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Metal free synthesis of tetrahydrobenzo[*a*] xanthenes using orange peel as a natural and low cost efficient heterogeneous catalyst

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In this work, a facile, efficient and metal free catalytic system has been developed for the synthesis of tetrahydrobenzo[*a*]xanthene derivatives *via* a one-pot three-component condensation of various aldehydes, 2-naphthol, and dimedone. For the first time, the orange peel as a green, acidic, and low cost natural catalyst with high porosity and high efficiency was used in tetrahydrobenzo[*a*]xanthenes synthesis procedure. This environmental-friendly novel catalytic system led to the desired products in high to excellent yields under solvent free conditions at 120 °C.

1. Introduction

Over the past decade, much attention has been given to the development of new procedures in organic synthesis for environmentally benign processes due to increasing green chemistry concerns.[1] Also, highly efficient and clean techniques of synthesis such as solvent-free and multicomponent reactions (MCRs) are highly regarded. Multi-component reactions (MCRs) are excellent tools in synthetic organic chemistry and drug discovery due to their product diversity, high efficiency, simple procedures, convergence, less energy consumption, decreased reaction steps and time saving.[2] Therefore, the new MCRs which meet the credentials of green chemistry aspects as well as cost effectiveness have gained much attention in organic chemistry.[3]

Xanthene and its derivatives have acquired immense attention because of their diverse range of biological and pharmaceutical properties such as anti-inflammatory,[4] antibacterial[5] and antimalarial agents.[6] The importance of xanthene derivatives clearly was realized from their usage as dyes,[7] fluorescent materials for visualization of biomolecules,[8] sensitizers in photodynamic therapy for destroying the tumor cells in laser technologies[9] and useful materials for photodynamic therapy.[10] The tetrahydrobenzo[*a*]xanthene, because of their wide range of pharmacological, industrial and synthetic applications are of utmost importance[11] and many methods for the synthesis of these xanthenes have been reported in the literature. One of these methods is the condensation reaction of aldehydes, 2-naphthol and cyclic 1,3-dicarbonyl compounds, with various catalysts such as $NaHSO_4 \cdot SiO_2$,[12] strontium triflate,[13] $Zr(HSO_4)_4$,[14] dodecan tungstophosphoric acid (PWA),[15] iodine,[16] $InCl_3/P_2O_5$,[17] *p*-toluenesulfonic acid/ionic liquid ([bmim]BF_4),[18] trichloroacetic acid,[19] tetradecyl trimethyl ammonium bromide (TTAB),[20] cyanuric chloride,[21] silica sulfuric acid (SSA),[22] trityl chloride (TrCl),[23] tetra(*n*-butyl)ammonium fluoride (TBAF),[24] proline triflate,[25] perchloric acid,[26] and $Cr(SO_4)_2 \cdot 4H_2O$.[27] These methods suffer from many drawbacks including the use of expensive and toxic metals, high-cost reagents, long reaction times in combination with high reaction temperatures, strong Lewis acids, low yield, harsh reaction conditions, organic solvents and tedious work-up processes and difficulty in separation and recovery of the catalyst.

Nowadays, using metal catalysts are not always eco-friendly and for this reason, serious environmental pollution often occurs.[28] Because of the strict environmental, there is an immense demand for metal-free, green and safe synthetic methods that reduce the use of toxic waste and stop the formation of inorganic wastes leading to high yield of the desired product.[29] Therefore, it is extremely important to explicate a protocol which can construct such complex molecules in a single step using reusable heterogeneous, inexpensive, metal-free and green catalyst in a simple procedure under solvent free conditions with excellent yields. In this paper, we report an efficient metal free synthesis of tetrahydrobenzo[*a*] xanthenes in the presence of orange peel as green heterogeneous catalyst.

