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Synthesis of Substituted Coumarins Catalyzed by Sawdust-SO_3H. An Efficient and Environmentally Benign Solid Acid Catalyst under Solvent-Free Conditions[1]

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Abstract—The sulfonated sawdust (SD-SO_3H) was easily prepared by treatment of sawdust, a biomass waste material, with chlorosulfonic acid and characterized by elemental analysis, SEM and TGA. The bio-degradable solid acid catalyst has been applied to the Pechmann condensation reaction of phenols with β-ketoesters for the synthesis of coumarin derivatives under solvent-free conditions. This environmentally benign and inexpensive method has such advantages as simplicity in operation, high yields, low catalyst loading and short reaction time. The catalyst can be efficiently recycled with insignificant loss of activity.

Keywords: coumarin, sawdust-SO_3H, Pechmann condensation, solvent free conditions, recyclable catalyst

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INTRODUCTION

Coumarins are important oxygen containing fused heterocyclic compounds found in nature that have been used in food and cosmetic industry [1] and possess biological activities such as antitumor [2], antimicrobial [3] and anticancer [4]. There are several methods of their synthesis such as Perkin [5], Knoevenagel [6, 7], Reformatsky [8], Pechmann [9], and Wittig [10] reactions that involve acidic as well as basic catalysts. However, the Pechmann condensation is one of the simplest and most popular procedures for synthesis of coumarins due. It involves the reaction of phenols with β-ketoesters that leads to 4-substituted coumarins. In a typical procedure the mineral acids such as sulfuric [11], polyphosphoric [12], and Lewis ($InCl_3$ [13], $ZrCl_4$ [14]) were used as catalysts. In the Pechmann condensation a number of solid acids have been used including Alumina sulfuric acid (ASA) [15], Nafion-H [16], poly(4-vinylpyridinium)hydrogen sulfate [17], H_2SO_4/silica gel [18], Amberlyst-15 [19], succinimide-*N*-sulfonic acid [20], montmorillonite clay [21], melamine trisulfonic acid [22], zeolite H-BEA [23], modified zirconia [24], and most recently $In(OTf)_3$ [25]. Although the above methods are suitable for certain synthetic applications, some of the procedures are associated with certain disadvantages such as high cost, involvement of corrosive reagents and long reaction time.

The lignocellulose waste material such as wood sawdust, a waste by-product of the timber industry, is one of the most abundant materials in the world that has low or no economic value as it is. It contains cellulose, hemicelluloses and lignin that have big number of available reactive functional groups: hydroxyl, phenolic and carboxylic.

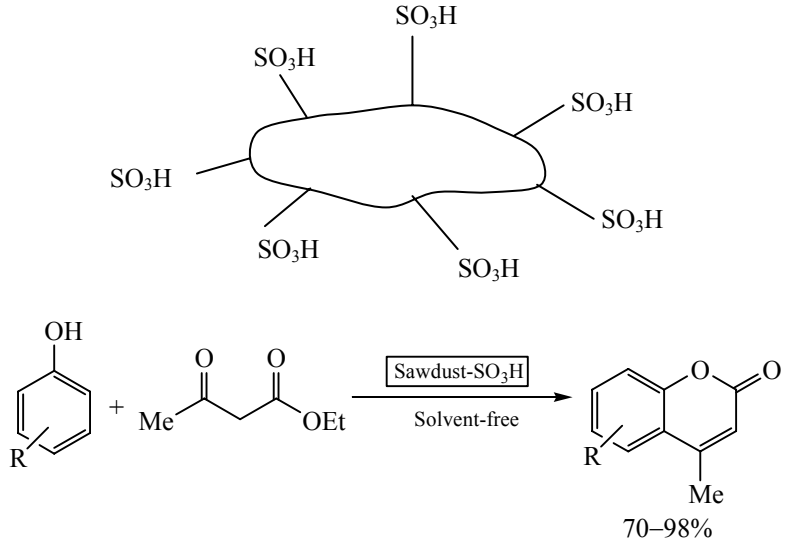
As the development of our earlier studies on modified sawdust [26, 27] we report here an efficient and simple procedure for the preparation of substituted coumarins via the Pechmann condensation using sawdust sulfonic acid under solvent free conditions (Scheme 1). The sulfonated sawdust (SD-SO_3H) can be easily prepared by treatment of sawdust with chlorosulfonic acid.

RESULTS AND DISCUSSION

The product of the sawdust-SO_3H treatment by chlorosulfonic acid was characterized by SEM, TGA and elemental analysis. The total acid site of SD–SO_3H was 4.8 mmol/g as determined by titration (NaOH).

