Article

Efficient synthesis of 1,8-dioxo-octahydroxanthenes catalyzed by *β*-cyclodextrin grafted with butyl sulfonic acid in aqueous media

Kai Gong [a],*, Hualan Wang [b], Shuxin Wang [a], Ying Wang [a], Jinghua Chen [a]

[a] *School of Pharmaceutical Science, Jiangnan University, Wuxi 214122, Jiangsu, China*

[b] *Key Laboratory of Organosilicon Chemistry and Material Technology, Ministry of Education, Hangzhou Normal University, Hangzhou 311121, Zhejiang, China*

ARTICLE INFO

ABSTRACT

β-Cyclodextrin was functionalized with butyl sulfonic acid to give an efficient, eco-friendly catalyst for the synthesis of 1,8-dioxo-octahydroxanthenes via the one-pot condensation of aromatic aldehydes and active methylene carbonyl compounds in aqueous media. This new methodology offers several advantages such as excellent yields, short reaction time, a simple procedure and mild reaction conditions. Furthermore, the catalyst can be readily recovered and reused up to five times without a significant loss in its activity.

1. Introduction

Xanthenes and its derivatives have received considerable attention owing to their interesting pharmacological properties, including their anti-bacterial [1], antiviral [2] and anti-inflammatory activities [3]. As well as their pharmacological properties, xanthenes have also been widely used as dyes [4], as well as additives in pH-sensitive fluorescent materials [5] and laser technologies [6]. In particular, xanthenediones constitute a structural unit that can be found in a large number of natural products [7]. Compounds belonging to this structural class have been used as versatile synthons for the synthesis of complex systems because of the inherent reactivity of their inbuilt pyran ring [8]. In light of their wide range of pharmaco-logical, industrial and synthetic applications, many methods for the preparation of xanthenes and xanthenediones have been reported in the literature [9].

One of the most commonly used methods reported for the synthesis of 1,8-dioxo-octahydroxanthene derivatives involves the condensation of aromatic aldehydes and active methylene carbonyl compounds. This reaction can be carried out in the presence of a protic acid or Lewis acid, such as *p*-dodecylbenzenesulfonic acid [10], Amberlyst-15 [11], Fe^{3+}-montmorillonite [12], $HClO_4$–SiO_2 [13], SiO_2 [14], nano-TiO_2 [15], $[Et_3NH][HSO_4]$ [16], I_2 [17], L-proline [18], $CaCl_2$ or HBr [19], nanosized MCM-41-SO_3H [20], ceric ammonium nitrate-supported HY-zeolite [21], Fe_3O_4@SiO_2-imid-$H_3PMo_{12}O_{40}$ nanoparticles [22] and cellulose sulfonic acid [23]. Xanthenediones

have also been synthesized under microwave [24] and ultrasound [20] irradiation conditions. However, the general usefulness of these methods has been limited by several disadvantages, such as low yields, difficulties associated with the availability or preparation of the starting materials, prolonged reaction times, the use of toxic organic solvents, the requirement for a large excess of reagents or catalysts and harsh reaction conditions. The development of simple, efficient, high-yielding and environmentally friendly methods for the synthesis of xanthenes using novel catalysts is therefore still in great demand.

The level of interest in the exploration of catalytic reactions in aqueous media has been increasing dramatically during the last few years because of advantages associated with performing reactions in water, such as improved reactivity and selectivity characteristics. Performing reactions in water can also lead to simplified workup procedures, making it easier to recycle the catalyst, as well as allowing for the use of mild reaction conditions [25]. Hence, considerable research efforts have been directed towards the design of novel ligands/catalysts to promote aqueous organic transformations. One of the most commonly used methods reported for the synthesis of phase transfer catalysts involves the combination of efficient homogeneous ligands/catalysts with water-soluble polymers (polyethylene glycol) or salts (sulfonate salt or quaternary ammonium salt) [26–30]. In this regard, cyclodextrin (CD) has received a particularly high level of attention because of its excellent water solubility and special hydrophobic cavity. Indeed, CDs and their derivatives have shown excellent performance characteristics in a broad range of aqueous organic reactions, including oxidation, cycloaddition, coupling and hydroformylation reactions [31–36]. In our group, we are especially interested in the use of CDs as catalyst supports and the use of these supported catalysts in aqueous biphasic reactions.

