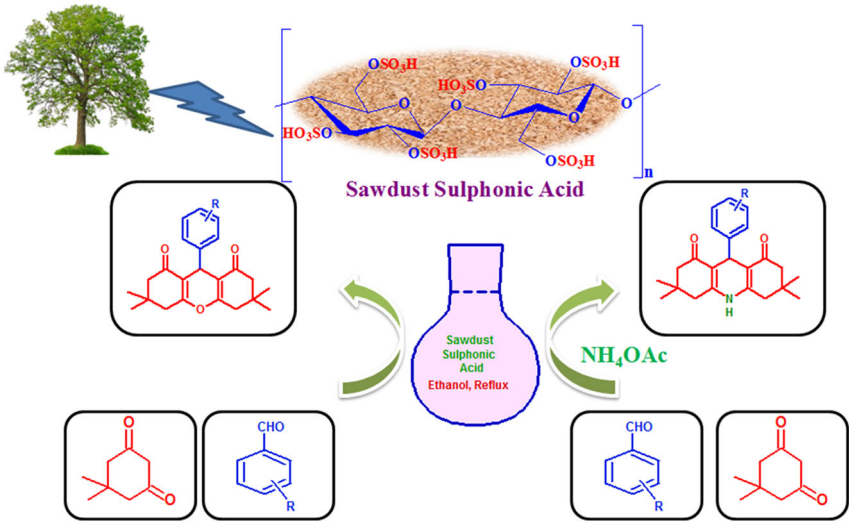
Graphical Abstract



Keywords Biomass · Renewable bioresources · Sawdust sulphonic acid · Green protocol

Introduction

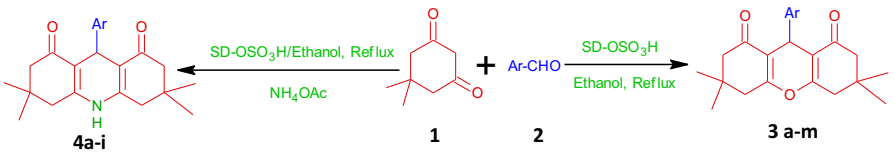
The heterogeneous solid acid catalysts have received captivating attention from both environmental and economical points of view [1, 2]. The unique attributes of heterogeneous solid acid catalysts such as a non-toxic nature, exceptional air stability, low cost, easy availability, immiscibility with common organic solvents, exceptional catalytic performance and facile recyclability makes the process simple and eco-friendly [3–6]. The recent quest towards the sustainable development has spurred considerable interest in employing renewable bioresources as a support material in heterogeneous catalytic technology [7]. In this regard, biomass represents the most promising renewable bioresource that has been already employed as a precursor to synthesize fuels, value added chemicals and useful materials [8]. Further, the functional structure of biomass provides the opportunities to generate different functionalities [9]. Cellulose, a linear polysaccharide made up of β-D-glucose units linked by 1,4 glycosidic bonds, is the most abundant organic biopolymer on the earth which is derived from biomass [10, 11]. Owing to its easy availability and a wide range of beneficial physical and chemical properties, cellulose has become the most common sustainable feedstock to produce materials for catalytic applications [12–14]. In the recent years, sporadic strides have been made to employ various natural sources of cellulose instead of refined cellulose [15]. Sawdust is a natural, renewable, biodegradable and easily available natural

source of cellulose obtained from wood as a waste by-product. Owing to hydrophilic nature, it is widely used as a promising adsorbent for removing heavy metals, acidic and basic dyes, and other unwanted materials from waste water [16, 17]. The unique accredit of sawdust is that it contains cellulose, hemicelluloses and lignin which include a wide variety of hydroxyl groups that can be used as active sites for the preparation of heterogeneous catalysts. Recently, functionalized sawdust in the form of sulphonated sawdust (SD-OSO_3H) has been employed as an excellent heterogeneous Bronsted acid catalyst for mediating significant organic transformations [18–20]. However, despite impressive catalytic potential, its utility in synthetic chemistry is not fully exploited. This spurred us to investigate the compatibility of sawdust sulphonic acid as a catalyst in the synthesis of biological relevant heterocyclic scaffolds.