[1] The text was submitted by the authors in English.

Scheme 1. Synthesis of coumarins catalyzed by SD-SO_3H under solvent-free conditions.



Elemental analysis indicated high sulfur content (6.0 mmol/g). According to the above methods data most of sulfur containing species on the surface of samples were in the form of SO_3H.

The catalytic performance of SD-SO_3H in the Pechmann condensation of coumarins was tested initially in the reaction of α-naphtol **1** with ethyl acetoacetate **2** (Table 1) for optimization of the process conditions. The most efficient amount of SD-SO_3H that led to 72% yield was 0.05 g.

The following reaction was carried out with the optimum amount of the catalyst in various solvents and at different temperatures. The reaction proceeded efficiently under solvent-free conditions (Table 2, entry 1). The processes carried out in the media of $CHCl_3$, CH_3CN or CH_2Cl_2 did not give high yields (Table 2, entries 2–4), while some solvents demonstrated no inefficiency (Table 2, entries 5–7). It was determined that the condensation of α-naphtol **1** with ethyl acetoacetate **2** proceeded the most efficient way under solvent free conditions, catalysis by SD-SO_3H (0.05 g) at 110°C (Table 2, entry 9). Similar conditions were applied to various phenols with ethyl acetoacetate and led to good or high yields of the corresponding coumarins (Table 3, compounds **3a–3j**).

The plausible mechanism of formation of 7-hydroxy-4-methylcoumarin (**3a**) consists of activation of

Table 1. Influence of SD-SO_3H catalyst concentration on the yield of product **3i**[a]

Entry	Catalyst, g	*T*, ºC	Time, min	Yield, %
1	–	90	120	0
2	0.025	90	120	40
3	0.05	90	75	72
4	0.075	90	120	70
5	0.1	90	120	60
6	0.15	90	120	60

[a] Solvent-free reaction of α-naphtol (1 mmol) with ethyl acetoacetate (1 mmol).

Table 2. Effect of solvents and temperature on the synthesis of product **3i**[a]

Entry	Solvent	*T*, ºC	Time, min	Yield, %
1	–	90	75	72
2	$CHCl_3$	Reflux	200	35
3	CH_3CN	Reflux	200	10
4	CH_2Cl_2	Reflux	200	20
5	THF	Reflux	200	0
6	MeOH	Reflux	200	0
7	H_2O	Reflux	200	0
8	–	70	120	70
9	–	110	25	91
10	–	130	25	92

[a] Reaction of α-naphtol (1 mmol) with ethyl acetoacetate (1 mmol). The catalyst amount: 0.05 g.

Table 3. Coumarins and their synthesis data. Reaction conditions: solvent-free and SD-SO_3H catalysis at 110ºC

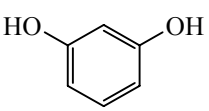
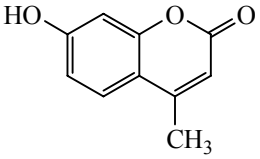
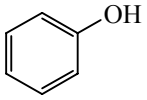
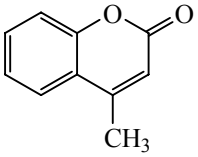
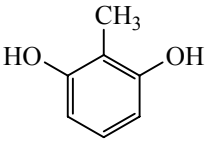
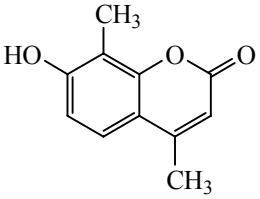
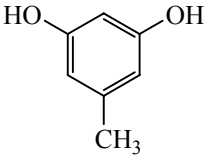
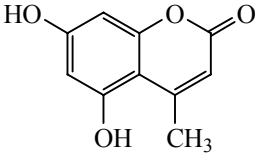
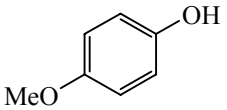
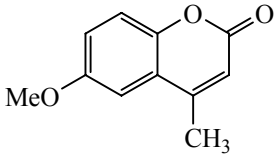
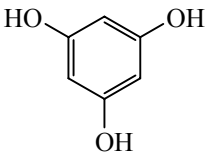
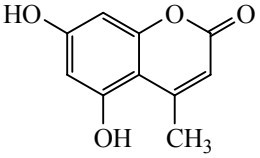
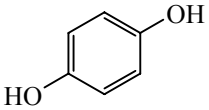
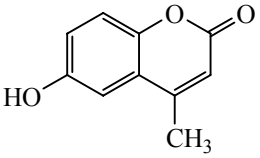
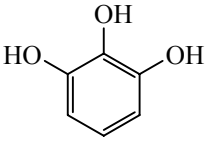
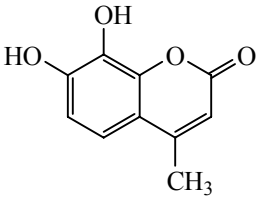
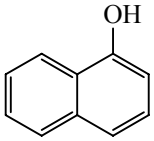
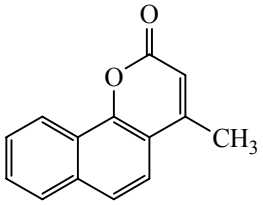
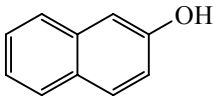
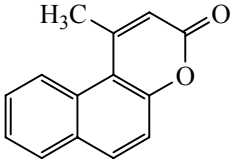
Comp. no.	Phenol	Product	Time, min	Yield, %[a]	mp, ºC
3a			9	98	185–187 186–187 [28]
3b			65	70	82–84 83–84 [29]
3c			6	95	259–264 264 [30]
3d			10	94	257–259 257–258 [31]
3e			25	91	165–167 165 [32]
3f			15	92	283–284 280–283 [33]
3g			20	90	239–240 241–242 [34]
3h			25	87	245–247 254–255 [35]
3i			25	91	154–155 153–155 [36]

