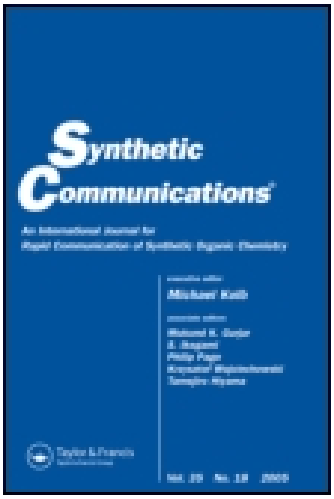


Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Perchloric Acid-Catalyzed Synthesis of 9-Aryl Xanthenes-9H-3,6-diol and 1,3,6,8-Tetraol in Water

Nikhil Vidyasagar [a] , Rabindra Nanda [a] , Rajesh Mangal [a] & Muthu K. Kathiravan [b]

[a] Padmashree Dr. D. Y. Patil Institute of Pharmaceutical Sciences and Research , Pimpri , Pune , India

[b] Sinhgad College of Pharmacy , Pune , India

Accepted author version posted online: 10 Jan 2012.Published online: 17 Aug 2012.

To cite this article: Nikhil Vidyasagar , Rabindra Nanda , Rajesh Mangal & Muthu K. Kathiravan (2012) Perchloric Acid-Catalyzed Synthesis of 9-Aryl Xanthenes-9H-3,6-diol and 1,3,6,8-Tetraol in Water, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 42:21, 3157-3165, DOI: 10.1080/00397911.2011.578326

To link to this article: http://dx.doi.org/10.1080/00397911.2011.578326

Synthetic Communications®, 42: 3157–3165, 2012

ISSN: 0039-7911 print/1532-2432 online
DOI: 10.1080/00397911.2011.578326

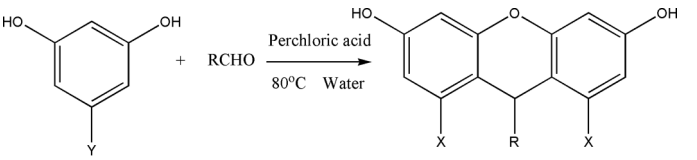
Taylor & Francis
Taylor & Francis Group

PERCHLORIC ACID–CATALYZED SYNTHESIS OF 9-ARYL XANTHENES-9*H*-3,6-DIOL AND 1,3,6,8-TETRAOL IN WATER

Nikhil Vidyasagar,[1] Rabindra Nanda,[1] Rajesh Mangal,[1] and Muthu K. Kathiravan[2]

[1]*Padmashree Dr. D. Y. Patil Institute of Pharmaceutical Sciences and Research, Pimpri, Pune, India*
[2]*Sinhgad College of Pharmacy, Pune, India*

GRAPHICAL ABSTRACT



X = H-Resorcinol and X = OH- Phloroglucinol

Abstract *Efficient syntheses of xanthenes have been described using a catalytic amount of perchloric acid in water. The high temperature and lengthy reaction time normally required for formation of xanthenes derivatives are not necessary when using a catalytic amount of perchloric acid. The method is relatively inexpensive, easily available, nonvolatile, nonexplosive, and thermally robust to catalyze the reaction at 80 °C by simple heating with good to excellent yields. The advantages of the reaction involve simple reaction protocol, simple workup, and improved synthesis in the presence of perchloric acid as catalyst.*

Keywords Perchloric acid; phloroglucinol; resorcinol; water; xanthenes

INTRODUCTION

The reaction between aldehydes and phenols is generally catalyzed by an acid or base to give cyclic oligomers.[1] Homogeneous acid catalysts such as H_2SO_4, HCl, and BF_3 are commonly used for organic synthesis. Xanthenes and benzoxanthenes are oxygen-containing heterocyclic ring systems possessing therapeutic and pharmaceutical properties such as antiviral,[2] antibacterial,[3] and anti-inflammatory activities.[4] They are also used as leuco-dyes in laser technology,[5] as antagonists of the paralyzing action of zoxazolamine,[6] and in fluorescent materials for visualization of biomolecules.[7] Photodynamic therapy (PDT) is a method of treating tumors

Received December 3, 2010.

