

Fabrication of activated carbon sulfuric acid as an excellent and novel solid acid catalyst, evaluating its catalytic activity in synthesizing 1,8-dioxo-octahydroxanthenes and 14-aryl-14*H*-dibenzo[a,j]xanthenes

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Abstract

In this work, for the first time, a novel and innovative procedure has been utilized to chemically functionalize activated carbon (AC) based on the sulfonation reaction, which can be used in catalytic reactions as a strong solid acid. For this aim, AC must pass three steps of oxidation, reduction, and sulfonation, respectively. Therefore, the AC first was oxidized, then reduced by lithium aluminum hydride, and eventually participate in the sulfonation reaction with chlorosulfonic acid. We utilized diverse analytical techniques such as FT-IR, XRD, TGA, XPS, and neutralization titration to characterize and confirm our claim that activated carbon was functionalized. The analysis results indicate that sulfonic acid groups were successfully anchored with covalent bonds on the AC's surface. The resulting catalyst was used to synthesize 1,8-dioxo-octahydroxanthenes and 14-aryl-14*H*-dibenzo[a,j]xanthenes and showed good activity and stability in these reactions. Also, the produced products showed acceptable and good yields (87–97%). Reusability without loss of catalytic activity and simple fabrication method are other advantages of this catalyst.

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Graphic abstract



Keywords Solid acid · Activated carbon · Xanthene · Green chemistry · Heterogeneous catalyst

Introduction

It is vivid to everyone that more attention should pay to more environmentally friendly processes in today's world, especially in the chemical industry [1, 2]. This trend focuses on what is known as "Green Chemistry" or "Sustainable Technology" [3, 4]. Catalysts can be considered one of the Green Chemistry pillars because they can be directed to advanced technologies to reduce chemical processes waste [1, 5–10]. For example, sulfuric acid is an extensively versatile catalyst for producing various chemicals in the industry. Over 15 million tons of this substance is exerted annually as a non-recyclable catalyst in different industries to produce various chemicals [11]. Remaining this catalyst in the reaction medium may cause problems such as corrosion and damage to equipment, and the separation of this catalyst and its reuse requires unique and costly methods [12, 13]. So a lot of products and energy are wasted. Among the types of catalysts, acid catalysts have a significant role in producing various industrial materials. Many reactions are catalyzed by traditional mineral acids such as H_2SO_4 , AlCl₃, HF, and HCl. These reactants have many problems, including toxicity, transport hazards,

storage, corrosivity, environmental damage, separation and cooling problems, and regeneration costs [14–18]. These acids are usually soluble in the organic reaction medium or remain as a separate phase and are eliminated during the water's cooling phase and require a significant alkali volume for subsequent neutralization. These problems limit the use of these catalysts in industry and necessitate replacing these catalysts with more advanced ones [1]. Replacing traditional mineral acids with solid acids is the right solution because solid acids do not have the traditional mineral acid problems that cause limit their use in industry. In recent decades, solid acids have been considered by many researchers. These types of catalysts can be utilized in many different reactions of acid-promoted [1, 11, 18-23]. They are green, stable, clean, and low-cost catalysts with low corrosion and higher selectivity and can be reused multiple times without loss of activity and easily removed from the reaction system for later use [24-28]. It has been specified that the type of support material utilized in solid acids is a vital factor in the efficiency of the generated supported catalyst in chemical reactions. There are diverse organiclinorganic supports that can be utilized for this purpose, such as silica, hydroxyapatite, zeolites, zirconia, polymers, and carbons [1]. Today, carbonaceous materials play an undeniable role in green chemistry and environmental studies [29-31]. Carbon-based solid acids are important for several reasons, including their inexpensive, phase compatibility with organic environments, abundance, and hydrophobicity. Amorphous carbon with sulfonic acid sites is a promising embedment for the sulfuric acid catalyst [22].