Xanthene derivatives are privileged heterocyclic motifs possessing a highly reactive inbuilt pyran ring. They are key intermediates in number of natural products as well as important synthons in synthetic organic chemistry [21]. They have garnered increasing attention because of their potential applications in biological and pharmacological regions [22–24]. Furthermore, this structural motif is also used as a corrosion inhibitor [25], in photodynamic therapy [26], laser technologies [27], fluorescent materials for the visualization of biomolecules [28] as well as selective positive allosteric modulators of metabotropic glutamate receptors [29]. Owing to their unique biological profile, numerous methodologies have been developed for the synthesis of 1,8-dioxo-octahydroxanthenes [30–44]. The most popular method involves the reaction between dimedone and aryl aldehydes. A wide array of catalysts has been reported to catalyze this transformation. However, many of the reported protocols are, although efficient, a few of them suffer from the drawbacks of tedious preparation of the catalyst, high reaction temperature, longer reaction time, low yields, excess use of reagents as well as toxic or expensive catalysts. This spurred us to develop an efficient, green and easily adaptable protocol for the synthesis of 1,8-dioxo-octahydroxanthenes.

Acridindiones are the polyfunctionalized and symmetrical derivatives of 1,4-dihydropyridines (1,4-DHPs) which represent a significant class of aza-heterocyclic compounds having potential biological and pharmacological applications [45–49]. In addition, they are also employed as excellent building blocks for the synthesis of antitubercular agents [50] and also serve as potential drug candidates for the treatment of congestive heart failure [51]. The most common approach for the synthesis of 1,8-dioxo-decahydroacridines involves the reaction of dimedone and NH_4OAc with aromatic aldehydes. A plethora of catalysts have been reported to catalyze this transformation [52–58]. However, there is a still scope for improvement, especially towards developing a facile protocol using robust heterogeneous catalyst.

In continuation of our research work in the development of sustainable methodologies for the bioactive heterocycles [59–61], we report herein an efficient strategy for the synthesis of 1,8-dioxo-octahydroxanthenes and 1,8-dioxo-decahydroacridines using sawdust sulphonic acid as a reusable heterogeneous acid catalyst (Scheme 1).



Scheme 1 Sawdust sulphonic acid catalyzed one-pot synthesis of 1,8-dioxo-octahydroxanthenes and 1,8-dioxo-decahydroacridines

Experimental

Dimedone (Thomas Baker), chlorosulphonic acid (Spectrochem) and aldehydes (Spectrochem and Thomas Baker) were used as received. The NMR spectra were recorded on a Bruker AC (300 MHz for ^{1}H NMR and 75 MHz for ^{13}C NMR) spectrometer using TMS as an internal standard in $CDCl_3$. Chemical shifts (δ) are expressed in ppm. Solid state CP/MAS ^{13}C-NMR spectra were recorded on JEOL-ECX400 spectrometer under prescribed operating conditions. The mass spectra were recorded on a Shimadzu QP2010 gas chromatograph mass spectrometer. The FT-IR spectra were measured on a Bruker ALPHA FT-IR spectrometer in between the frequency range 500–4000 cm^{-1}. The size and morphology of pristine sawdust and sawdust sulphonic acid were observed by using a FE-SEM of MIRA3 TESCAN microscope with an accelerating voltage of 10 kV.

General procedure for synthesis of 1,8-dioxo-octahydroxanthenes

A mixture of dimedone (2 mmol), aromatic aldehyde (1 mmol) and sawdust sulphonic acid (0.05 g) was refluxed in ethanol (3 mL). After completion of reaction as indicated by thin layer chromatography (TLC), the reaction mixture was diluted with hot ethanol (5 mL) and filtered to remove the catalyst. After evaporation of solvent in *vacuo,* the crude product was recrystallized from ethanol to afford the desired 1,8-dioxo-octahydroxanthenes.