Address correspondence to Muthu K. Kathiravan, Department of Pharmaceutical Chemistry, AISSMS's College of Pharmacy, Kennedy Road, Near RTO, Pune 411001, India. E-mail: drmkkathir@gmail.com

by combined use of a photosensitizer and light. These compounds are used as sensitizers in PDT.[8] In this method, photosensitizers are injected directly into malignant tissue and a specific wavelength of light that excites the photosensitizer drug is used, thereby killing the tumor cells.[9] The xanthene dyes are utilized as agricultural bactericides and also extracted from the natural sources such as soil and plants such as *Indigofera longeracemosa.*[10]

The literature methods for the synthesis of benzoxanthenes include the reaction of 2-naphthol with formamide,[11] 2-naphthol-1-methanol,[12] and carbon monoxide.[13] Certain improvements suggested to overcome the hazards associated with these reactions include mixing 2-naphthol with aldehydes in the presence of a catalyst, such as amberlyst,[14] sulfamic acid,[15] molecular iodine,[16] and AcOH–H_2SO_4.[1] All of these methods suffer from one of the following drawbacks, such as long reaction time, toxic reagents, solvents, and poor yields.[16–17]

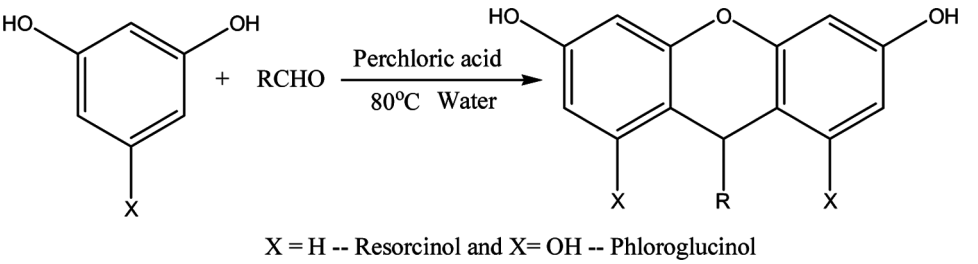
Other methods for the synthesis of xanthenes are (1) inter- or intramolecular trapping of arynes by phenols or aldehydes,[18] (2) Pd-catalyzed cyclization of polycyclic aryl triflate esters,[19] (3) Yb-catalyzed reaction of 2-naphthol and aldehydes,[20] and (4) reaction of 2-tetralone and salicylaldehydes under acidic conditions.[21] Although these methods are efficient for the synthesis of xanthenes, the application scope is limited to the synthesis of either 9-aryl- or 9-alkyl-substituted xanthenes. Therefore, the development of a general method for the synthesis of both 9-aryl- and 9-alkyl-substituted xanthenes is highly desirable for chemical library synthesis. Recently iron-catalyzed, microwave-promoted cascade benzylation–cyclization of phenols is reported in which benzyl acetates, benzyl bromides, and benzyl carbonates are used as benzylating reagents.[22]

The organic reactions in aqueous media have attracted much attention in synthetic organic chemistry, because water is one of the most abundant, cheapest, and environmentally friendly solvents and it exhibits unique reactivity and selectivity.[23] Recently Bigdeli et al. reported synthesis of benzoxanthenes under solvent-free condition at 125 °C.[24]

In continuation of our work exploring water as a solvent,[25] we herein report for the first time perchloric acid–catalyzed synthesis of 9-aryl xanthenes-9*H*-3,6-diol and 9-aryl xanthenes-9*H*-1,3,6,8-tetraol (Scheme 1) derivatives in water.

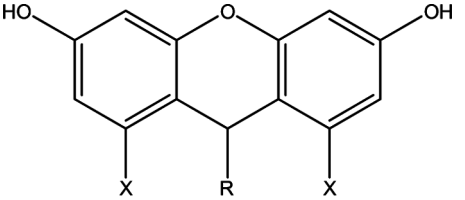
RESULTS AND DISCUSSION

An efficient method using catalytic amount of perchloric acid for the synthesis of 9-aryl xanthenes-9*H*-3,6-diol and 9-aryl xanthenes-9*H*-1,3,6,8-tetraol in water is reported. Aromatic aldehydes carrying different functional groups including electron-donating (EDG) and electron-withdrawing groups (EWG) were subjected to study with resorcinol and phloroglucinol. The investigated reaction was compared under similar reaction conditions in the presence of three different catalysts, oxalic acid, alum, and perchloric acid. The results are presented in Table 1. The reaction employing perchloric acid as catalyst is substantially faster (25–30 min), gives better yields (75–88%), and is nearly quantitative after 25 min. In this event, the choice of catalyst was crucial for an efficient reaction. Among the catalysts examined so far, perchloric acid gave the best result and the possible mechanism is depicted in Scheme 2. Perchloric acid protonates the aldehyde carbonyl group, which is followed