For the first time in this paper, we utilized activated carbon and generated activated carbon sulfuric acid (ACSA; AC-OSO₃H) as a heterogeneous solid acid. Due to the small pore size, board pore distribution, and high specific surface area, activated carbon has been utilized as an efficient and functional material in this catalyst. Affluence, availability, cost-effectiveness, non-toxic, phase compatibility with organic media, and hydrophobicity are other advantages of activated carbon. Benzoxanthenes and xanthenes are among the compounds that are of great importance due to their vast and vital applications in the biological and industry, such as anti-inflammatory activities [32], antibacterial [33], antiviral [34], anticancer [35], leuco dyes [36], laser technology [37], and sensitizers in photodynamic therapy [38]. Many methods have been reported to synthesize these two matters, but these methods have drawbacks such as harsh reaction conditions, prolonged reaction time, excessive use of catalysts, and low efficiency [39-43]. Nowadays, multi-component reactions (MCRs) have been considered to synthesize various compounds, including xanthenes [44]. In multi-component reactions, three or more reactants are combined in the same pot to produce the desired product. These reactions do not require intermediate separation, so energy consumption and reaction time are reduced. Compared to the multistage synthetic procedure, MCRs are a powerful synthetic method for synthesizing heterocyclic compounds due to their simplicity and high efficiency [45-47]. Therefore, in this paper, we fabricate sulfuric acid-based activated carbon and investigate its catalytic activity in synthesizing benzoxanthenes and xanthenes derivatives.

Experimental

Materials and equipment

All chemicals utilized in this work were of the utmost purity purchased by Merck. Activated carbon powder was (particle size: < 100 μ m, about 90%) purchased from Merck. Deionized distilled water was used throughout the work; X-ray diffractometer analysis was performed by (XRD) (38066 RIVA, d/G. Via M. Misone, 11/D (TN) ITALY) at room temperature. Mettler-TG 50 thermal analyzer was utilized for TGA analysis, and temperature range and condition analysis were 25–400 °C and a heating rate of 10 °C/min under the nitrogen atmosphere. FT-IR spectra were obtained from the Bruker IFS 66 FT-IR spectrometer in 400–4000 cm⁻¹. X-ray information was gauged on an STOE IPDS-II two-circle diffractometer at 120 K for high-resolution scans and survey scans. The pass energies were 20 eV and 160 eV, respectively. Titration was used to gauge the acidity of solid samples.

Treatment of AC

Oxidation of AC

In order to manufacture the desired catalyst, the oxidation treatment process must first be accomplished on activated carbon. Oxidation treatment was done with nitric acid because previous research has shown that nitric acid utilization makes the carbon further acidic [48]. The reason for oxidation is to create sites and moieties on the surface of activated carbon. Before oxidation, the purchased activated carbon was first rinsed with HCl (0.1 M) and NaOH (0.1 M) solutions to remove alkaline and acidic impurities, respectively. In the next step, the washed activated carbon was refluxed for 2 h in a solution of 30% w–v nitric acid. Eventually, it was rinsed with distilled water to achieve a neutral pH.

Reduction of AC

Lithium aluminum hydride (LiAlH₄) was utilized to reduce oxidized AC. For this purpose, 20 mg of oxidized AC was dispersed in toluene by ultrasonic apparatus (in a water bath) for 30 min, and then 5.0 mg of LiAlH₄ is added gradually. The resulting solution was stirred for an hour at ambient temperature, and then followed 2.0 mL of HCl (2 N) was added to the solution until it removed the remaining lithium and aluminum. Finally, the solution was filtered, rinsed with solvents of toluene, absolute ethanol, and acetone, respectively, and was placed in a vacuum oven at 80 °C overnight until the reduced AC was produced.

Sulfonation of AC

The equipment utilized for sulfonation of reduced AC was: Vacuum flask attached to the constant pressure dropping funnel and gas inlet tube. 220.5 mg (1.892 mmol) of chlorosulfonic acid was added dropwise to 1000 mg of reduced AC for 30 min at ambient temperature. HCl gas was immediately emitted from the reaction container and removed through the gas inlet tube, and directed to water as the adsorbent solution. After completion of the reaction, the creating compound was shaken for 30 min. Finally, a black solid of activated carbon sulfuric acid (ACSA) was generated (Fig. 1).

Catalytic reaction

Synthesize of 14-aryl-14H-dibenzo[a,j]xanthenes

The combination includes 2-naphthol (1 mmol), aldehyde (0.5 mmol), and activated carbon sulfuric acid (0.03 g) as catalyst was heated at 80 °C. TLC evaluated the reaction progress. After ending the reaction, the obtained mixture was rinsed with ethyl acetate. Then, to separate and recover the catalyst, the mixture was filtered.