2. Experimental

2.1 Materials

All compounds were obtained from Sigma-Aldrich and Merck in analytical grade and used without further purification. The melting points of products were determined with an Electro thermal Type 9100 melting point apparatus. The FT-IR spectra

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were recorded on an Avatar 370 FT-IR Therma Nicolet spectrometer. The NMR spectra were provided on Brucker Avance 400 MHz instruments in chloroform ($CDCl_3$). Mass spectra were recorded with Agilent Technologies (HP) 5973 Network Mass Selective Detector and Shimadzu GC-MS-QP5050 instruments at 70 eV. Elemental compositions were determined with a Leo 1450 VP scanning electron microscope spectrometer (SEM). Inductively coupled plasma (ICP) was carried out on a Varian, VISTA-PRO, CCD, Australia. All yields refer to isolated products after purification by recrystallization.

2.2 Catalyst preparation

In order to prepare the catalyst, the orange peel was powdered, washed with distilled water and dried at 80 °C for 2 h.

2.3 General procedure for the preparation of 12-substituted-8,9,10,12-tetrahydro benzoxanthen-11-ones

Powdered orange peel (0.05 g) was added to the mixture of aromatic aldehyde **1** (1 mmol), 2-naphthol **2** (1 mmol), and dimedone **3** (1 mmol) under solvent free condition. The mixture was stirred at 120 °C for the appropriate time which was presented in Table 2. The progress of the reaction was monitored by thin-layer chromatography (TLC) in ethyl acetate : *n*-hexane, 1 : 4. After completion of the reaction (monitored by TLC), boiling ethanol was added to the reaction mixture. The catalyst was filtered off and the reaction mixture was cooled to room temperature. The precipitated crude product was then removed by filtration and recrystallized from absolute ethanol to give pure product. The spectral data for selected product are presented as follows:

9,9-Dimethyl-12-phenyl-8,9,10,12-tetrahydro-11*H*-benzo[*a*]xanthen-11-one (4a). White powder, mp 149–150 °C, yield 95%. IR (KBr) ν_{max}/cm^{-1}: 3054, 2957–2886, 1651. ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 0.99 (s, 3H, CH_3), 1.15 (s, 3H, CH_3), 2.25–2.36 ($AB_{quartet}$, $^2J_{HH}$ = 16.4 Hz, $^2J_{HH}$ = 16.4 Hz, 2H, C=C–CH_AH_B), 2.60 (s, 2H, CH_2), 5.74 (s, 1H, CH), 7.08 (tt, J = 7.2, 1.2 Hz, 1H, arom-H), 7.20 (t, J = 8 Hz, 2H, arom-H), 7.35–7.48 (m, 5H, arom-H), 7.77–7.83 (m, 2H, arom-H), 8.03 (d, J = 8.4 Hz, 1H, arom-H).

12-(4-Bromophenyl)-9,9-dimethyl-8,9,10,12-tetrahydro-11*H*-benzo[*a*]xanthen-11-one (4c). White powder, mp 187–189 °C, yield 95%. IR (KBr) ν_{max}/cm^{-1}: 3.064, 2.962, 1.643, 1.593, 1.515, 1.484, 1.374, 1.222, 1.175, 1.010, 837, 811, 755 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.00 (s, 3H, CH_3), 1.02 (s, 3H, CH_3), ($AB_{quartet}$, 2H, $^2J_{HH}$ = 16.4 Hz, $^2J_{HH}$ = 16.4 Hz C=C–CH_AH_B), 2.60 (s, 2H, CH_2), 5.70 (s, 1H, CH), 7.23–7.25 (m, 2H, arom-H), 7.30–7.36 (m, 5H, arom-H), 7.79–7.83 (m, 2H, arom-H), 7.93 (d, J = 8.4 Hz, 1H, arom-H).

12-(4-Chlorophenyl)-9,9-dimethyl-8,9,10,12-tetrahydro-11*H*-benzo[*a*]xanthen-11-one (4f). White powder, mp 191–193 °C, yield 95%. IR (KBr) ν_{max}/cm^{-1}: 3.071, 2.960, 1.640, 1.594, 1.488, 1.376, 1.225, 1.181, 1.146, 1.092, 838, 811, 747 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 0.99 (s, 3H, CH_3), 1.15 (s, 3H, CH_3), 2.25–2.36 ($AB_{quartet}$, 2H, $^2J_{HH}$ = 16.4 Hz, $^2J_{HH}$ = 16.4 Hz C=C–CH_AH_B), 2.602 (s, 2H, CH_2), 5.71 (s, 1H, CH), 7.15–7.17 (m, 2H, arom-H), 7.31–7.49 (m, 5H, arom-H), 7.79–7.83 (m, 2H, arom-H), 7.94 (d, J = 8 Hz, 1H, arom-H).