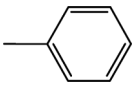
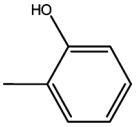
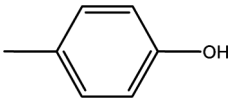
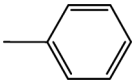
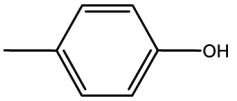


Scheme 1. Synthesis of 9-aryl xanthenes-9*H*-3,6-diol and 9-aryl xanthenes-9H-1,3,6,8-tetraol.

Table 1. Comparisons of the methods for the synthesis of the 9-aryl xanthenes-9*H*-3,6-diol and 9-aryl xanthenes-9*H*-1,3,6,8-tetraol



X = H--**1a-c**
X = OH--**2a-b**

Compound	R	Oxalic acid		Alum		Perchloric acid	
		Reaction time (min)	Yield[a] (%)	Reaction time (min)	Yield[a] (%)	Reaction time (min)	Yield[a] (%)
1a		110	76	160	78	30	86
1b		100	74	150	80	30	88
1c		105	78	140	80	25	85
2a		110	75	160	64	30	75
2b		105	78	140	72	25	80

[a]Isolated yields.

by the attachment of the phenolic aromatic ring. Attack of another H^+ ion from perchloric acid to hydroxyl group forms a carbocation and thus initiates the attachment of the other phenolic ring. Thus the xanthenes ring is formed finally by the removal of a molecule of water from its intermediate.

The other reactions gave only 64–80% yield after 2–3 h. This effect might be due to the effect of the perchloric acid used, which is known for its complexing ability. Further reactions were carried out using a catalytic amount of perchloric acid. However, the reaction mixture was heated at 80 °C for the synthesis of xanthenes.

In all cases, the desired products were synthesized in good yields within a short period of time. Another advantage of the reaction is the workup procedure, which is simple and includes basic filtration to separate the product. The reaction worked well with aromatic aldehydes (Table 2), giving products in 82–96% yields.

The presence of EWG (20 min, 84%) on the aromatic aldehydes went to completion at faster rate than EDG donating groups. Also the presence of o-EWG (20 min, 80%.) accelerated the reaction rate more than m,p-EWG (25 min, 83%). The reaction is general, tolerates a variety of functional groups, and is applicable to aldehydes containing EWG as well as EDG. The increase in bulkiness of the substituents has no significant effect on rate of reaction.