In this context, we wish to report the synthesis of a functionalized *β*-cyclodextrin bearing butyl sulfonic acid (*β*-CD-BSA) groups and the subsequent application of this material as a catalyst for the synthesis of 1,8-dioxo-octahydroxanthenes (**3**) by the one-pot condensation of various aldehydes (**1**) with dimedone (**2a**) or 1,3-cyclohexanedione (**2b**) in aqueous media (Scheme 1). To the best of our knowledge, the work described in this study represents the first reported example of the synthesis of *β*-CD-BSA and its use as a catalyst for the preparation of 1,8-dioxo-octahydroxanthenes.

2. Experimental

2.1. General

All of the reagents used in the current study were purchased from commercial sources and used without further purification. Melting points were determined on an X6-data microscopic melting points apparatus and were uncorrected. Fourier transform infrared (FT-IR) spectra were recorded on a Bruker Vecter 22 spectrometer as KBr disks. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance III (400 MHz) spectrometer using D$_2$O or CDCl$_3$ as a solvent with TMS as internal reference
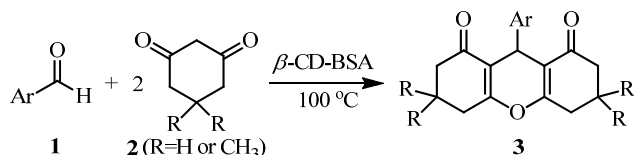
Scheme 1. Synthesis of 1,8-dioxo-octahydroxanthenes.

standard.

2.2. Synthesis of β-CD-BSA

β-CD (2 g) was dissolved in a solution of NaOH (20 mL, 5 mol/L), and the resulting solution was heated at 75 °C. 1,4-Butane sultone (2.4 g) was then added to the reaction in a dropwise manner, and the resulting mixture was stirred for 3 h at 75 °C. The reaction was then cooled to room temperature and the pH was adjusted to neutral using a HCl solution (3 mol/L). The neutral mixture was then dropped into ethanol to afford sulfobutyl ether *β*-cyclodextrin (SBE-*β*-CD) as a white solid, which was collected by filtration.

Acidic resin was activated in a saturated aqueous solution of NaCl for 24 h, treated with an aqueous solution of NaOH (2.5 wt%) for 80 min, washed with distilled water until the pH of the washings reached 7.0 and then treated with an aqueous solution of HCl (5.0 wt%) for 12 h. After this treatment process, the resin was transferred to a column and washed with deionized water until the pH of the eluent reached 7.0.

A portion of the sodium salt of SBE-*β*-CD (1.0 g) was dissolved in water (100 mL), and the resulting solution was allowed to flow through the acidic resin column at a speed of 20 drops/min. The acidic eluent was then collected and freeze-dried for 12 h to the give the *β*-CD-BSA product.

IR (KBr, cm^{-1}): 3454, 3419, 2963, 2924, 2361, 2342, 1655, 1636, 1613, 1383, 1217, 1192, 1136, 1051, 818, 705, 689, 612, 560. ^{1}H NMR (400 MHz, D$_2$O): *δ* 1.70 (m, −OCH$_2$*CH$_2$CH$_2$*CH$_2$SO$_3$H), 2.88 (m, −OCH$_2$CH$_2$−CH$_2$*CH$_2$*SO$_3$H), 3.49–3.8 (m, −O*CH$_2$*−CH$_2$CH$_2$CH$_2$SO$_3$H and C*H*), 5.01–5.14 (m, C$_1$−H).

2.3. Typical procedure for the synthesis of 1,8-dioxo-octahydroxanthenes

A mixture of aromatic aldehyde **1** (2 mmol), 5,5-dimethyl-1,3-cyclo-hexanedione or 1,3-cyclohexanedione (4 mmol) and *β*-CD-BSA (1 mol%) in H$_2$O (2 mL) was stirred at 100 °C for the appropriate length of time. Upon completion of the reaction, as determined by TLC, the resulting solid material was filtered and washed with H$_2$O (10 mL). The crude products were purified by recrystallization from EtOH (95%).

Analytical data for selected compounds are presented below.