12-(4-Fluorophenyl)-9,9-dimethyl-8,9,10,12-tetrahydro-11*H*-benzo[*a*]xanthen-11-one (4g). White powder, mp 185–186 °C, yield 95%. IR (KBr) ν_{max}/cm^{-1}: 3.071, 2.961, 1.639, 1.594, 1.473, 1.377, 1.225, 1.181, 1.159, 1.148, 839, 810, 767, 745 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 0.99 (s, 3H, CH_3), 1.15 (s, 3H, CH_3), 2.25–2.36 ($AB_{quartet}$, 2H, $^2J_{HH}$ = 16.4 Hz, $^2J_{HH}$ = 16.4 Hz C=C–CH_AH_B), 2.60 (s, 2H, CH_2), 5.73 (s, 1H, CH), 6.88 (t, J = 8.8 Hz, 2H, arom-H), 7.30–7.50 (m, 5H, arom-H), 7.81 (t, 2H, arom, H), 7.95 (d, J = 8.0 Hz, 1H, arom-H).

9,9-Dimethyl-12-(*p*-tolyl)-8,9,10,12-tetrahydro-11*H*-benzo[*a*]xanthen-11-one (4i). White powder, mp 175–177 °C, yield 92%. IR (KBr) ν_{max}/cm^{-1}: 3.073, 2.954, 2.870, 1.650, 1.598, 1.465, 1.372, 1.227, 1.185, 1.148, 1.111, 813, 757 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.01 (s, 3H, CH_3), 1.15 (s, 3H, CH_3), 2.22 (s, 3H, CH_3), 2.25–2.36 ($AB_{quartet}$, 2H, $^2J_{HH}$ = 16.4 Hz, $^2J_{HH}$ = 16.4 Hz C=C–CH_AH_B), 2.60 (s, 2H, CH_2), 5.69 (s, 1H, CH), 7.00 (d, J = 8.0 Hz, 2H, arom-H), 7.25 (d, J = 8.0 Hz, 2H, arom-H), 7.34 (d, J = 8.8 Hz, 1H, arom-H), 7.37–7.49 (m, 2H, arom-H), 7.79 (t, J = 8.8 Hz, 2H, arom-H), 8.03 (d, J = 8.4 Hz, 1H, arom-H).

9,9-Dimethyl-12-(3-nitrophenyl)-8,9,10,12-tetrahydro-11*H*-benzo[*a*]xanthen-11-one (4k). White powder, mp 170–172 °C, yield 90%. IR (KBr) ν_{max}/cm^{-1}: 3.072, 2.958, 1.650, 1.596, 1.530, 1.468, 1.375, 1.349, 1.225, 1.193, 1.177, 1.145, 1.094, 812 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.99 (s, 3H, CH_3), 1.17 (s, 3H, CH_3), 2.25–2.38 ($AB_{quartet}$, 2H, $^2J_{HH}$ = 16.4 Hz, $^2J_{HH}$ = 16.4 Hz C=C–CH_AH_B), 2.64 (s, 2H, CH_2), 5.85 (s, 1H, CH), 7.38–7.50 (m, 4H, arom-H), 7.84–7.98 (m, 5H, arom-H), 8.15 (t, J = 1.6 Hz, 1H, arom-H).

3. Results and discussion

The FT-IR spectrum of orange peel and the 5th recovered orange peel was shown in Fig. 1. As shown in Fig. 1a, broad bands centred at 3400 cm^{-1} attributed to stretching vibration of hydroxyl groups. The absorption bands at 1738 cm^{-1} are assigned to C=O carbonyl group. As shown in Fig. 1b, shape, position and relative intensity of all characteristic peaks are well preserved. These results indicated that no considerable changes were observed on the chemical structure of functional groups and the hydrogen bonding network (Fig. 1).