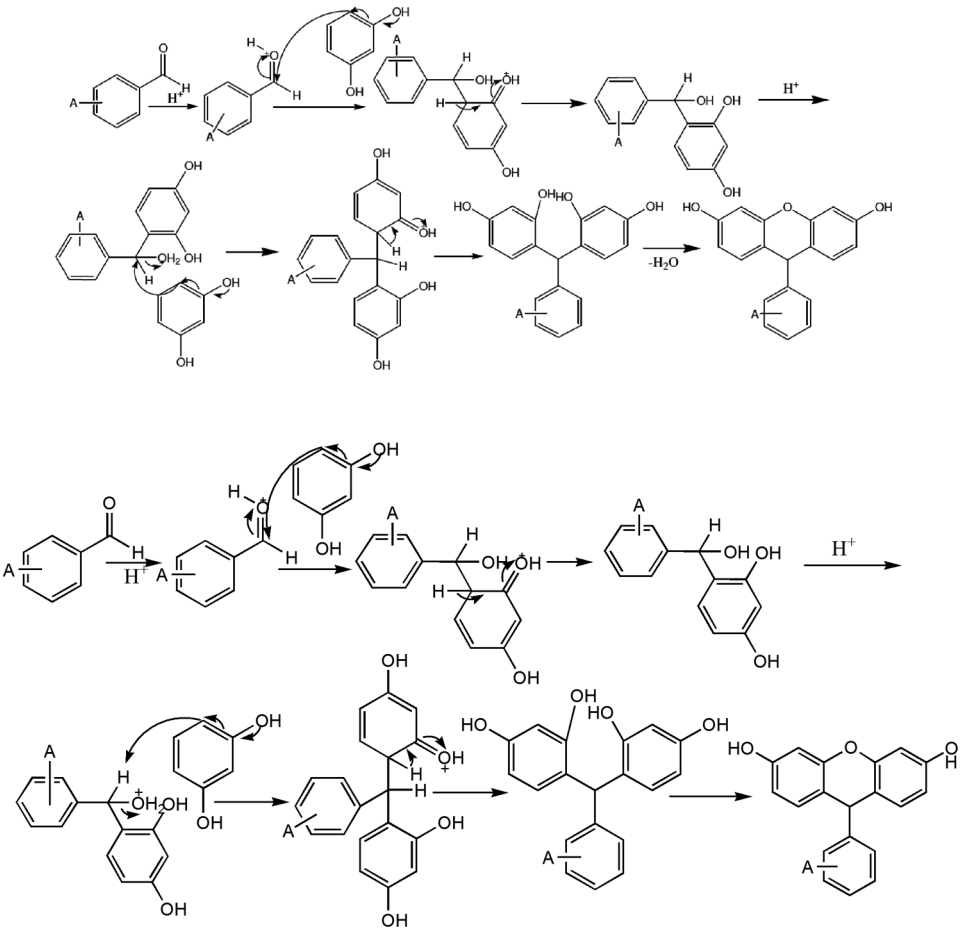
The condensation was achieved under classical heating with water as solvent in the presence of oxalic acid, alum, and perchloric acid, the latter being a much more efficient procedure. No products could be isolated with the same temperature conditions with oxalic acid and alum after 30 min, but lesser yields were obtained after an extended period (2–3 h) at high temperatures (Table 1). The high temperatures and lengthy reaction time required for formation of xanthenes derivatives are easily obtained with in a shorter time using a catalytic amount of perchloric acid. The process is amenable to scale-up and can be gainfully employed to synthesize a library of xanthene analogs.

EXPERIMENTAL

Melting points were determined with a Veego melting-point apparatus (VMP PM, 32/1104) and are uncorrected. Thin-layer chromatography (TLC) was carried out using silica gel (G-60 mesh). An Rf value was calculated for each compound using n-hexane–ethyl acetate (1:1) as solvent, and the spots were located using iodine vapor. Infrared (IR) spectra in KBr were recorded on a Fourier Transform (FT)–IR spectrophotometer with diffuse reflectance attachment (Shimadzu 8400S). ^{1}H NMR spectra were obtained using Bruker Avance II 400 NMR spectrometer with dimethylsulfoxide (DMSO-d_6) as solvent. Chemical shifts were expressed in parts per million relative to tetramethylsilane (TMS) as internal standard. Mass spectra ware obtained on a double-focusing magnetic sector mass spectrometer using direct insertion probe with electron impact ion source operating at 70 eV.

Synthesis of 9-Aryl Xanthenes-9*H*-3,6-diol and 9-Aryl Xanthenes-9*H*-1,3,6,8-tetraol

In a typical procedure, resorcinol/phloroglucinol (10 mmol) and substituted aldehydes (10 mmol) were dissolved in water (5 ml) and stirred. A catalytic amount



Scheme 2. Reaction mechanism.

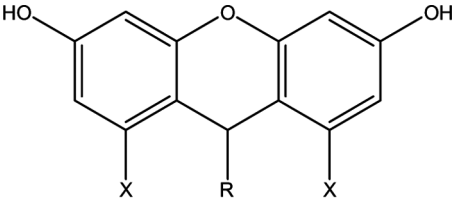
of perchloric acid 60% (two drops) was added to the stirred solution. The reaction mixtures were heated at 80 °C for an appropriate time. Solid precipitate starts separating after 20 min. The progress of the reaction was monitored by thin-layer chromatography (TLC). The solid precipitate obtained was filtered, washed with water, dried, and recrystallized from ethanol.