Compound **3a**: white crystals, mp 202–204 °C (204–205 °C [12]). FT-IR (KBr, cm^{-1}): 3427, 2958, 2915, 2870, 1662, 1625, 1578, 1468, 1454, 1382, 1361, 1202, 1166, 1154, 1141, 1127, 1002, 700; ^{1}H NMR (400 MHz, CDCl$_3$): *δ* 0.99 (s, 6H, CH$_3$), 1.10 (s, 6H, CH$_3$), 2.14–2.25 (m, 4H, CH$_2$), 2.47 (s, 4H, CH$_2$), 4.75 (s,

1H, CH), 7.08–7.12 (t, 1H, ArH), 7.19–7.23 (t, 2H, ArH), 7.28–7.30 (d, 2H, ArH); ^{13}C NMR (100 MHz, CDCl$_3$): δ 196.42, 162.26, 144.11, 128.40, 128.07, 126.39, 115.68, 50.75, 40.88, 32.23, 31.85, 29.31, 27.35.

Compound **3i**: white crystals, mp 217–219 °C (216–218 °C [13]). FT-IR (KBr, cm^{-1}): 3444, 2962, 2874, 1677, 1625, 1511, 1468, 1412, 1391, 1360, 1198, 1166, 1140, 1126, 1001, 840; ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.99 (s, 6H, CH$_3$), 1.10 (s, 6H, CH$_3$), 2.14–2.25 (m, 7H, CH$_2$ and Ar-CH$_3$), 2.45 (s, 4H, CH), 4.71 (s, 1H, CH), 7.02 (d, J = 8.0 Hz, 2H, ArH), 7.17 (d, J = 8.0 Hz, 2H, ArH); ^{13}C NMR (100 MHz, CDCl$_3$): δ 196.45, 162.11, 141.21, 135.79, 128.81, 128.26, 115.78, 50.78, 40.89, 32.23, 31.45, 29.30, 27.40, 21.09.

Compound **3u**: yellow crystals, mp 286–287 °C. FT-IR (KBr, cm^{-1}): 3428, 2923, 2850, 1659, 1606, 1591, 1521, 1423, 1384, 1361, 1347, 1174, 1128; ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.94–2.11 (m, 4H, CH$_2$), 2.34–2.37 (m, 4H, CH$_2$), 2.57–2.73 (m, 4H, CH$_2$), 4.88 (s, 1H, CH), 7.48 (d, J = 8.0 Hz, 2H, ArH), 8.09 (d, J = 8.0 Hz, 2H, ArH); ^{13}C NMR (100 MHz, CDCl$_3$): δ 196.46, 164.59, 151.73, 146.48, 129.44, 123.46, 115.77, 36.83, 32.23, 27.16, 20.24.

Compound **3y**: yellow crystals, mp 288–290 °C. FT-IR (KBr, cm^{-1}): 3382, 2949, 1662, 1610, 1597, 1515, 1446, 1430, 1387, 1361, 1275, 1242, 1207, 1193, 1172, 1130, 961, 835, 632, 609; ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.97–2.07 (m, 4H, CH$_2$), 2.28–2.41 (m, 4H, CH$_2$), 2.56–2.67 (m, 4H, CH$_2$), 4.74 (s, 1H, CH), 4.81 (bs, 1H, Ar–OH), 6.67 (d, J = 8.0 Hz, 2H, ArH), 7.16 (d, J = 8.0 Hz, 2H, ArH); ^{13}C NMR (100 MHz, CDCl$_3$): δ 196.77, 163.79, 154.05, 136.84, 129.57, 117.07, 115.02, 36.99, 30.79, 27.15, 20.33.

3. Results and discussion

A schematic illustration of the steps involved in the preparation for β-CD-BSA is shown in Scheme 2. Briefly, commercially available β-CD was reacted with 1,4-butane sultone in a NaOH solution to afford sulfobutyl ether β-cyclodextrin, which was treated with acidic resin to give β-CD-BSA. The resulting β-CD-BSA material was characterized by FT-IR spectroscopy and ^{1}H NMR. The average degree of substitution for the sulfobutyl ether group on the β-CD-BSA material was found to be 7 [37].