The morphology of orange peel was studied with scanning electron microscopy (SEM). The smooth amorphous morphology

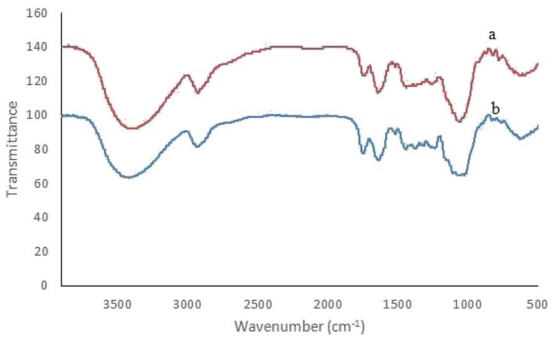


Fig. 1 FTIR spectra of (a) orange peel, (b) recovered orange peel.

of orange peel surface was shown in (Fig. 2a). Also, SEM image of powdered orange peel showed high porosity in comparison with non-powdered orange peel (Fig. 2b). High porosity of powdered orange peel could provide an adequate morphology for organic materials and various solvents adsorption for catalytic purposes. The main ingredients of 7 g orange peel contain 5.8 calories, water (4.4 g), protein (0.1 g), total fat (0.0 g), total carbohydrate (1.5 g), fiber (0.6 g), ash (0.0 g), and minerals. Elemental content of the catalyst (0.242 g of orange peel) was characterized by inductively coupled plasma analyses (ICP), which resulted in the following output: Al (90.719 ppm), Cu (9.998 ppm), Se (0.334 ppm), Ni (21.075 ppm), Pb (11.040 ppm), Zn (64.341 ppm), Mg (824.002 ppm), K (185.674 ppm), Na (273.493 ppm), P (290.394 ppm), Cr (18.120 ppm), Mn (4.783 ppm), Mo (6.885 ppm), S (858.694 ppm), Si (4.409 ppm), Fe (472.723 ppm), Ca (7726.53 ppm). It also contained different vitamins, such as vitamin C (ascorbic acid; 14%), vitamin A (1%), vitamin B6 (1%), soluble sugars, cellulose, hemicellulose, and pectin as the main components. The composition of the orange peel varies with geographical, cultural and seasonal harvesting and processing. Because of significant amounts of ascorbic acid in orange peel, it has acidic property with pH 5.1 and hence it would act as acid catalyst for these reactions. Therefore, we have used this natural catalyst for synthesis of tetrahydrobenzo[*a*]xanthenes.[30] The results of the current study indicated that orange peel as a natural material with multifunctional properties and high porosity possessed high efficiency in green synthesis of tetrahydrobenzo[*a*]xanthenes. In order to remove the pollutions from the surface of orange peel, it was powdered, washed with distilled water and dried at 80 °C for 2 h before use (Scheme 1).

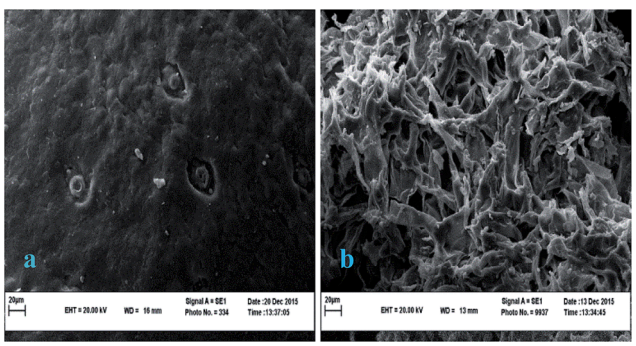
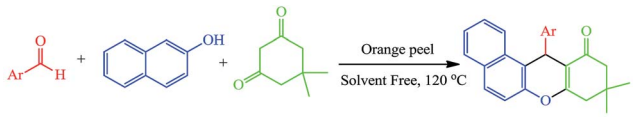


Fig. 2 SEM image of (a) non-powdered orange peel, (b) powdered orange peel.