General procedure for synthesis of 1,8-dioxo-decahydroacridines

To the well-stirred mixture of benzaldehyde (1 mmol) and sawdust sulphonic acid (0.05 g) in ethanol (3 mL), dimedone (2 mmol) and NH_4OAc (1.5 mmol) were added, and the resultant reaction mixture was refluxed for an appropriate time. After completion of reaction (monitored by TLC), the reaction mixture was diluted with hot ethanol (5 mL) and filtered to remove the catalyst. After evaporation of solvent in *vacuo,* the crude product was recrystallized from ethanol to afford corresponding 1,8-dioxo-decahydroacridines.

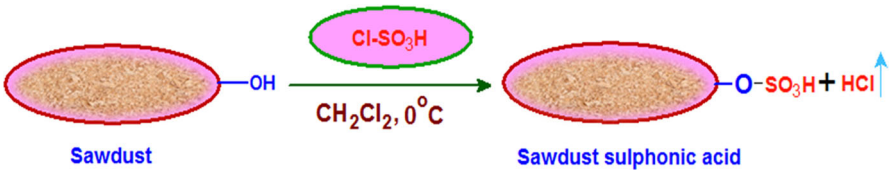


Fig. 1 Preparation of sawdust sulphonic acid

Result and discussion

Our initial strides began with the preparation of sawdust sulphonic acid by adopting the literature procedure [19]. In general, sawdust obtained from the local timber industry was washed with a copious amount of distilled water to remove the adhered surface impurities and dried at 60 °C for 24 h. The dried sawdust was finely pulverized and passed through 1 mm sieve to get fine powder. The sulphonic acid groups were introduced with the help of hydroxyl groups in sawdust by reacting with chlorosulfonic acid in dichloromethane at 0 °C. The product obtained was filtered, washed with diethyl ether, dried and further pulverized to get the desired sawdust sulphonic acid as fine powder (Fig. 1).

Sawdust sulphonic acid was characterized on the basis of FT-IR, solid state ^{13}C CP-MAS, FE-SEM and EDX techniques. In the FT-IR spectrum (Fig. 2), cellulose and hemicellulose units are present in sawdust sulphonic acid displaying C–H stretching vibrations at 2940 and 2891 cm^{-1} while the phenyl ring of lignin showed C=C stretching peaks at 1660 and 1625 cm^{-1}. In addition, the FT-IR spectrum also displayed characteristic peaks at 3327 cm^{-1} (OH stretching of SO_3H), 1157,