Scheme 2. Synthesis of β-CD-BSA.
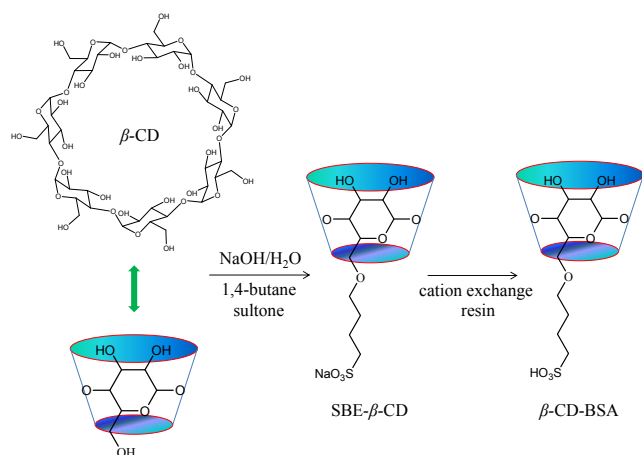
The reaction of benzaldehyde (**1a**) with dimedone (**2a**) was initially selected as a model reaction to optimize the reaction conditions for the formation of 1,8-dioxo-octahydroxanthenes using a variety of solvents, temperatures, reactions times and catalyst loadings. The results of these optimization experiments are summarized in Table 1. These results showed that none of the desired 1,8-dioxo-octahydroxanthene product was detected when a mixture of benzaldehyde and dimedone was heated at 100 °C for 120 min in the absence of the catalyst (Table 1, entry 1). Furthermore, no activity was observed in the presence of β-CD (Table 1, entry 2). When SBE-β-CD was used as the catalyst, the product was obtained in low yield (Table 1, entry 3). Pleasingly, however, the use of a small amount of β-CD-BSA as the catalyst gave the desired product in excellent yield over a much shorter reaction time (Table 1, entry 4). The best result was achieved when the reaction was carried out with a 1 mol% loading of β-CD-BSA (Table 1, entry 5). The use of a higher loading of the catalyst did not lead to further improvements in the yield or reaction time (Table 1, entry 6).

The results of the optimization experiments indicated that the nature of the solvent had a significant impact on the outcome of the reaction (Table 1, entries 7–14). It is noteworthy that the use of a non-polar solvent such as toluene or cyclohexane gave moderate yields of the desired product (65% and 70%, respectively). The use of a polar aprotic solvent such as THF or MeCN led to a slight improvement in the yield (76% and 85%, respectively). In the absence of a solvent, the reaction proceeded smoothly to give the desired product in a yield of 86%, although an extended reaction time of 60 min was required. Performing the reaction in a polar solvent therefore afforded improved yields of the product as well as enhancing the reaction rate. The use of polar protic solvents such as water and ethanol accelerated the reaction within a minimum reaction time at 100 °C to give the desired product **3a** in 93% and 91% yields, respectively. According to the principles of green chemistry, water was selected as the best reaction medium for further evaluation. Based on these experiments, the optimal

Table 1

Optimization of the reaction conditions for the synthesis of **3a**.

Entry	Solvent	T (°C)	Catalyst (mol%)	Time (min)	Yield [a] (%)
1	H$_2$O	100	0	120	NR [b]
2	H$_2$O	100	β-CD (1)	30	NR [b]
3	H$_2$O	100	SBE-β-CD (1)	30	56
4	H$_2$O	100	β-CD-BSA (0.5)	30	85
5	H$_2$O	100	β-CD-BSA (1)	30	93
6	H$_2$O	100	β-CD-BSA (2)	30	93
7	—	100	β-CD-BSA (1)	60	86
8	Toluene	100	β-CD-BSA (1)	100	65
9	Cyclohexane	Reflux	β-CD-BSA (1)	100	70
10	THF	Reflux	β-CD-BSA (1)	60	76
11	MeCN	Reflux	β-CD-BSA (1)	60	85
12	DMF	100	β-CD-BSA (1)	60	82
13	CH$_3$CH$_2$OH	Reflux	β-CD-BSA (1)	30	91
14	HOCH$_2$CH$_2$OH	100	β-CD-BSA (1)	30	90

Reaction conditions: benzaldehyde (2 mmol), dimedone (4 mmol), solvent-free or solvent (2 mL).

[a] Isolated yield.

[b] No reaction was observed.

reaction conditions for the formation of 1,8-dioxo-octahy-droxanthenes were determined to be 1 mol% of the β-CD-BSA catalysts in water at 100 °C.