Table 3. (Contd.)

Comp. no.	Phenol	Product	Time, min	Yield, %[a]	mp, ºC
3j			25	88	184–187 183–184 [29]

[a] Yields upon recrystallization.

the carbonyl group of ethyl acetoacetate by the Brønsted acid sites of the catalyst (SD-SO_3H) leading to the formation of **1**. The nucleophilic attack of **1** by resorcinol gives the intermediate **2** which rapidly undergoes cyclization via intramolecular condensation forming **3a** via the Pechmann condensation (Scheme 2).

Comparison of catalytic activity of SD-SO_3H with several other catalysts in the synthesis of 7-hydroxy-4-methyl coumarin **3a** via the Pechmann condensation (Table 4) exhibited some technological and economical advantages of the former system.

According to our study of SD-SO_3H in the reaction of α-naphtol with ethyl acetoacetate at 110ºC the catalyst can be recycled and used efficiently in three and more cycles. Upon completing the model reaction the catalyst was filtered off, washed with dichloromethane and reused after drying at 50ºC for 4 h. The fresh SD-SO_3H catalyst led to the yield 91% of the product **3i**, upon recovery the catalyst gave the yields of 89, 87, and 87% respectively in three subsequent cycles.

EXPERIMENTAL

All chemicals were commercially available and used without further purification. The reactions were monitored by TLC and the yields refer to the isolated

Scheme 2. The plausible mechanism of formation of 7-hydroxy-4-methylcoumarin **3a**.