Synthesize of 1,8-dioxo-octahydroxanthenes

The manner resembled that explained for synthesize 14-aryl-14*H*-dibenzo[a,j]xanthenes with the exclusion that 2-naphthol was supplanted with 5,5-dimethyl-1,3-cyclohexanedione.



Fig. 1 Preparation of ACSA

Results and discussion

Characterization of catalyst

FT-IR analysis

The FT-IR spectra obtained from AC at diverse stages of manufacturing are shown in Fig. 2. The 3436 cm⁻¹ and 1158 cm⁻¹ bands are assigned to the O–H stretch band and the C–O stretch band, respectively, which proves hydroxyl (-OH) groups' on the AC surface in the pristine AC (Fig. 2a). The reason for the hydroxyl groups' presence seems to the loading of atmospheric moisture on the surface or the oxidation of raw materials during refining [49]. Other bands at 1639 cm⁻¹, 1562 cm⁻¹, 1384 cm⁻¹, and 1406 cm⁻¹ are attributed to the C=O stretching vibration mode of quinone groups, C=C stretching vibration mode of aromatic rings, C–O–H bending vibration mode, respectively. For the oxidized AC (Fig. 2b), two bands emerged at 1717 cm⁻¹ and 1233 cm⁻¹, ascribed to the C=O and C–O stretching vibrations modes carboxylic groups, respectively. After oxidation, increasing hydroxyl groups has led to increased relative intensities of peaks at 1233 cm⁻¹ and 3425 cm⁻¹. This



Fig. 2 FT-IR spectra of pristine (a), acid-treated (b), reduced (c), and sulfonized (d) ACs

evidence confirms that the surface of the AC is activated by acid treatment and functionalized. Reduction of the COOH groups to OH groups in the reduced AC (Fig. 2c) confirmed by the band's vanish at 1715 cm⁻¹ and the advent of a band at 942 cm⁻¹, allocated to the stretching vibration mode of C–O. The sulfonation of AC (Fig. 2d) shows the O=S=O asymmetric and symmetric stretching bands at 1190–1220 cm⁻¹ and 1080–1109 cm⁻¹, respectively, and a peak at 600–700 cm⁻¹ that related to the S–O stretching mode. The spectrum also displays a broad OH stretching band around 3700 cm⁻¹ and 2800 cm⁻¹.

XRD analysis

XRD pattern of sample AC and its sulfonated derivative are depicted in Fig. 3, and the identical peaks are perceived in both the pristine and sulfonic acid-anchored AC. These results mean that the structure of the AC core is preserved within the sulfonation process. The peaks in the XRD pattern corresponding to the Miller index value ascribed to the amorphous carbon.

TGA/DGT analysis

The thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) curve of the sulfonic acid functionalized AC are shown in Fig. 4. TGA and DGT were used to determine the stability of the support layer on the catalyst. Two weightloss peaks in the temperature range of 120 $^{\circ}$ C and 250 $^{\circ}$ C can be seen in Fig. 4,



Fig. 3 XRD diffraction pattern of AC and ACSA



Fig. 4 TGA and DTG pattern for ACSA

which could be due to the removal of moisture adsorbed on the surface of the catalyst and the degradation and removal of sulfonic acid groups, respectively.

XPS analysis

X-ray photoelectron spectroscopy (XPS) facilitates us to be aware of the presence of elements inside the material or elements that cover the surface of the material. XPS (C 1s) spectra for pristine AC, acid-treated AC, reduced AC, and sulfonated AC are shown in Fig. 5. The C 1s peaks shown in the pristine AC (Fig. 5a) can be converted to 285.0, 286.4, 287.8, 288.8, and 289.9 eV [50, 51]. The contribution of plasmon at 291.0 eV was negligible. In the acid-treatment curve (Fig. 5b), the peaks at around 288.1 and 289.6 eV are ascribed to the CO and COO groups, respectively. These peaks depict 6.78% and 4.55% carbon signals larger and more significant than the pristine AC (Table 1). Due to the enhancement in atomic oxygen content from 4.73% (pristine AC) to 14.03 % (acid-treated AC), it can be concluded that the acid treatment process has been successful and has led to the creation of more functional groups at the surface of AC (Table 2). After reduction, AC depicted the identical pattern with the attendance of O 1s and C 1s peaks (Fig. 5c). The reduction of carboxylic acid groups to alcoholic groups can be understood by decreasing the acidic ingredient at 289.6 eV and increasing the alcoholic components at 287.2 eV (Table 1). AC sulfonate (Fig. 5d) depicts the same pattern as the reduced pattern, except that a new peak (single S 2p) emerges at 168 eV corresponding to S–O with