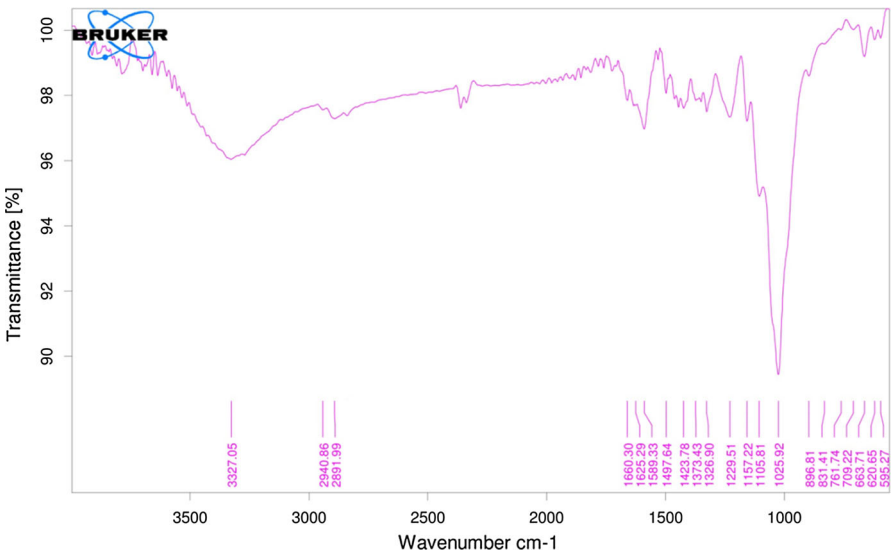


Fig. 2 The FT-IR spectrum of sawdust sulphonic acid

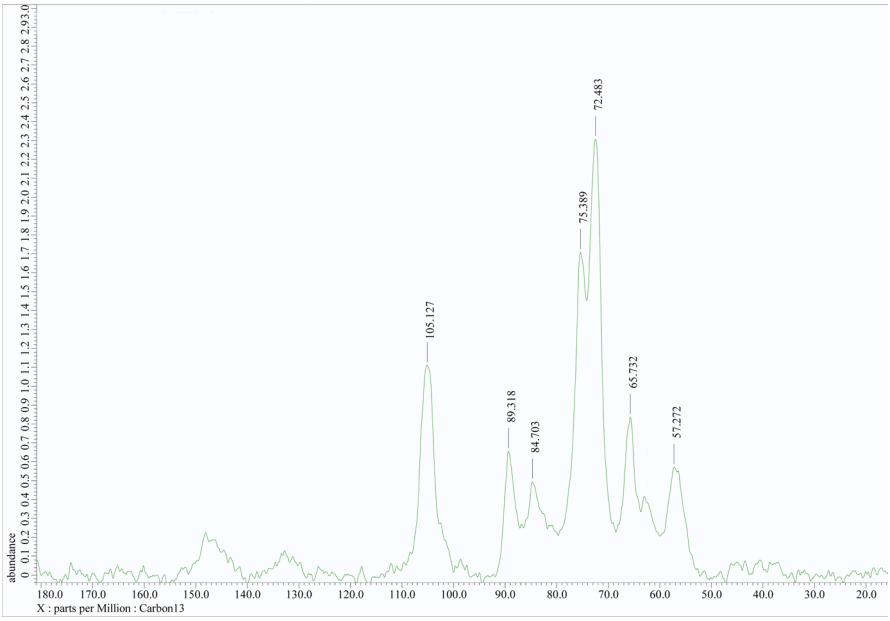


Fig. 3 Solid state CP-MAS ^{13}C-NMR spectrum of sawdust sulphonic acid

1025 cm^{-1} (asymmetric and symmetric stretching of SO_2), 896 cm^{-1} (S–OH bending) and 663 cm^{-1} (S–O symmetric stretching) indicating the successful grafting of sulphonic acid in the matrix of sawdust.

The solid state ^{13}C CP-MAS spectrum (Fig. 3) of sawdust sulphonic acid displayed peaks at 105.12 (bs, cellulose-C_1), 89.32 (bs, cellulose-C_4), 72.48–75.38 (m, cellulose-C_2, C_3, C_5), 65.73 (bs, cellulose-C_6) which is in concordance with the proposed catalyst.

The elemental mapping of pristine sawdust and sawdust sulphonic acid was done by using energy dispersive X-ray (EDX) analysis. The EDX analysis of sawdust (Fig. 4a) revealed carbon and oxygen as the major elements while that of sawdust sulphonic acid recognized the peaks for carbon, oxygen and sulfur as shown in Fig. 4b. The presence of sulfur in its respective energy position at 2.30 keV also