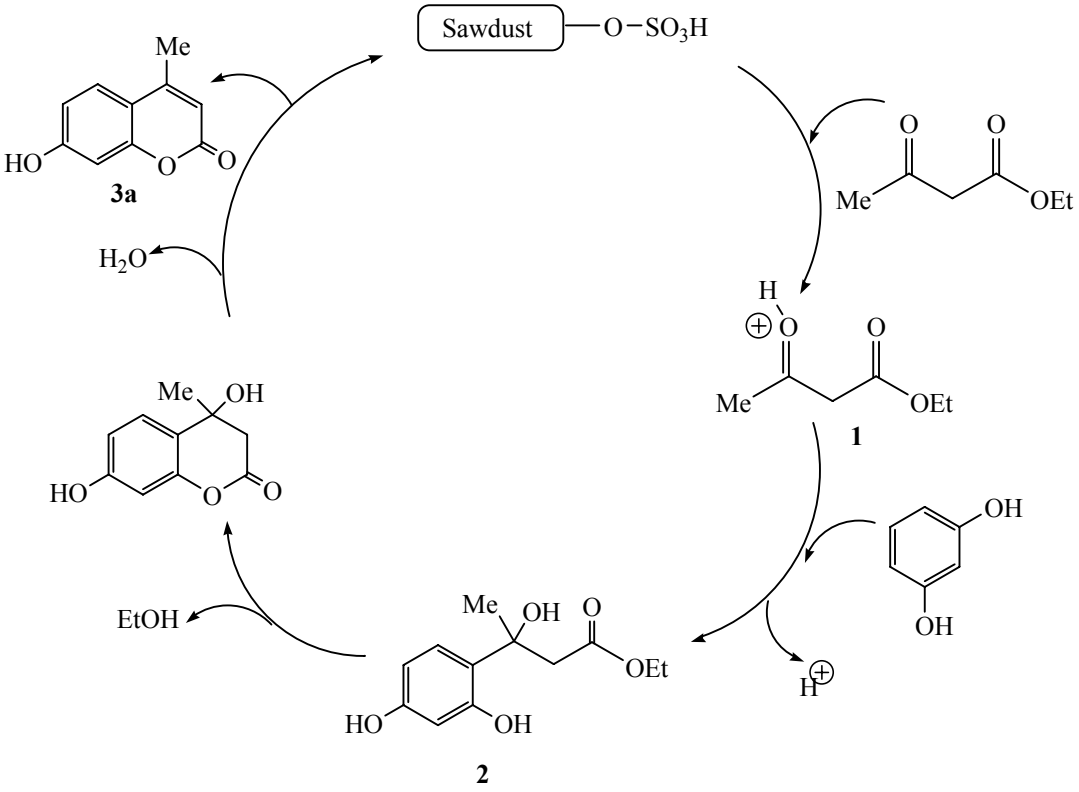


Table 4. Comparison of catalytic activity of SD-SO_3H with some other catalysts

Entry	Catalyst	*T*, °C	Time, min	Yield, %	References
1	SD-SO_3H	110	9	98	This work[a]
2	m-ZrP	160	240	94	[37]
3	SCZ	120	143	87	[38]
4	ASA	100	30	98	[32]
5	CMK-5-SO_3H	130	20	95	[39]
6	$H_6P_2W_{18}O_{62}\cdot 24H_2O$	130	42	87	[40]
7	Zeolite- E4a	110[b]	180	97	[41]
8	$HClO_4\cdot SiO_2$	130	35	95	[42]

[a] Reaction condition: resorcinol (1 mmol), ethyl acetoacetate (1 mmol) and a catalyst (0.05 g) without a solvent.
[b] Toluene as solvent.

products. Melting points were measured on an Electrothermal apparatus and the elemental analysis was performed with an Elementar Analysensysteme GmbH VarioEL CHNS mode. The ^1H NMR spectra were measured on a Bruker DRX-400Avance spectrometer using TMS as internal standard. Scanning electron microphotographs (SEM) were obtained on a LEO 1455VP-SEM. The thermogravimetric analysis (TGA) of the sawdust-SO_3H was performed on LINSEIS PT 1600 and sample was heated from 30 to 600°C at a scanning rate of 10°C/min under the atmosphere of nitrogen.

Catalyst preparation. The sawdust was collected from the local Sawmill and washed continuously with distilled water to remove the surface impurity and water soluble materials, and dried under sunlight. The resulting material was ground and sieved (50 mesh size), washed with distilled water and dried at 50°C for 2 h. A 50 mL suction flask charged with 2.0 g of sawdust and 10 mL CH_2Cl_2 was equipped with a constant-pressure dropping funnel containing chlorosulfonic acid (2 mL) and a gas inlet tube for driving HCl gas out of the flask into water. Chlorosulfonic acid was added dropwise to the mixture at 0°C and mixed until no HCl was evolved. Upon completion of the process the mixture was shaken for 1 h at room temperature. The product was filtered off, washed with CH_2Cl_2 (20 mL) and dried at 50°C to produce sawdust sulfuric acid (SD-SO_3H) as a brown powder. Complete experimental details are available online as the Supplementary Materials of this paper.

General procedure for substituted coumarins. A well stirred mixture of a phenol derivative (1.0 mmol), ethyl acetoacetate (1.2 mmol) and SD-SO_3H (0.05 g, 0.24 mmol) was heated at 110°C under solvent-free conditions. Upon completion of the reaction, as indicated by TLC, $CHCl_3$ was added and the catalyst was filtered off. The filtrate was evaporated and the residue purified by recrystallization from ethanol to give the corresponding pure product. Melting points and ^1H NMR spectra of the products were compared with and matched well the reference data.

CONCLUSIONS

Various substituted coumarins were synthesized with high yield and purity by condensation of different phenols with ethyl acetoacetate (the Pechmann condensation) under solvent free conditions using SD-SO_3H as a heterogeneous, green, highly efficient, recyclable, and inexpensive catalyst.

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