Fig. 5 C 1 s XPS spectrum of pristine (a), acid-treated (b), reduced (c), and solfunized (d) ACs

•		u U	e		
Binding energy (eV) and assignation	C SP ² 285	C SP ³ 286–286.4	C–O 287–287.2	-C=O 288.48-288.69	CO–O 289.3–289.9
Pristine	74.03	8.6	3.08	2.21	2.01
Acid-treated	69.13	12.08	6.78	5.62	4.55
Reduced	69.44	11.67	7.30	5.83	4.17
Sulfonized	70.25	11.38	7.27	4.63	4.89

 Table 1
 Summary of the relative percentage of carbon and assignation

Table 2Summary of theelement composition of the ACs

Element (Atom%)	С	0	S
Pristine	95.27	4.73	_
Acid-treated	85.97	14.03	-
Reduced	86.06	13.94	-
Sulfonized	75.76	63.8	3.10

an elemental percentage of 3.1%. Accordingly, after the sulfonation process, the catalyst contains SO₃H groups, and all sulfur atoms exist in SO₃H groups [52]. Due to the increase in the atomic percentage of oxygen in the sulfonated state (63.8%) compared to the pristine state (4.37%), it is quite evident that the sulfonic groups were immobilized on the AC.

Neutralization titration

Based on the neutralization titration results, the acidity of this catalyst is equal to 2.385 mmol.g⁻¹, which demonstrates that the fabricated catalyst acts as a robust solid acid with a high density of acidic sites.

Catalytic activity

As a first attempt to study the yield and reaction time, one equivalent of 2-naphthol and 0.5 equivalent of 4-chlorobenzaldehyde was examined at 80 °C under the solvent-free conditions, and low yield (< 30%) was obtained after 9 h (Table 3, Entry 1). In order to optimize the reaction and meliorate the product's efficiency, ACSA (0.2 g) was added, and the reaction was performed under the same conditions. A remarkable betterment was observed in the reaction time and product yield (Table 3, Entry 2). With this promising result, more evaluations about the optimal reaction conditions were performed, and the reaction was accomplished with diverse amounts of catalysts. When the catalyst amount was reduced from 0.2 to 0.03 g, the reaction time was improved from 45 to 20 min, and the product's yield was improved from 80 to 97% (Table 3). By further reducing the amount of catalyst to 0.02, the efficiency even reached 97%, but suddenly the reaction time increased to 85 min (Table 3, Entry 5), so the optimal amount of catalyst for this reaction was 0.03 g.

The next step after optimizing the amount of catalyst is to specify the application range of the ACSA. An extensive range of aromatic aldehydes was exposed to react with 2-naphthol in the attendance of the optimum amount of ACSA, at 80 °C under the solvent-free conditions to produce corresponding 14-aryl-14*H*-dibenzo[a,j]xanthenes (Fig. 6). The results are summarized in Table 4. It is specified that various

Table 3Influence of the amountof ACSA on the synthesisof 14-aryl-14H-dibenzo[a,j]xanthenes	Entry	ACSA (g)	Time (min)	Yield (%) ^a
	1	_	540	Trace
	2	0.2	45	80
	3	0.1	30	85
	4	0.05	24	92
	5	0.03	20	97
	6	0.02	85	97

4-chlorobenzaldehyde-2-naphthol = 0.5:1, Solvent-free, 80 °C ^aRefers to isolated yields



Fig. 6 Synthesis of 14-aryl-14H-dibenzo[a,j]xanthene catalyzed by ACSA

substitutions in the aryl group of aldehydes have not shown much impact on the generation of the ultimate product and afford the anticipated product in good yields.