Ar=C_6H_5, 3-Br-C_6H_4, 4-Br-C_6H_4, 2-Cl-C_6H_4, 4-Cl-C_6H_4, 4-F-C_6H_4, 3-Me-C_6H_4, 4-Me-C_6H_4, 4-OMe-C_6H_4, 3-NO_2-C_6H_4, 4-NO_2-C_6H_4, 2-OH-C_6H_4, 4-OH-C_6H_4, 4-CN-C_6H_4, 1-Naphythyl, 2-Naphthyl, 4-$N(Me)_2$-C_6H_4

Scheme 1 Synthesis of tetrahydrobenzo[*a*]xanthene derivatives in the presence of orange peel.

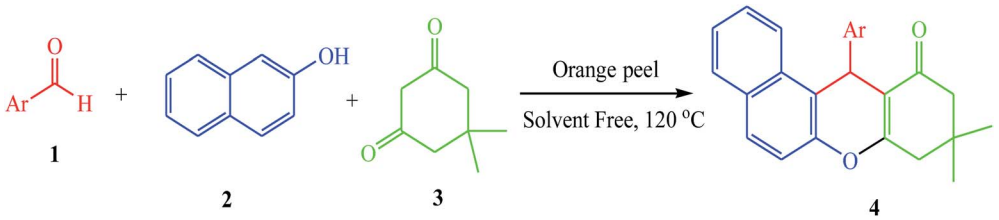
As a model reaction, condensation of benzaldehyde, 2-naphtol and dimedone was carried out in the presence of orange peel. For optimization of the reaction conditions various parameters such as catalyst amount, solvent and reaction temperature were investigated as shown in Table 1. Desired product was produced only with 13% yield when the reaction was carried out without catalyst under solvent free condition at 120 °C (Table 1, entry 1), under the same reaction condition, 98% yield was obtained after 60 min in the presence of 0.05 g of orange peel (Table 1, entry 3). In order to evaluate the effect of solvent, different solvents including H_2O, EtOH, CH_2Cl_2, toluene, $CHCl_3$, THF, and EtOAc were used under reflux in the presence of orange peel (Table 1, entries 6–12). The results of these experiments revealed that in the presence of these solvents the yield of the desired product was decreased in comparison with the solvent-free conditions. To optimise the catalyst amount, the reaction was carried out under solvent free conditions at 120 °C in the presence of different amount of catalyst (0.03 g, 0.05 g, and 0.07 g). The results indicated no significant increase in yield with increasing the catalyst amount (Table 1, entries 2, 3, and 5). Based on these results, solvent free condition in the presence of 0.05 g catalyst at 120 °C was chosen as the optimized conditions.

The catalytic activity of orange peel in the synthesis of various tetrahydrobenzo[*a*]xanthene derivatives under the optimized conditions was also studied (Table 2). Versatility of the optimized condition was demonstrated by three-component condensation reaction of a range of aromatic aldehydes, 2-naphthol and dimedone under solvent-free condition at 120 °C in the presence of a catalytic amount of orange peel. All aromatic aldehydes with electron-withdrawing and electron-releasing groups were converted to the related products in high to excellent yields (Table 2). The results showed that the catalytic system was efficient with various substituents on the benzaldehyde. The conversion of benzaldehydes with electron withdrawing groups (Table 2, entries 2–7, 11, 12 and 15) was faster than the electron donating groups analogue (Table 2, entries 8–10, 13, and 14).