The structures of the synthesized xanthene analogs and their characteristic properties are given in Table 2.

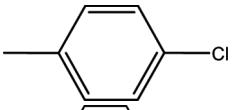
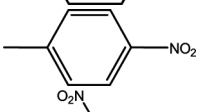
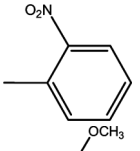
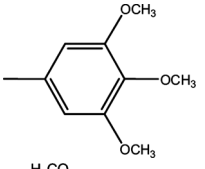
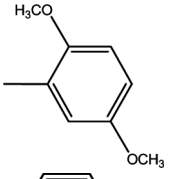
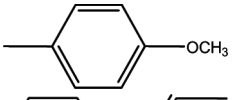
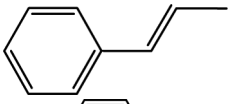
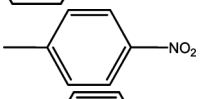
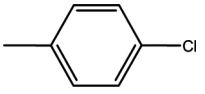
Data for Compounds 1a–1e

9-Phenyl-9H-xanthene-3,6-diol (1a). Orange powder; IR (KBr): υ/cm^{-1} = 3475–3224 (OH), 3091–3029 (CH), 1610, 1514, 1429 (ring C=C), 1076 (ether C-O) 840, 748, 702 (CH); ^{1}H NMR (DMSO-d_6, 300 MHz): δ ppm = 5.15 (b.s, 2H, -OH), 5.76 (s, 1H, CH), 6.21–7.10 (m, 11H, Ar-H), 6.32 (s, 2H), 6.39 (s, 2H), 6.90

Table 2. Physical properties of 9-aryl xanthenes-9*H*-3,6-diol and 9-aryl xanthenes-9*H*-1,3,6,8-tetraol synthesized using perchloric acid

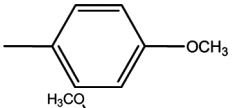
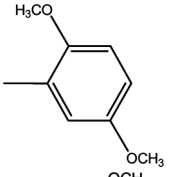
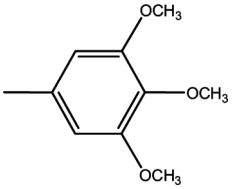
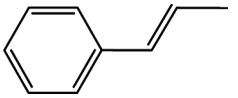


X = H--**1a-j**
X=OH--**2a-h**

Compound	R	Reaction time (min)	Melting point (°C)[a]	Yield (%)[b]
1d		25	210–211	84
1e		25	214–215	83
1f		20	190–191	80
1 g		35	222–224	90
1 h		35	200–202	86
1i		35	145–146	88
1j		30	255–257	90
2c		25	213–214	78
2d		25	270–271	82

(*Continued*)

Table 2. Continued

Compound	R	Reaction time (min)	Melting point (°C)[a]	Yield (%)[b]
2e		35	180–182	90
2f		35	232–233	86
2 g		30	244–246	85
2 h		30	240–242	89

[a]Melting points are uncorrected.
[b]Isolated yields.

(d, 2H, $J = 4.32$ Hz), 7.08 (s, 1H), 7.10 (s, 2H). EIMS (70 eV, m/z) 290 (M+, base peak), Anal. calcd. for $C_{19}H_{14}O_3$ C: 78.61; H, 4.86. Found: C, 78.21; H, 4.66.

9-(2-Hydroxyphenyl)-9H-xanthene-3,6-diol (1b). Off-white powder ; IR (KBr): $\upsilon/cm^{-1} = 3463–3205$ (OH), 3151–3037 (CH), 1606, 1508, 1454 (ring C=C), 1087 (ether C-O), 837, 756 (CH); ^{1}H NMR (DMSO-d_6, 300 Mz): δ ppm = 5.43 (s, 3H, -OH), 5.63 (s, 1H, CH), 6.21–6.87 (m, 10H, Ar-H), 6.27 (s, 2H), 6.49 (d, 2H, $J = 5.20$ Hz), 6.86 (d, 2H, J = 11.88 Hz). EIMS (70 eV, m/z) 306 (M+, base peak). Anal. calcd. for $C_{19}H_{14}O_4$: C, 74.50; H, 4.61. Found: C, 74.34; H, 4.51.