The reaction of diverse aromatic aldehydes with 5,5-dimethyl-1,3-cyclohexanedione instead of 2-naphthol was performed in solvent-free conditions at 80 °C caused 1,8-dioxo-octahydroxanthene derivatives were created with excellent yield and after a short time (Fig. 7, Table 5).

All products were separated by filtration and were identified by spectroscopic methods such as FT-IR, ¹HNMR, ¹³CNMR, and CHN and compared with reference data (Figures 1S–38S). Also, product **5g** (Entry 8, Table 5) was adopted to determine the structure by X-ray single-crystal diffraction (Fig. 8).

Mechanism of reactions

Possible and acceptable mechanisms for 14-aryl-14*H*-dibenzo[a,j]xanthene and 1,8-dioxo-octahydroxanthene synthesis are proposed in Schemes 1 and 2, respectively. Both mechanisms are almost identical and generally involve a Knoevenagel condensation, a Michael addition, and finally, a cyclocondensation reaction. Also, the role of ACSA catalyst in these two mechanisms is similar: to enhance the carbonyl group's electrophilicity by protonation and promote the addition of nucleophiles to the aldehyde. In the generation process of 14-aryl-14*H*-dibenzo[a,j]xanthene (Scheme 1), first, due to the nucleophilic addition of a β -naphthol molecule to an ACSA-activated aldehyde, intermediate **I** is formed, and then after dehydration, intermediate **II** is created (Knoevenagel condensation). The nucleophilic attack of the second β -naphthol on the β -carbon of the existing α,β -unsaturated carbonyl group in activated intermediate **II** results in the formation of intermediate **III**, which ultimately desired product **IV** is generated by the conversion of intermediate **III** by a cyclocondensation reaction.

The same is true of the 1,8-dioxo-octahydroxanthene synthesis mechanism. For this purpose, the aldehyde first is activated by the ACSA catalyst and attacked by the dimedone molecule as the nucleophile, forming an intermediate **I**. Then, by removing a molecule of water, the Knoevenagel condensation is completed, and the intermediate of **II** is created. Another dimedone molecule then reacts with intermediate **II** by Michael addition, resulting in produced intermediate **III**. Finally, the conversion of intermediate **III** to the 1,8-dioxo-octahydroxanthene **IV**

Entry	Aromatic aldehyde	Product	Time (min)	Yield (%) ^b
1	СНО		30	95
2	H ₃ C CHO	CH ₃ 4b	40	92
3	CI CHO		20	97
4	CI CHO	CI CI CI CI CI CI CI CI CI CI CI CI CI C	70	93
5	O ₂ N CHO		17°	94
6	CHO	NO, O 4f	30	90
7	F CHO		10	98
8	NC	CN CN CN CN CN CN CN CN CN CN CN CN CN C	50°	92
9	Br	Br U U U U U U U U U U U U U U U U U U U	21	89
10	MeO	OMe CHARACTER 4j	100	87
11	CI CHO		20	94

 Table 4
 ACSA catalyzed synthesis of 14-aryl-14H-dibenzo[a,j]xanthene^a

Table 4 (continued)

^aSome of the products were characterized by IR, ¹H NMR, and ¹³C NMR spectroscopic data, CHN, and melting points

^bYields refer to isolated products

^cThe reactants and catalyst were grinding thoroughly before heating



Fig. 7 Synthesis of 1,8-dioxo-octahydroxanthene catalyzed by ACSA

is done through the cyclocondensation reaction. In general, it can be declared that the catalyst facilitates the formation of an intermediate of I in both reactions by activating the aldehyde and enhancing the nucleophilic attack on it, improving the rate of both reactions.

Catalytic activity comparison

In order to compare the catalytic activity of ACSA with other works for the synthesis of 14-aryl-14*H*-dibenzo[a,j]xanthene and 1,8-dioxo-octahydroxanthene compounds, a summary of the results was gathered in Tables 6 and 7, respectively. Table 6 shows that the yield and time required for 14-phenyl-14*H*-dibenzo[a,j] xanthene (**4a**) synthesis are lower than the other catalysts.

To compare the catalytic activity of the catalyst with other works, we adopted product 5a as a representative of the 1,8-dioxo-octahydroxanthene, and the results of this comparison are summarized in Table 7. As can be observed, the reaction yield of this catalyst is better than other catalysts, and the reaction time is faster than others.