Table 1 Optimization of model reaction catalysed by heterogeneous orange peel green catalyst

Entry	Catalyst (g)	Solvent	Temperature (°C)	Time (h)	Isolated yield%
1	—	Solvent free	120	1	13
2	0.03	Solvent free	120	1	80
3	0.05	Solvent free	120	1	98
4	0.05	Solvent free	100	1	80
5	0.07	Solvent free	120	1	98
6	0.05	H_2O	Reflux	1	50
7	0.05	EtOH	Reflux	1	60
8	0.05	CH_2Cl_2	Reflux	1	30
9	0.05	Toluene	Reflux	1	20
10	0.05	$CHCl_3$	Reflux	1	25
11	0.05	THF	Reflux	1	35
12	0.05	EtOAC	Reflux	1	35

Table 2 Three-component condensation reaction of various substrates enhanced by orange peel catalyst[a]



					Mp (°C)		
Entry	Ar	Product	Time (min)	Yield (%)	Found	Reported	Reference
1	C_6H_5	**4a**	40	95	149–150	151–153	31
2	3-Br-C_6H_4	**4b**	30	90	170–171	161–164	32
3	4-Br-C_6H_4	**4c**	30	95	187–189	186–188	33
4	2-Cl-C_6H_4	**4d**	40	95	175–176	173–174	34
5	3-Cl-C_6H_4	**4e**	40	90	173–174	175–177	35
6	4-Cl-C_6H_4	**4f**	30	95	191–193	187–188	36
7	4-F-C_6H_4	**4g**	30	95	185–186	191–193	37
8	3-Me-C_6H_4	**4h**	55	85	173–175	176–177	38
9	4-Me-C_6H_4	**4i**	40	92	175–177	173–175	34
10	4-OMe-C_6H_4	**4j**	60	85	201–203	204–205	31
11	3-NO_2-C_6H_4	**4k**	40	90	170–172	168–172	39
12	4-NO_2-C_6H_4	**4l**	20	98	176–178	174–175	36
13	2-OH-C_6H_4	**4m**	50	83	132–133	135–137	40
14	4-OH-C_6H_4	**4n**	50	90	216–217	213–214	41
15	4-CN-C_6H_4	**4o**	35	95	201–203	196–199	42
16	1-Naphthyl	**4p**	90	82	191–193	184–188	43
17	2-Naphthyl	**4q**	75	85	235–237	231–233	41
18	4-$N(Me)_2$-C_6H_4	**4r**	90	80	201–202	200–202	44

[a] Reaction conditions: aromatic aldehyde (1 mmol), 2-naphtol (1 mmol), dimedone (1 mmol).

The efficiency of the presented protocol was compared with different heterogeneous catalysts reported previously in the literature. The results are shown in Table 3. Based on these results, all previously reported methods suffer from long reaction times to achieve appropriate yields as well as use of strong Lewis acids, expensiveness and toxic metals with tedious work-up procedure. Also, orange peel gives better yield in shorter reaction time than other heterogeneous catalysts.

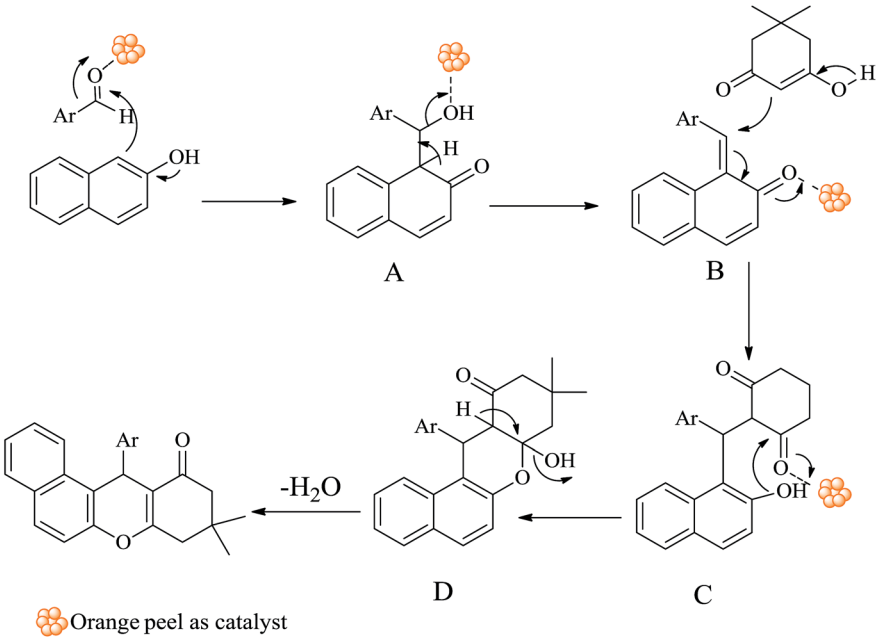
A plausible mechanism for the reaction methodology under current development is shown in Scheme 2. In the absence of the catalyst, the reaction of benzaldehyde and 2-naphthol with dimedone could be carried out but the product was obtained with a very poor yield after a prolonged time (Table 1, entry 1).