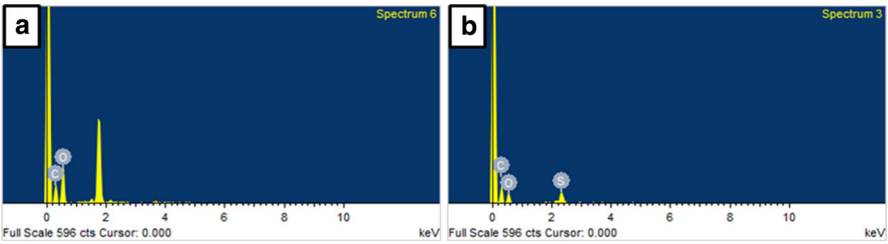


Fig. 4 EDX: **a** pristine sawdust; **b** sawdust sulphonic acid

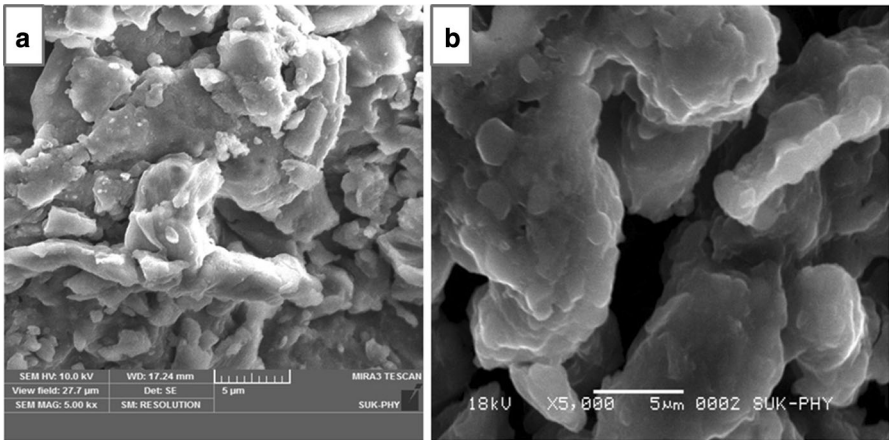


Fig. 5 SEM images: **a** pristine sawdust; **b** sawdust sulphonic acid

supports the formation of sawdust sulphonic acid. The loading of SO_3H as determined by EDX was found to be 0.123 mmol/g of sawdust.

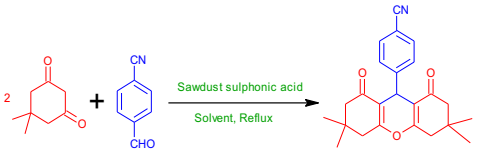
The surface morphology of pristine sawdust and sawdust sulphonic acid was studied by scanning electron microscopy (SEM). The SEM images (Fig. 5a, b) clearly indicate irregular morphology having a particle size in the micrometer range. The sawdust sulphonic acid (Fig. 5b) exhibits smooth and uniform particles with sufficient voids having a shape mimicking pristine sawdust.

The acidic sites on sawdust sulphonic acid were quantified by the ion exchange method and were found to be 1.88 mmol H^+/g of catalyst [62].

Initially, the catalytic potential of sawdust sulphonic acid has been screened for the synthesis of 1,8-dioxo-octahydroxanthenes. In this regard, the dimedone and 4-cyanobenzaldehyde were chosen as model substrates for optimization of reaction conditions. In order to optimize the solvent, a model reaction in the presence of sawdust sulphonic acid (0.05 g) was carried out in various organic solvents at different temperature conditions (Table 1). High yield was achieved in the presence of ethanol under reflux conditions (Table 1, entry 11). Since, it is relatively safe and can be used to dissolve many organic compounds. Unfortunately, the model reaction afforded lower yields of desired product in toluene, chloroform, dichloromethane, acetonitrile, EDC, THF, DMF, and acetone (Table 2, entries 1–8). Furthermore, use of n-propanol gave the desired product in moderate yield (Table 2, entry 9). On the contrary, the reaction gave the desired product in trace amount in *n*-butanol (Table 2, entry 10).

Furthermore, in order to optimize the catalyst loading, the model reaction was carried using different quantities of sawdust sulphonic acid (Table 2). It was observed that the optimum amount of catalyst turns out to be 0.05 g in order to obtain the best result (Table 2, entry 5). However, a catalyst quantity lower than 0.05 g did not lead to quantitative yield of the product (Table 2, entries 1–4). Furthermore, an increase in catalyst quantity beyond 0.05 g did not increase the yield of product significantly (Table 2, entry 6).