Reusability of catalyst

Catalyst recycling is an essential issue for heterogeneous catalysts so that the catalyst can be removed with a simple decanter, and after rinsing with acetone and air drying without the need for any deactivation, it can be used five times (Table 8).

Er	ntry	Aromatic aldehyde	Product	Time (min)	Yield (%) ^b
	1	CHO		40	97
	2	H ₃ C CHO	CH ₃ 0 0 0 5b	60	95
	3	CI CHO		55	95
	5	O ₂ N CHO	NO ₂	30 °	90
	6	NO ₂ CHO	5e	40	91
	7	F CHO	5f	20	92
	8	NC	SN Sg	53 °	97
	9	Br	Br O O O O Sh	90	97
:	10	CI		40	92

 Table 5
 ACSA catalyzed synthesis of 1,8-dioxo-octahydroxanthene^a

Table 5 (continued)

^aSome of the products were characterized by IR, ¹H NMR, and ¹³C NMR spectroscopic data, CHN, and melting points

^bYields refer to isolated products

^cThe reactants and catalyst were grinding thoroughly before heating



Fig. 8 X-ray structure of 5 g

Conclusion

Based on the demands of industries for cost-effective and green methods, recycling and recovery of sulfuric acid are important issues in developed countries and industries. This study is the first, which illustrates the utilization of the activated carbon as a support for sulfuric acid and shows its application in the synthesis of 14-aryl-14*H*-dibenzo[a,j]xanthenes and 1,8-dioxo-octahydroxanthenes. Features that make the catalyst stand out are stability and high catalytic activity, easy and fast preparation method, and cost-effectiveness. This catalyst was confirmed by FT-IR, XRD, TGA, XPS, and neutralization titration technique, and product synthesis was authenticated with information of FT-IR, ¹HNMR, ¹³CNMR, and CHN spectroscopy. The functionalization of activated carbon by hydroxyl groups also opens up new approaches to their modification.



[Proposed mechanism for 14-aryl-14*H*-dibenzo [a,j] xanthenes synthesis]

Scheme 1 Proposed mechanism for 14-aryl-14*H*-dibenzo[a,j]xanthene synthesis



[Proposed mechanism for 1,8-dioxo-octahydroxanthenes synthesis]

Scheme 2 Proposed mechanism for 1,8-dioxo-octahydroxanthene synthesis

Entry	Catalyst	Conditions	Time	Yield (%)	Ref
1	SBA-15/SO ₃ H	Dichloroethane, 85 °C	24 h	95	[42]
2	FeCl ₃	Solvent-free, 100 °C	10 h	91	[39]
3	Sulfamic acid	Solvent-free, 125 °C	8 h	93	[53]
4	Selectfluor TM	Solvent-free, 125 °C	8 h	93	[54]
5	Silica sulfuric acid	Solvent-free, 80 °C	45 min	89	[55]
6	PPA/SiO ₂	Solvent-free, 120 °C	30 min	90	[40]
7	ACSA	Solvent-free, 80 °C	30 min	95	This work

Table 6 Comparison of ACSA with other works for 14-phenyl-14H-dibenzo[a,j]xanthene synthesis

 Table 7
 Comparison of ACSA with other works for the 1,8-dioxo-octahydroxanthene synthesis

Entry	Catalyst	Conditions	Time	Yield (%)	Ref
1	Nickel NPs@N-doped TiO ₂	EtOH, 80 °C, reflux	2.5 h	85	[56]
2	SA@Sawdust	Ethanol/reflux	50 min	92	[57]
3	[Bmim]HSO ₄	Solvent-free, 80 °C	3 h	85	[58]
4	Silica sulfuric acid	Solvent-free, 80 °C	1 h	97	[55]
5	ACSA	Solvent-free, 80 °C	40 min	97	This work

Table 8 Reusability of ACSA in the synthesis of xanthenes derivatives	Run	1	2	3	4	5
	Yield (%) ^a	97	97	95	92	92

4-chlorobenzaldehyde-2-naphthol = 0.5:1, Solvent-free, 80 °C ^aRefer to isolated yields

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Declaration

Conflict of interest All authors are aware of the submission and agree to its publication, and have no conflicts of interest.

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