Chemical Science Review and Letters ISSN 2278-6783

Research Article

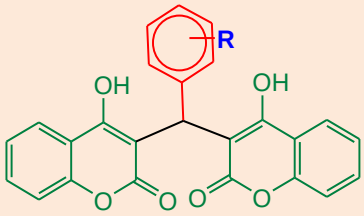
Mild and Efficient one pot synthesis of bis (4-hydroxy coumarins) derivatives using EPZ-10 catalyst at room temperature by simple grinding technique

Omprakash S. Chavan[1], Santosh A. Jadhav[2], Mahesh G. Shioorkar[2], Shivaji B. Chavan[1], and Mohammad A. Baseer[1]*

[1]Organic Synthesis Laboratory, Department of Chemistry, Yashwant College, Nanded, M.S., India
[2]P.G.Department of Chemistry, Vivekanand College, Aurangabad, M.S., India

Abstract

A simple one pot green highly efficient condition for synthesis of bis-coumarins involving simple grinding technique of 4-hydroxy coumarins and substituted aromatic aldehyde under solvent free condition, at room temperature catalysed by biodegradable, naturally occurring heterogeneous solid acid catalyst EPZ-10 has been described. The remarkable features of this environmentally benign protocol are short reaction time, use of commercially in expensive heterogeneous EPZ-10 catalyst by simple grinding technique at room temperate with high yield of product by simple experimental procedure.



Biscoumarin

R= -H, -4-NO_2, -2-Cl, -4-Cl, -4-OMe, -2-Br, -4-Br, -4-Me,-2-OH,-4-OH.

Keywords: biscoumarins, solvent free condition, grinding technique, EPZ-10 catalyst, room temperature

***Correspondence**
Author: Mohammad A. Baseer
Email: drmohammadabaseer@gmail.com

Introduction

Coumarins [1] and their derivatives form an elite class of compounds, occurring and important role in the region of natural product and synthetic organic chemistry. The coumarins have variable biological activities like inhibition of platelet aggregation, [2] anticancer, [3] antibacterial, [4] anti-inflammatory, [5] antipyretic, antifungal [6] and also reported for exhibiting photochemical properties. [7]

Biscoumarins is an important class of coumarins derivatives due to their pronounced pharmacological activities. [8–11] In literature survey, different methods are reported for synthesis of biscoumarins from 4-hydroxycoumarins and substituted aromatic aldehydes in various catalyst like Ruthenium (III) chloride [12], Nanosilica chloride [13], Cobalt (II) chloride [14], Trichloroacetic acid [15], DBSA [16], Cellulose sulphuric acid [17], Magnesium oxide nanoparticles [18] etc.

In continuation of our research study, [19–23] here, we report the synthesis of biscoumarins by simple grinding technique at room temperature catalysed by EPZ-10 as a biodegradable green catalyst with the help of 4-hydroxycoumarins and aromatic aldehydes. Envirocat EPZ-10 is the clay catalyst, have many advantage like Ease of handling, non-corrosiveness, low cost, regeneration etc. This clay catalyst having strong Lewis acid site as promising surface for developing new synthetic methods for heterocyclic compounds. [24–27]

Experimental

General

All the compounds used in synthesis were of analytical grade, the melting points of the compounds were determined in open head capillary and are uncorrected. The IR spectra of the compounds were recorded in the region of 4000-400

cm-[1] by using KBr pallet on FT-IR Perkin spectrophotometer. [1]H NMR spectra were recorded on a DRX-300 Bruker FT-NMR spectrophotometer in $CDCl_3$. Satisfactory elemental analysis was obtained on a Perkin Elmer CHN analyzer. The values of chemical shift are expressed in δ ppm as a unit. All the compounds were checked for purity by thin layer chromatography (TLC).

Chemistry

A series of biscoumarins derivatives (**3a-3j**) has been synthesised by condensation of substituted aromatic aldehydes with 4-hydroxy coumarins with the help of commercially available EPZ-10 as a clay catalyst by simple grinding technique with mortar and pestle at room temperature. All the synthesised biscoumarins derivatives were characterised on the basis of their spectral and analytical studies.