To assess the efficiency and the generality of the catalyst, we applied the optimal protocol to a variety of substituted aromatic aldehydes and active methylene carbonyl compounds, and the results of these experiments are summarized in Table 2. It revealed that aromatic aldehydes bearing an electron-donating or electron-withdrawing substituent reacted smoothly with dimedone or 1,3-cyclohexanedione to give the corresponding 1,8-dioxo-octahydroxanthene products in high yields. The results also showed that aromatic aldehydes bearing electron-withdrawing groups reacted at a greater rate to give higher yields of the 1,8-dioxo-octahydroxanthene products than those bearing electron-donating groups.

The efficiency of our newly synthesized catalyst for the synthesis of 1,8-dioxo-octahydroxanthenes was further evaluated by comparing its performance with several other catalysts reported in the literature. These comparison experiments were based on the synthesis of compounds **3h** from 4-nitrobenzaldehyde and dimedone, and the results are listed in Table 3. The results revealed that β-CD-BSA performed much more effectively than the other catalysts in terms of providing a very short reaction time, mild conditions and a high yield of the product.

Based on the results described above, we have proposed a plausible mechanism for the synthesis of 1,8-dioxo-octahydroxanthenes using the β-CD-BSA catalyst (Scheme 3). Considering the protic and acidic nature of β-CD-BSA, it was envisaged that one molecule of the enol tautomer of dimedone would be react with the activated aldehyde **I** to give the *ortho*-quinone methide (*o*-QMs) **II** via a Knoevenagel reaction. Intermediate **II** would then react with another molecule of dimedone via a Michael addition reaction to give intermediate **III**, which would undergo a cyclodehydration reaction to give the expected product **3**. In this case, the β-CD-BSA material would not only function as a protic acid but would also perform as a phase transfer catalyst [38,39].The β-CD-BSA material would therefore catalyze the reaction and participate in the formation of stable colloidal particles in the presence of the substrates in water, which would play an important role in accelerating the rate of the reaction. The formation of colloidal particles could be the main reason that β-CD-BSA exhibited such a high level of

Table 2

β-CD-BSA-catalyzed synthesis of 1,8-dioxo-octahydroxanthenes.

Entry	Ar	R	Product	Time (min)	Yield [a] (%)
1	C_6H_5	CH_3	**3a**	30	93
2	$2\text{-Cl-}C_6H_5$	CH_3	**3b**	30	94
3	$4\text{-Cl-}C_6H_5$	CH_3	**3c**	20	97
4	$2,4\text{-Cl}_2\text{-}C_6H_5$	CH_3	**3d**	30	95
5	$4\text{-F-}C_6H_5$	CH_3	**3e**	20	96
6	$2\text{-NO}_2\text{-}C_6H_5$	CH_3	**3f**	25	96
7	$3\text{-NO}_2\text{-}C_6H_5$	CH_3	**3g**	20	97
8	$4\text{-NO}_2\text{-}C_6H_5$	CH_3	**3h**	15	95
9	$4\text{-CH}_3\text{-}C_6H_5$	CH_3	**3i**	45	90
10	$4\text{-CH}_3\text{O-}C_6H_5$	CH_3	**3j**	60	95
11	$4\text{-OH-}C_6H_5$	CH_3	**3k**	40	90
12	$2\text{-OH-}C_6H_5$	CH_3	**3m**	40	88
13	$4\text{-N(CH}_3)_2\text{-}C_6H_5$	CH_3	**3n**	60	93
14	C_6H_5	H	**3l**	30	88
15	$2\text{-Cl-}C_6H_5$	H	**3o**	20	95
16	$4\text{-Cl-}C_6H_5$	H	**3p**	20	96
17	$2,4\text{-Cl}_2\text{-}C_6H_5$	H	**3q**	20	90
18	$4\text{-F-}C_6H_5$	H	**3r**	20	93
19	$2\text{-NO}_2\text{-}C_6H_5$	H	**3s**	20	92
20	$3\text{-NO}_2\text{-}C_6H_5$	H	**3t**	15	92
21	$4\text{-NO}_2\text{-}C_6H_5$	H	**3u**	15	94
22	$4\text{-CH}_3\text{-}C_6H_5$	H	**3v**	45	91
23	$4\text{-CH}_3\text{O-}C_6H_5$	H	**3w**	60	95
24	$2\text{-OH-}C_6H_5$	H	**3x**	60	90
25	$4\text{-OH-}C_6H_5$	H	**3y**	60	92
26	$4\text{-N(CH}_3)_2\text{-}C_6H_5$	H	**3z**	60	90

Reaction conditions: aldehyde (2 mmol), dimedone or 1 3-cyclohexanedione (4 mmol), β-CD-BSA (0.02 mmol), H_2O (2 mL), 100 °C.
[a] Isolated yield.

catalytic activity towards this reaction.