9-(4-Hydroxyphenyl)-9h-xanthene-3,6-diol (1c). Off-white powder, IR (KBr): $\upsilon/cm^{-1} = 3292–3178$ (OH), 3129–3076 (CH) 1604, 1510, 1431 (ring C=C), 1076 (ether C-O), 844, 577 (CH); ^{1}H NMR (DMSO-d_6, 300 MHz): δ ppm = 5.48 (s, 1H,-OH), 5.69 (s, 2H, -OH), 5.77 (s, 1H, CH), 6.13–6.82 (m, 8H, Ar-H), 6.37 (s, 2H), 6.53 (d, 2H, $J = 2.79$ Hz), 6.63 (d, 2H, $J = 6.36$ Hz), 6.82 (d, 2H, J = 6.36 Hz). EIMS (70 eV, m/z) 306 (M+, base peak). Anal. calcd. for $C_{19}H_{14}O_4$: C, 74.50; H, 4.61. Found: C, 74.34, H, 4.51.

9-(4-Chlorophenyl)-9H-xanthene-3,6-diol (1d). Yellow crystals; IR (KBr): $\upsilon/cm^{-1} = 3510–3328$ (OH), 3192–3045 (CH), 1612, 1496, 1431 (ring C=C), 1087 (ether C-O), 844, 767 (CH); 725 (C-l); ^{1}H NMR (DMSO-d_6, 300 MHz): δ ppm = 5.28 (s, 2H), 5.45 (s, 1H), 6.21–6.68 (m, 6H, Ar-H), 6.24 (s, 2H), 6.68 (d, 2H, $J = 2.31$ Hz), 6.90, 6.93 (d, 2H, $J = 8.01$ Hz), 7.18, 7.21 (d, 2H, $J = 10.14$ Hz). EIMS (70 eV, m/z) 324 (M+, base peak). Anal. Calcd. for $C_{19}H_{13}ClO_4$: C, 70.27; H, 4.03. Found: C, 70.21; H, 4.01.

9-(4-Nitrophenyl)-9H-xanthene-3,6-diol (1e). Yellow crystals; IR (KBr): $\upsilon/cm^{-1} = 3321–3228$ (OH), 3116–3078 (CH), 1604, 1512, 1431 (ring C=C), 1345 (symmetric NO), 1091 (ether C-O), 844 (symmetric NO), 744, 702, 628 (CH); ^{1}H NMR (DMSO-d_6, 300 MHz): δ ppm = 5.38 (s, 2H), 5.63 (s, 1H), 6.30–6.90 (m, 6H, Ar-H), 6.30 (s, 2H), 6.37 (s,2H), 6.83, 6.88 (d, 2H, $J = 16.14$ Hz), 7.30, 7.33 (d, 2H, $J = 8.37$ Hz), 8.18, 8.21 (d,2H, $J = 10.14$ Hz); EIMS (70 eV, m/z) 335 (M+, base peak), 305, 289, 179, 122, 107, 101, 93, 77, 30. Anal. calcd. for $C_{19}H_{13}NO_5$: C, 68.06; H, 3.91; N, 4.18. Found: C, 68.02; H, 3.78; N, 4.11.

Data for Compound 2a–2e

9-Phenyl-9H-xanthene-1,3,6,8-tetraol (2a). Brown powder; IR (KBr): $\upsilon/cm^{-1} = 3315–3203$ (OH), 3098–3024 (CH), 1610, 1492, 1444 (ring C=C), 1076 (ether C-O), 827, 748, 698 (CH); ^{1}H NMR (DMSO-d_6, 300 MHz): δ ppm = 5.10 (b.s, 4H, -OH), 5.41 (s, 1H, CH), 5.70 (s, 2H, CH), 5.88 (s, 2H, CH), 7.01–7.20 (m, 5H), 7.01 (d, 2H), 7.08 (s, 1H), 7.20 (d, 2H). EIMS (70 eV, m/z) 322 (M+, base peak). Anal. calcd. for $C_{19}H_{14}O_5$: C, 70.80; H, 4.38. Found C, 70.71; H, 4.30.