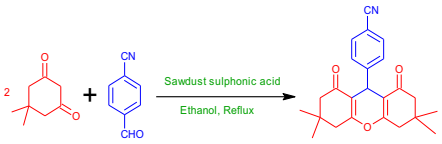
Table 1 Solvent optimization in the synthesis of 1,8-dioxo-octahydroxanthenes



Entry	Reaction condition	Reaction time (min)	Isolated yield (%)
1	Toluene/Reflux	30	25
2	Chloroform/Reflux	30	28
3	DCM/Reflux	30	30
4	Acetonitrile/Reflux	30	33
5	EDC/Reflux	30	35
6	THF/Reflux	30	37
7	DMF/Reflux	30	43
8	Acetone/Reflux	30	58
9	*n*-propanol/Reflux	30	53
10	*n*-butanol/Reflux	30	Trace
11	Ethanol/Reflux	30	92

Reaction conditions: Dimedone (2 mmol), 4-cyanobenzaldehyde (1 mmol) and sawdust sulphonic acid (0.05 g, 0.0061 mmol) in solvent (3 mL) at given condition

Table 2 Catalyst loading studies in the synthesis of 1,8-dioxo-octahydroxanthenes

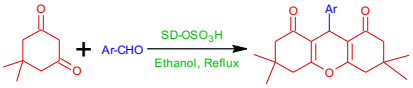


Entry	Catalyst amount (g)	Reaction time (min)	Isolated yield (%)
1	0.01	30	59
2	0.02	30	62
3	0.03	30	70
4	0.04	30	85
5	0.05	30	92
6	0.10	30	93

Reaction conditions: Dimedone (2 mmol), 4-cyanobenzaldehyde (1 mmol) and catalyst in ethanol (3 mL) at reflux condition

To explore the scope of the present protocol, several structurally diverse aldehydes were treated with dimedone under optimized reaction conditions, and the results are summarized in Table 3. In all the cases, reaction proceeded smoothly, affording corresponding 1,8-dioxo-octahydroxanthenes as the sole products and no anomalies like tetraketones were noted [63]. The aromatic aldehydes bearing electron-donating as well as electron-withdrawing substituents reacted efficiently

Table 3 Sawdust sulphonic acid catalyzed synthesis of 1,8-dioxo-octahydroxanthenes from dimedone and aryl aldehydes



Entries	Aryl aldehyde (2)	Product (3)	Time (min)	Yield (%)[a]	Mp (°C)
1	Benzaldehyde	**3a**	50	88	200–202
2	4-Cyanobenzaldehyde	**3b**	30	92	218–222
3	4-Chlorobenzaldehyde	**3c**	45	82	230–233
4	4-Bromobenzaldehyde	**3d**	50	85	238–240
5	4-Nitrobenzaldehyde	**3e**	35	90	226–230
6	4-Hydroxybenzaldehyde	**3f**	55	88	249–252
7	4-Methylbenzaldehyde	**3g**	50	88	217–220
8	4-Methoxybenzaldehyde	**3h**	45	83	246–248
9	3-Methoxybenzaldehyde	**3i**	50	80	160–162
10	2-Nitrobenzaldehyde	**3j**	40	86	248–251
11	2,5-Dimethoxybenzaldehyde	**3k**	50	80	171–173
12	3,4,5-Trimethoxybenzaldehyde	**3l**	55	81	206–208
13	Thiophene-2-carboxaldehyde	**3m**	55	82	162–165

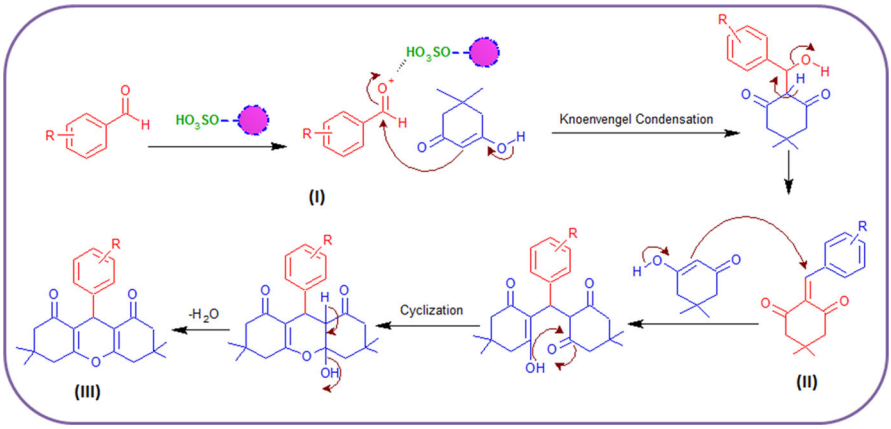
Reaction conditions: Dimedone (2 mmol), aryl aldehyde (1 mmol) and sawdust sulphonic acid in ethanol (3 mL) at reflux condition