The ability of a catalyst to be recovered and reused is becoming increasingly important for the development of green processes. With this in mind, we evaluated the reusability of our newly developed catalyst using 4-nitrobenzaldehyde and dimedone as model substrates. After the separation of the products, the filtrate containing the catalyst was distilled to dryness under vacuum to allow for the removal of the water, and the resulting catalyst was used directly in the next run. As shown in Fig. 1, the results of these experiments revealed that the catalyst could be recycled up to five times without any significant decrease in the catalytic activity and yields in the range of 95% to 90%.

Table 3

Comparison of different catalysts for the synthesis of **3h**.

Entry	Catalyst	Condition	Time	Yield (%)	Ref.
1	β-CD-BSA	H_2O	15 min	95	This work
2	DBSA	H_2O/100 °C	6 h	94	[10]
3	[Et$_3$NH][HSO$_4$]	Solvent-free/100 °C	30 min	92	[16]
4	Cellulose sulfonic acid	Solvent-free/110 °C	5 h	95	[23]
5	MCM-41-SO$_3$H	H_2O/90 °C	60 min	50	[20]
6	HClO$_4$-SiO$_2$	H_2O/100 °C	1 h	68.2	[13]
7	Amberlyst-15	CH$_3$CN/reflux	5 h	94	[11]
8	L-Proline	ClCH$_2$CH$_2$Cl/60 °C	6 h	78	[18]
9	Fe^{3+}-montmorillonite	EtOH/100 °C	6 h	93	[12]
10	CAN supported HY-zeolite	Solvent-free/80 °C	45 min	93	[21]
11	Fe$_3$O$_4$@SiO$_2$-imid-PMA	EtOH/reflux	1.25 h	94	[22]
12	nano-TiO$_2$	Solvent-free/100 °C	15 min	96	[15]
13	CaCl$_2$	DMSO/90 °C	5 h	87	[19]
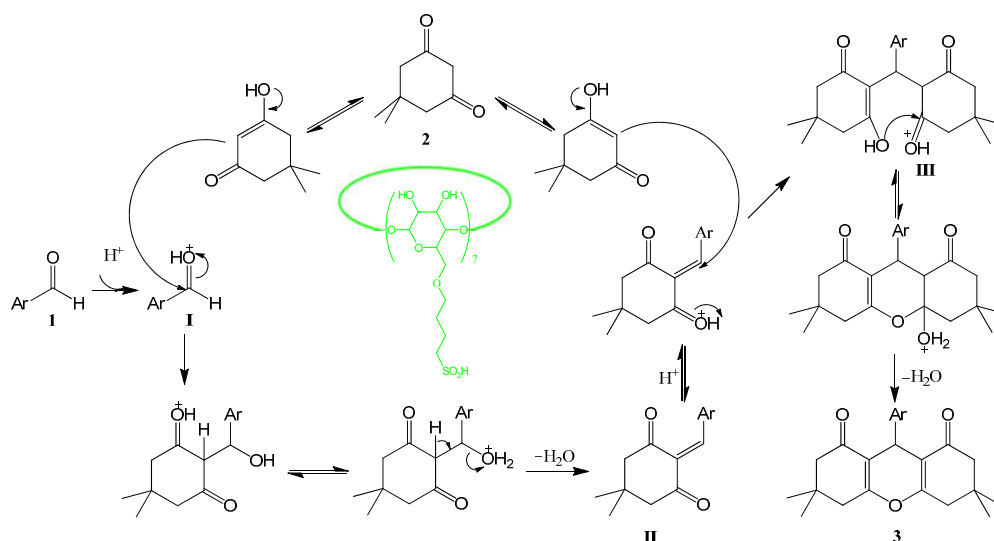
Scheme 3. Possible mechanism for the synthesis of 1,8-dioxo-octahydroxanthenes catalyzed by *β*-CD-BSA.
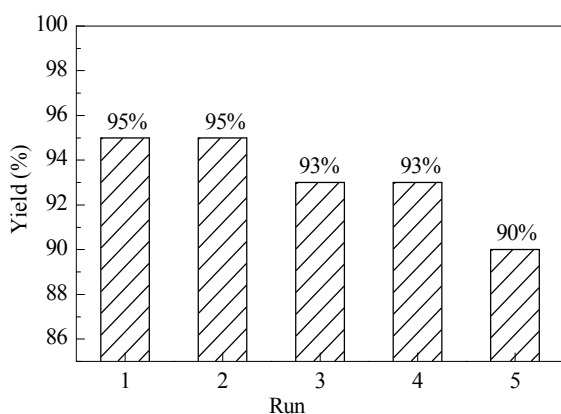
Fig. 1. Recyclability experiments using *β*-CD-BSA for the synthesis of **3h**.