General method

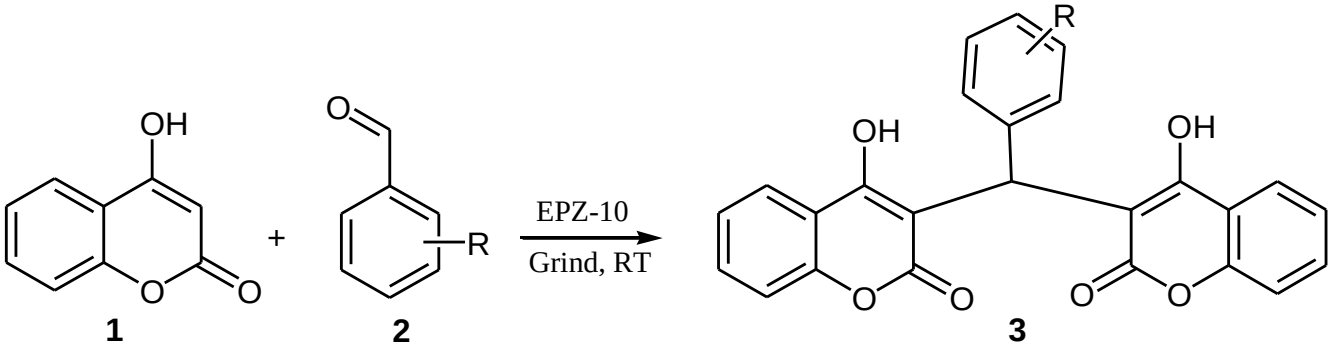
Synthesis of Biscoumarins derivatives were prepared by following method.

A mixture of 4-hydroxy coumarin (0.021 mol, 3.40 gm), substituted aromatic aldehydes (0.01 mol) and EPZ-10 (20 mol %) was mixed into a mortar and grind by pestle for the period of appropriate time (**Table 1**) the completion of reaction was monitor by TLC, after completion of reaction, 10 mL of ethyl acetate was added to mixture and extracted, organic layer was filtered to removed clay catalyst, organic layer evaporated to obtained solid product, followed by recrystallization using proper solvent. Synthetic pathway for preparation of biscoumarin compound is as shown in **scheme 1**. Physical data of synthesised compounds given in **Table 2**.

Table 1 Optimisation of reaction condition[b] for synthesis of biscoumarin (**3g**) using EPZ-10 catalyst by simple grinding technique.

Entry	Catalyst	Mol %	Time (min.)	Yield[a] (%)
1.	Silica	20	10	55
2.	$AlCl_3$	20	10	82
3.	$ZnCl_2$	20	10	67
4.	**EPZ-10**	**20**	**10**	**93**
5.	Montmorillonite	20	20	70
6.	PMA	20	20	40
7.	BF_3:OEt_2	20	12	32
8.	EPZ-10	05	20	53
9.	EPZ-10	10	20	69
10.	EPZ-10	30	05	90

[a] Isolated yield, [b] reaction condition: 4-hydroxy coumarins (**1,** 0.021 mol), 4-bromo benzaldehyde (**2**, 0.01 mol) and EPZ-10 catalyst, grinding at r.t.



Scheme 1 Synthesis of biscoumarin derivatives by simple grinding techniques using EPZ-10 as clay catalyst.

3,3'-(benzylidene)-bis-[4-hydroxycoumarin] (3a): Yield 89 %; IR (KBr, cm^{-1}): 3034, 1652, 1608, 754; [1]H NMR (300 MHz, $CDCl_3$): δ 6.18 (s, 1H, CH), 6.82 to 7.56 (m, 13H, Ar), 10.72 (br s, 2H, OH) ppm.

Table 2 Physical data of biscoumarin derivatives.