9-(4-Hydroxyphenyl)-9H-xanthene-1,3,6,8-tetraol (2b). Off-white powder; IR (KBr): $\upsilon/cm^{-1} = 3292–3196$ (OH), 3103–3076 (CH) 1612, 1510, 1438 (ring C=C), 1071 (ether C-O), 815, 567 (CH); ^{1}H NMR (DMSO-d_6, 300 MHz): δ ppm = 5.30 (s, 5H, -OH), 5.42 (s, 1H, CH), 5.71 (s, 2H, Ar-H), 5.83 (s, 2H, Ar-H), 6.61 (d, 2H), 6.88 (d, 2H). EIMS (70 eV, m/z) 338 (M+, base peak). Anal. calcd. for $C_{19}H_{14}O_6$: C, 67.45; H, 4.17. Found: C, 67.35; H, 4.12.

9-(4-Nitrophenyl)-9H-xanthene-1,3,6,8-tetraol (2c). Yellow powder; IR (KBr): $\upsilon/cm^{-1} = 3282–3191$ (OH), 3130–3078 (CH) 1608, 1512, 1451 (ring C=C), 1056 (ether C-O), 844, 577 (CH); ^{1}H NMR (DMSO-d_6, 300 MHz): δ ppm = 5.25 (s, 4H, -OH), 5.48 (s, 1H), 5.85 (s, 2H, CH), 5.92 (s, 2H), 7.50 (d, 2H, Ar-H), 8.10 (d, 2H, Ar-H), EIMS (70 eV, m/z) 367 (M+, base peak). Anal. calcd. for $C_{19}H_{13}NO_7$: C, 62.13; H, 3.57; N, 3.81. Found: C, 62.01; H, 3.48, N, 3.43.

9-(4-Chlorophenyl)-9H-xanthene-1,3,6,8-tetraol (2d). Yellow powder; IR (KBr): $\upsilon/cm^{-1} = 3286–3130$ (OH), 3192–3045 (CH) 1610, 1488, 1448 (ring C=C), 1095 (ether C-O), 831, 767 (CH); ^{1}H NMR (DMSO-d_6, 300 MHz): δ ppm = 5.28 (s, 4H, -OH), 5.45 (s, 1H), 5.95 (s, 2H), 6.10 (s, 2H), 7.21 (d, 2H), 7.46 (d, 2H). EIMS (70 eV, m/z) 356 (M+, base peak). Anal. calcd. for $C_{19}H_{13}ClO_5$: C, 63.97; H, 3.67. Found: C, 63.81; H, 3.51.

9-(4-Methoxyphenyl)-9H-xanthene-1,3,6,8-tetraol (2e). Buff powder; IR (KBr): $\upsilon/cm^{-1} = 3321–3106$ (OH), 3116–3078 (CH) 2877–2837 (OCH_3) 1604, 1508, 1442 (ring C=C), 1081 (ether C-O), 744, 702, 628 (CH); ^{1}H NMR (DMSO-d_6, 300 MHz): δ ppm = 3.80 (s, 3H, OCH_3), 5.30 (s, 4H, -OH), 6.10 (s, 2H), 6.30 (s, 2H) 6.75 (d, 2H), 6.95 (d, 2H), EIMS (70 eV, m/z) 352 (M+, base peak). Anal. calcd. for $C_{20}H_{16}O_6$: C, 64.07; H, 4.89. Found: C, 64.01, H, 4.81.

CONCLUSION

An efficient synthetic route for synthesis of diverse xanthenes was developed. The products obtained contain no impurities and are isolated with a simple procedure. The reaction products were obtained in good yields, in spite of starting materials with various functional groups. Biological evaluation of xanthene derivatives as antimicrobial, anti-inflammatory agents is currently in progress. Finally, the results provide further scope for the generation of chemical libraries and can be utilized as potential therapeutic agents. Thus, perchloric acid could efficiently catalyze the condensation reaction of phenols and aldehydes and may be helpful for catalyst design of xanthene derivatives.