[a] Isolated yield

forming 1,8-dioxo-octahydroxanthenes in good to excellent yields (80–92%) highlighting general applicability of the protocol (Table 3, entries 2–5 and 6–9). Remarkably, good yields (80–86%) were obtained with the sterically hindered aldehydes such as 2-nitrobenzaldehyde and 2,5-dimethoxybenzaldehyde under the optimized reaction condition (Table 3, entries 10–11). Interestingly, highly substituted aromatic aldehyde such as 3,4,5-trimethoxybenzaldehyde (Table 3, entry 12) was also well tolerated furnishing comparatively moderate yield (81%) of the desired product. Fascinatingly, hetero-aromatic aldehyde like thiophene-2-carbaldehyde (Table 3, entries 13) was found to be equally effective furnishing the anticipated product in good yields (82%).

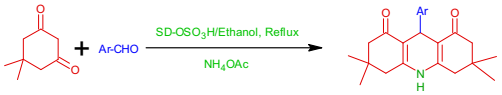
The tentative mechanism for sawdust sulphonic acid catalyzed synthesis of 1,8-dioxo-octahydroxanthenes is outlined in Scheme 2. Initially, sawdust sulphonic acid protonated aryl aldehyde (**I**) and undergoes facile knoenvengel condensation with dimedone to form intermediate (**II**). Next, Michael addition of another dimedone molecule on (**II**) forms intermediate (**III**) which on further cyclodehydration furnishes the desired 1,8-dioxo-octahydroxanthenes.

The hot filtration test was carried out to validate the heterogeneous nature of sawdust sulphonic acid. After the 50% completion (GC) of the model reaction of 1,8-dioxo-octahydroxanthenes, catalyst was removed from the reaction mixture by simple filtration and the filtrate was refluxed for an additional 1 h. The reaction did not push forward beyond 50% of product yield. This clearly indicates that during the



Scheme 2 Plausible mechanistic pathway for the formation of 1,8-dioxo-octahydroxanthenes

Table 4 Sawdust sulphonic acid catalyzed synthesis of 1,8-dioxo-decahydroacridines



Entry	Aryl aldehyde (2)	Product (4)	Time (min)	Yield (%)[a]	Mp (°C)
1	Benzaldehyde	**4a**	50	88	190–192
2	4-Cyanobenzaldehyde	**4b**	30	92	>300
3	4-Chlorobenzaldehyde	**4c**	45	82	297–299
4	4-Bromobenzaldehyde	**4d**	50	85	241–243
5	4-Nitrobenzaldehyde	**4e**	35	90	283–285
6	4-Hydroxybenzaldehyde	**4f**	55	88	>300
7	4-Methylbenzaldehyde	**4g**	50	86	>300
8	4-Methoxybenzaldehyde	**4h**	45	83	298–300
9	3,4,5-Trimethoxybenzaldehyde	**4i**	55	81	260–262

Reaction conditions: Dimedone (2 mmol), aryl aldehyde (1 mmol), NH_4OAc (1.5 mmol) and sawdust sulphonic acid in ethanol (3 mL) at reflux condition

[a] Isolated yield

course of reaction, SO_3H units are held firmly to the cellulosic matrix of sawdust and are not being leached out. This confirms that catalytic process takes place exclusively under heterogeneous conditions.