4. Conclusions

We have developed a novel eco-friendly procedure for the synthesis of 1,8-dioxo-octahydroxanthenes via the one-pot condensation of aromatic aldehydes and active methylene carbonyl compounds using *β*-CD-BSA as a catalyst. The attractive features of this new protocol include a simple procedure, high catalytic activity, short reaction time, excellent yields, recyclable catalyst and its adaptability for the synthesis of a diverse set of 1,8-dioxo-octahydroxanthenes. This approach therefore represents a valuable addition to the existing processes for the synthesis of benzoxanthenes.

References

[1] Zelefack F, Guilet D, Fabre N, Bayet C, Chevalley S, Ngouela S, Lenta B N, Valentin A, Tsamo E, Dijoux-Franca M G. *J Nat Prod*, 2009, 72: 954

[2] Wang H K, Morris-Natschke S L, Lee K H. *Med Res Rev,* 1997, 17: 367

[3] Poupelin J P, Saint-Ruf G, Foussard-Blanpin O, Narcisse G, Uchida-Ernouf G, Lacroix R. *Eur J Med Chem*, 1978, 13: 67

[4] Zolfigol M A, Moosavi-Zare A R, Arghavani-Hadi P, Zare A, Khakyzadeh V, Darvishi G. *RSC Adv*, 2012, 2: 3618

[5] Liu J, Diwu Z, Leung W Y. *Bioorg Med Chem Lett*, 2001, 11: 2903

[6] Ahmad M, King T A, Ko D K, Cha B H, Lee J. *J Phys D,* 2002, 35: 1473

[7] Hatakeyma S, Ochi N, Numata H, Takano S. *J Chem Soc, Chem Commun*, 1988: 1202

[8] O'Callaghan C N, McMurry T B H. *J Chem Res Synop*, 1995: 214

[9] Li J J, Lu L M, Su W K. *Tetrahedron Lett*, 2010, 51: 2434

[10] Jin T S, Zhang J S, Xiao J C, Wang A Q, Li T S. *Synlett*, 2004: 866

[11] Das B, Thirupathi P, Mahender I, Reddy V S, Rao Y K. *J Mol Catal A,* 2006, 247: 233

[12] Song G Y, Wang B, Luo H T, Yang L M. *Catal Commun*, 2007, 8: 673

[13] Kantevari S, Bantu R, Nagarapu L. *J Mol Catal A*, 2007, 269: 53

[14] Soliman H A, Salama T A. *Chin Chem Lett*, 2013, 24: 404

[15] Khazaei A, Reza Moosavi-Zare A, Mohammadi Z, Zare A, Khakyzadeh V, Darvishi G. *RSC Adv*, 2013, 3: 1323

[16] Zhou Z Q, Deng X C. *J Mol Catal A*, 2013, 367: 99

[17] Mulakayala N, Murthy P V N S, Rambabu D, Aeluri M, Adepu R, Krishna G R, Reddy C M, Prasad K R S, Chaitanya M, Kumar C S, Rao M V B, Pal M. *Bioorg Med Chem Lett*, 2012, 22: 2186

[18] Das B, Kashanna J, Kumar R A, Jangili P. *Synth Commun*, 2012, 42: 2876

[19] Ilangovan A, Muralidharan S, Sakthivel P, Malayappasamy S, Karuppusamy S, Kaushik M P. *Tetrahedron Lett*, 2013, 54: 491