Compound	R	Molecular Formula	Molecular Weight	M.P. (°C) (Reported [28])	Yield (%)
3a	Ph-H	$C_{25}H_{16}O_6$	412	230 (231-34)	89
3b	Ph-4-NO_2	$C_{25}H_{15}NO_8$	457	233 (232-34)	72
3c	Ph-2-Cl	$C_{25}H_{15}ClO_6$	446	221 (224-26)	90
3d	Ph-4-Cl	$C_{25}H_{15}ClO_6$	446	251 (254-56)	92
3e	Ph-4-OMe	$C_{26}H_{18}O_7$	442	247 (246-48)	88
3f	Ph-2-Br	$C_{25}H_{15}BrO_6$	491	251 (256-58)	95
3g	Ph-4-Br	$C_{25}H_{15}BrO_6$	491	268 (266-68)	93
3h	Ph-4-Me	$C_{26}H_{18}O_6$	426	265 (266-68)	85
3i	Ph-2-OH	$C_{25}H_{16}O_7$	428	253 (254-56)	91
3j	Ph-4-OH	$C_{25}H_{16}O_7$	428	222 (222-24)	93

3,3'-(4-Nitrobenzylidene)-bis-[4-hydroxycoumarin] (3b): Yield 72 %; IR (KBr, cm^{-1}): 3033, 1652, 1615, 1529,1347, 761; ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.56 (s, 1H, CH), 7.13 to 8.38 (m, 12H, Ar), 11.22 (br s, 2H, OH) ppm.

3,3'-(4-Methoxybenzylidene)-bis-[4-hydroxycoumarin](3e): Yield 88 %; IR (KBr, cm^{-1}): 3443, 2926,1668, 1606,1563, 1510 ,767; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.71 (s, 3H, OCH_3), 6.31 (s, 1H, CH), 6.80–7.93(m, 12H, Ar), 8.16–8.78 (m, 2H, OH) ppm.

3,3'-(4-Methylbenzylidene)-bis-[4-hydroxycoumarin](3h): Yield 85%; IR (KBr, cm^{-1}): 3445, 3073, 1671, 1618, 1606, 1565, 1351, 763; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.23 (s, 3H, CH_3), 6.20 (s, 1H, CH), 7.01-7.89 (m, 12H, Ar), 11.86 (br s, 2H, OH) ppm.

Result and Discussion

Series of reactions arranged by keeping focus on verifying utility spectrum of heterogeneous catalyst by grinding method and using 4-hydroxy coumarin and 4-bromo benzaldehyde as model reaction. Various solid catalysts were used and found that EPZ-10 is most prominent among them, obtaining significant yield and easy to removed from reaction. Further, to optimizing amount of catalyst for biscoumarin synthesis, EPZ-10 used in various proportion (Table 1 Entry 8, 9, 10). Decreasing amount of catalyst to 5 and 10 mol % reaction yield was fall down with essentially increase in reaction time, whereas on increasing catalyst upto 30 mol % no significant improvement has observed in yield of product. Further derivatisation of synthesis of biscoumarin was done by found optimized condition, 20 mol % of EPZ-10 catalyst and grinding at room temperature for 10 minutes. All compounds were synthesised according to scheme 1 and characterised by comparison of their spectral data with reported literature.[28]

Conclusion

Herein, we report the synthesis of biscoumarin derivatives of 4-hydroxy coumarins and substituted aromatic aldehyde in the presence of EPZ-10 catalyst by simple grinding technique at room temperature. This present green approach offers several advantages such as, excellent yield, short reaction time, simple reaction procedure with solvent free condition by using commercially available green biodegradable EPZ-10 as a clay catalyst.
We believe that, this method found to be useful addition to present methodologies for the synthesis of biscoumarin derivatives.

Acknowledgement

Authors are thankful to the Principal, Yashwant Mahavidhyalaya, Nanded for constant encouragement and providing necessary facilities for this work and one of the author (Chavan O.S.) is thankful to WRO, UGC, Pune, for providing financial Assessment.

References

[1] R. O'Kennedy, R. D. Thornas, Coumarins: Biology, Application and Mode of Action, Wiley and Sons, Chichester, 1997.

[2] G.Cravetto, G.M. Namo, G. Plamisanom, S. Tagliapieta, Tetrahydron: asymmetry. 2001, 12, 707-710.

[3] Aoife Lacy and Richard O'Kennedy, Studies on Coumarins and Coumarin-Related Compounds to Determine their Therapeutic Role in the Treatment of Cancer, Current Pharmaceutical Design. 2004, 10, 3797-3811.

[4] Naceur Hamdi, Mustapha Saoud, Antonio Romerosa, Rached Ben Hassen, Synthesis, spectroscopic and antibacterial investigations of new hydroxy ethers and heterocyclic coumarin derivatives, J. Heterocyclic Chem. 2008, 45(6), 1835–1842,

[5] Yasser Abdelaal Selim, Nabil Hassan Ouf, Anti-inflammatory new coumarin from the Ammi majus L, Organic and Medicinal Chemistry Letters 2012, 2(1), 1-4.