REFERENCES

1. Sarma, R. J.; Baruah, J. B. *Dyes Pigm.* **2005**, *64*, 91–92.
2. Lambert, R. W.; Martin, J. A.; Merrett, J. H.; Parkes, K. E. B.; Thomas, G. J. *Wo PCT Int. Appl. 9706178, 1997; Chem. Abstr.* **1997**, *126*, 212377y
3. Hideo, T. Patent 56005480, 1981, *Chem. Abstr.* **1981**, *95*, 80922b.
4. Poupelin, J. P.; Saint-Rut, G.; Foussard-Blanpin, O.; Narcisse, G.; Uchida-Ernouf, G.; Lacroix, R. *Eur. J. Med. Chem.* **1978**, *13*, 67–71
5. Menchen, S. M.; Benson, S. C.; Lam, J. Y. L.; Zhen, W.; Sun, D.; Rosenblum, B. B.; Khan, S. H. U. S. Patent, 6,583,168, 2003, *Chem. Abstr.* **2003**, *139*, 54287f.
6. Saint-Ruf, G.; De, A.; Hieu, H. T. *Bull. Chim. Ther.* **1972**, *7*, 83–86
7. Bekaert, A.; Andrieux, J.; Plat, M. *Tetrahedron Lett.* **1992**, *33*, 2805–2806.
8. Ion, R. M.; Planner, A.; Wiktorowicz, K.; Frackowiak, D. *Acta Biochim. Pol.* **1998**, *45*, 833–846
9. Das, S. K.; Singh, R.; Panda, G. *Eur. J. Org. Chem.* **2009**, 4757–4761.
10. Licudine, P. J. A.; Kawate, M. K.; Li, Q. X. *J. Agric. Food Chem.* **1997**, *45*, 766–733.
11. Papini, P.; Cimmarusti, R. *Gazz. Chim. Ital.* **1947**, *77*, 142–147.
12. Sen, R. N.; Sarkar, N. *J. Am. Chem. Soc.* **1925**, *47*(4), 1079–1091.
13. Ota, K.; Kito, T. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1167–1168.
14. Ko, S.; Yao, C. F. *Tetrahedron Lett.* **2006**, *47*, 8827–8829.
15. Rajitha, B.; Kumar, B. S.; Reddy, Y. T.; Reddy, P. N.; Sreenivasulu, N. *Tetrahedron Lett.* **2005**, *46*, 8691–8693
16. (a) Das, B.; Ravikanth, B.; Ramu, R.; Laxminarayana, K.; Rao, B. V. *J. Mol. Catal. A: Chem.* **2006**, *255*, 74–77; (b) Pasha, M. A.; Jayashankara, V. P. *Bioorg. Med. Chem. Lett.* **2007**, *17*, 621–623.
17. Khosropour, A. R.; Khodaei, M. M.; Moghannian, H. *Syn. Lett.* **2005**, 955–958.
18. (a) Zhao, J.; Larock, R. C. *Org. Lett.* **2005**, *7*, 4273–4275; (b) Zhao, J.; Larock, R. C. *J. Org. Chem.* **2007**, *72*, 583–588; (c) Yoshida, H.; Watanabe, M.; Fukushima, H.; Ohshita, J.; Kunai, A. *Org. Lett.* **2004**, *6*, 4049–4051; (d) Okuma, K.; Nojima, K.; Matsunaga, N.; Shioji, K. *Org. Lett.* **2009**, *11*, 169–171; (e) Knight, D. W.; Little, P. B. *Syn. Lett.* **1998**, 1141–1143; (f) Knight, D. W.; Little, P. B. *J. Chem. Soc.* **2001**, *1*, 1771–1977.
19. Wang, J. Q.; Harvey, R. G. *Tetrahedron* **2002**, *58*, 5927–5931.
20. Su, W.; Yang, D.; Jin, C.; Zhang, B. *Tetrahedron Lett.* **2008**, *49*, 3391–3395.
21. Jha, A.; Beal, J. *Tetrahedron Lett.* **2004**, *45*, 8999–9001.
22. Xiaobing, X.; Xiaolei, X.; Hongfeng, L.; Xin, X.; Yanzhong, L. *Org. Lett.* **2010**, *12*, 100–103.
23. (a) Demko, Z. P.; Sharpless, K. B. *J. Chem. Rev.* **2005**, *105*, 3095–3166.
24. Bigdeli, M. A.; Heravi, M. M.; Mahdavinia, G. H. *J. Mol. Catal. A: Chem.* **2007**, *275*, 25–29.
25. Potewar, T. M.; Kathiravan, M. K.; Chothe, A. S.; Srinivasan, K. V. *Eur. J. Chem.* **2011**, *2*(2), 235–237.