[20] Rostamizadeh S, Amani A M, Mahdavinia G H, Amiri G, Sepehrian H. *Ultrason Sonochem*, 2010, 17: 306

[21] Sivaguru P, Lalitha A. *Chin Chem Lett*, 2014, 25: 321

[22] Esmaeilpour M, Javidi J, Dehghani F, Nowroozi Dodeji F. *New J Chem*, 2014, 38: 5453

[23] Oskooie H A, Tahershamsi L, Heravi M M, Baghernejad B. *E J Chem*, 2010, 7: 717

[24] Hua G P, Li T J, Zhu S L, Zhang X J. *Chin J Org Chem*, 2005, 25: 716

[25] Simon M O, Li C J. *Chem Soc Rev*, 2012, 41: 1415

[26] Shekouhy M. *Catal Sci Technol*, 2012, 2: 1010

[27] Pan X Y, Lu C F, Nie J Q, Chen Z X, Yang G C, Dong N G, Shi J W. *Catal Commun*, 2014, 53: 72

[28] Mohammad N R, Yasamin B. *Appl Catal A*, 2014, 469: 183

[29] Wang Y L, Luo J, Liu Z L. *Appl Organomet Chem*, 2013, 27: 601

Graphical Abstract

Efficient synthesis of 1,8-dioxo-octahydroxanthenes catalyzed by *β*-cyclodextrin grafted with butyl sulfonic acid in aqueous media

Kai Gong *, Hualan Wang, Shuxin Wang, Ying Wang, Jinghua Chen
Jiangnan University; Hangzhou Normal University
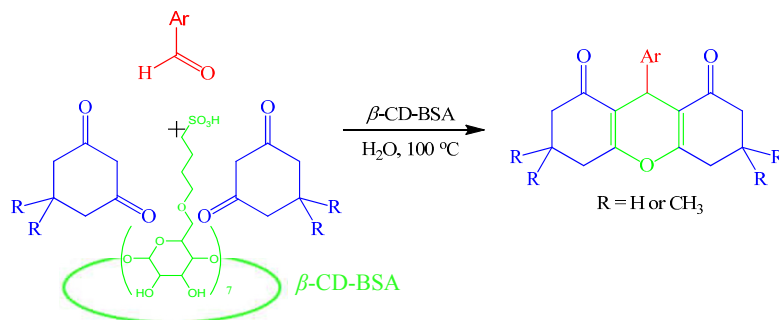
β-Cyclodextrin has been functionalized with butyl sulfonic acid to give an efficient eco-friendly catalyst (*β*-CD-BSA) for the synthesis of 1,8-dioxo-octahydroxanthenes via the one-pot condensation of aromatic aldehydes and active methylene carbonyl compounds in aqueous media.

[30] Ishii D, Ohashi C, Hayashi H. *Green Chem*, 2014, 16: 1764

[31] Bai L, Wyrwalski F, Lamonier J F, Khodakov A Y, Monflier E, Ponchel A. *Appl Catal B*, 2013, 138-139: 381

[32] Zhang G F, Luan Y X, Han X W, Wang Y, Wen X, Ding C R, Gao J R. *Green Chem*, 2013, 15: 2081

[33] Liu H M, Li Y M, Wu H, Liu J X, He D H. *Chin J Catal*, 2015, 36: 283

[34] Hapiot F, Bricout H, Menuel S, Tilloy S, Monflier E. *Catal Sci Technol*, 2014, 4: 1899

[35] Wu J, Du X L, Ma J, Zhang Y P, Shi Q C, Luo L J, Song B A, Yang S, Hu D Y. *Green Chem*, 2014, 16: 3210

[36] Asghari S, Tajbakhsh M, Kenari B J, Khaksar S. *Chin Chem Lett*, 2011, 22: 127

[37] Song A J, Wang J H, Liu C D, Deng L H. *Chin Sci Bull*, 2009, 54: 1362

[38] Blach P, Landy D, Fourmentin S, Surpateanu G, Bricout H, Ponchel A, Hapiot F, Monflier E. *Adv Synth Catal*, 2005, 347: 1301

[39] Kiasat A R, Nazari S. *Catal Sci Technol*, 2012, 2: 1056

Page numbers refer to the contents in the print version, which include both the English version and extended Chinese abstract of the paper. The online version only has the English version. The pages with the extended Chinese abstract are only available in the print version.