According to chemistry knowledge, orange peel, as an acid, activates the carbonyl group of substrates. As shown in Scheme 2, prior activation of the carbonyl group of aldehyde by orange peel followed by a nucleophilic attack from C_1 of β-naphthol, provides intermediate A, which serves as an electrophile, ready to be attacked by dimedone. Then, cyclodehydration of intermediate C and dehydration affords the desired product.

Furthermore, the recyclability of our proposed catalyst was studied in the model reaction. After completion of the

Table 3 Comparison of catalytic activity between orange peel and other reported catalysts

Entry	Catalyst	Solvent	Temperature (°C)	Other	Time (min)	Yield (%)	Reference
1	PEG-400	—	120	—	330–450	79–90	45
2	CAN	CH_2Cl_2/ETOH	26	Ultrasound	120–144	82–87	46
3	I_2	ACOH	80	—	150–180	70–89	47
4	P-TSA	$[bmim]BF_4$	80	—	120–210	83–95	48
5	$Sr(OTF)_2$	$ClCH_2CH_2Cl$	300–420	—	390	70–88	49
6	Sulfamic acid	—	120	—	115–136	79–84	50
7	$NaHSO_4$–SiO_2	$ClCH_2CH_2Cl$	Reflux	—	280–420	69–89	51
8	Orange peel	—	120	—	60	98	This work



Scheme 2 Plausible reaction pathway catalysed by orange peel.

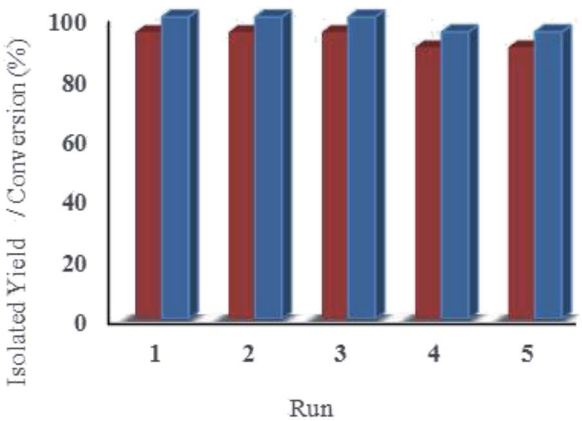


Fig. 3 Recyclability of orange peel catalyst in the synthesis of tetrahydrobenzo[*a*]xanthenes.

condensation reaction of benzaldehyde with β-naphtol and dimedone, orange peel was separated by simple filtration from the reaction mixture, washed with distilled water and ethanol several times to remove the organic products. The catalyst was dried at 100 °C for 1 h. The heterogeneous catalyst was used at least for 5 successive runs without significant decrease in product yield (Fig. 3).

4. Conclusion

In summary, we have described a convenient and highly efficient metal free synthesis of tetrahydrobenzo[*a*]xanthenes using orange peel as a green and effective catalyst by three-component one-pot condensation of various aldehydes with 2-naphthol and dimedone under solvent free condition. This new type of low cost and reusable catalyst plays a crucial role in "electrophilic activation". Excellent yields of product, short reaction time, mild reaction conditions, avoiding the use of organic solvent, a simple workup procedure, and reusability of the catalyst are the important and valuable features of this metal free methodology. The resulting tetrahydrobenzo[*a*]xanthene derivatives are of importance for organic and medicinal research.

Acknowledgements

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