In order to expand the scope of protocol, the reactions of dimedone, and NH_4OAc with different aldehydes for the synthesis 1,8-dioxo-decahydroacridine derivatives were undertaken in the presence of sawdust sulphonic acid (0.05 g) and the results are shown in Table 4. The aromatic aldehydes having electron-poor as well as electron-rich groups form corresponding 1,8-dioxo-decahydroacridines in good to

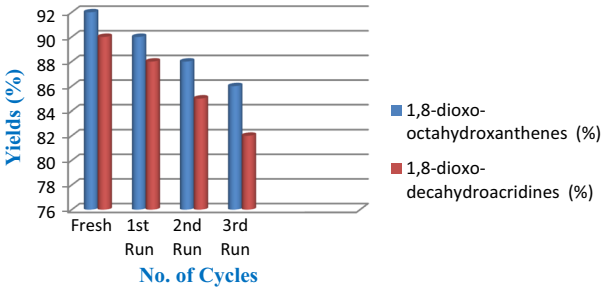


Fig. 6 Reusability of sawdust sulphonic acid in synthesis of 1,8-dioxo-octahydroxanthenes and 1,8-dioxo-decahydroacridines

Table 5 Comparison of the efficiency of sawdust sulphonic acid with reported catalysts for the synthesis of 1,8-dioxo-octahydroxanthenes and 1,8-dioxo-decahydroacridines[a]

Entry	Catalyst used	Reaction condition	1,8-dioxo-octahydroxanthenes		1,8-dioxo-decahydroacridines		Ref.
			Time	Yield (%)	Time	Yield (%)	
1	Sawdust Sulphonic acid (0.05 g)	Ethanol/ Reflux	50 min	88	55 min	90	This work
2	$SmCl_3$ (20 mol %)	Solvent-free/ 120 °C	9 h	98	–	–	[39]
3	Montmorillonite K-10 (0.3 g)	Solvent-free/ 100 °C	2 h	82	–	–	[42]
4	$HClO_4$–SiO_2 (0.05 g)	Solvent-free/ 140 °C	3 h	32	–	–	[43]
5	Cellulose Sulphonic acid (0.05 g)	Solvent-free/ 110 °C	6 h	95	–	–	[64]
6	KH_2PO_4 (5 mol %)	Ethanol:water/ 120 °C	–	–	5 h	94	[55]
7	Saccharose (20 mol %)	Solvent-free/ 80 °C	–	–	35 min	77	[56]
8	Silica bonded *N*-propyl sulfamic acid (0.03 g)	Ethanol/ Reflux	–	–	2 h	86	[57]
9	$[Et_3NH][HSO_4]$ (10 mol %)	Solvent-free/ 110 °C	–	–	20 min	88	[58]

[a] Based on benzaldehyde

excellent yield highlighting general applicability of the present protocol (Table 4, entries 2–8). Interestingly, good yields were obtained with the sterically hindered aldehyde such as 3,4,5-trimethoxybenzaldehyde under the optimized reaction conditions (Table 4, entry 9).

The reusability of catalyst is an important attribute from the perspective of green chemistry. The reusability sawdust sulphonic acid was investigated for synthesis of **3a** and **4a** under an optimized reaction condition (Fig. 6). The catalyst was easily recovered from the reaction mixture by simple filtration and reused for three times without significant decrease in the yield of the desired product. The slight decrease in the observed yield is attributed to inadequate recovery of the catalyst due to the attrition during filtration.

In order to show the advantage of sawdust sulphonic acid in comparison with other reported catalysts, we have summarized some of the previous reports for the preparation of 1,8-dioxo-octahydroxanthenes and 1,8-dioxo-decahydroacridines (Table 5). The comparison of results clearly proves that sawdust sulphonic acid is a highly effective catalyst in terms of reaction time and yield than other reported catalysts.

Conclusions

In summary, we have reported a highly efficient and cost-effective approach for the synthesis of 1,8-dioxo-octahydroxanthenes and 1,8-dioxo-decahydroacridines in the presence of environmentally benign sawdust sulphonic acid as a catalyst. The advantages of the present protocol includes high yields, short reaction time, eco-friendly solvent, cleaner reaction profile, operational simplicity, ease of preparation of the catalyst and facile reusability.

Supporting Information

A supplementary material which includes some of the scan copies of FT-IR, ^{1}H-NMR, ^{13}C-NMR and Mass analysis for this article can be accessed on the publisher's website.

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