[6] Razi Ahmad, Mohammad Asad, Zeba N Siddiqui, Anil kumar, Evolution of Antipyretic and Antinociceptive potential of new heterocyclic derivatives of 3- formyl-4-hydroxycoumarin in Rat, Int. Res J Pharm. App Sci. 2013, 3(5), 253-259.

[7] Ahmed A. Al-Amiery, Abdul Amir Hassan Kadhum, Abu Bakar Mohamad, Antifungal Activities of New Coumarins, Molecules 2012, 17, 5713-5723.

[8] Poonam kumar koppula, Nilini Purohit, Bis-(1H-2-benzopyran-1-one) derivatives: Synthesis and antimicrobial evaluation, J. Chem. Sci. 2013, 6, 125, 1535–1542.

[9] Bo. Jian Li , Chih Chia Chiang and Ling Yih Hsu, QSAR Studies of 3,3-(Substituted-benzylidene)-bis-4-hydroxycoumarin, Potential HIV-1 Integrase Inhibitor, J. Chin. Chem. Soc. 2010, 57, 742-749.

[10] Irena Kostova, Georgi Momekov, Tzvetomira Tzanova, Margarita Karaivanova, Synthesis, Characterization, and Cytotoxic Activity of New Lanthanum(III) Complexes of Bis-Coumarins., Bioinorg. Chem. App. 2006, 1–9.

[11] Anhar Abdel-Aziem, Synthesis and Antimicrobial Activity of Some Novel Thiazoles, 1,3,4-Thiadiazines, 1,3,4-Thiadiazoles Incorporating Coumarin Moiety, J. Heterocyclic Chem. 2015, 52, 251-553.

[12] Khalil Tabatabaeian, Hannaneh Heidari, Alireza Khorshidi, Manouchehr Mamaghani, Nosrat O. Mahmoodi, Synthesis of biscoumarin derivatives by the reaction of aldehydes and 4-hydroxycoumarin using ruthenium (III) chloride hydrate as a versatile homogeneous catalyst, J. Serb. Chem. Soc. 2012, 77 (4) 407–413.

[13] Ramin Karimian, Farideh Piri, Ali Asghar Safari, Seyed Javad Davarpanah, One-pot and chemoselective synthesis of bis(4-hydroxycoumarin) derivatives catalyzed by nano silica chloride, J. Nanostructure in Chem. 2013, 3(52), 1-6.

[14] Mohammad Reza Nazarifar, Cobalt (II) Chloride Hexahydrate as an Efficient and Inexpensive Catalyst for the Preparation of Biscoumarin Derivatives, Advances in Chem. 2014, 1-6.

[15] Zahed Karimi-Jaberi, Mohammad Reza Nazarifar, Efficient catalysts for the rapid synthesis of benzylidene bis(4- hydroxyl coumarins) derivatives in aquous media, Eur. Chem. Bull. 2014, 3(6), 512-514.

[16] Asiyeh Shamsaddini, Enayatollah Sheikhhosseini, Synthesis of 3,3-Arylidene Bis(4-Hydroxycoumarin) Catalyzed by p-Dodecylbenzenesulfonic Acid (DBSA) in Aqueous Media and Microwave Irradiation, Inter. J. Org. Chem. 2014, 4, 135-141.

[17] Masoumeh Sedighi, Naser Montazeri, Synthesis of Biscoumarin Derivatives as Biological Compounds Using Cellulose Sulfonic Acid, Adv. Stu. in Bio. 2015, 7(2), 89-95.

[18] Javad Safaei-Ghomi, Fahime Eshteghal, Mohammad Ali Ghasemzadeh, Solvent-free Synthesis of Dihydropyrano[3,2-c]chromene and Biscoumarin Derivatives Using Magnesium Oxide Nanoparticles as a Recyclable Catalyst, Acta Chim. Slov. 2014, 61, 703–708.

[19] Omprakash S. Chavan, Mohammad A. Baseer, Comparative study of various synthetic methods of 7-hydroxy-4-methyl coumarins via Pechmann reaction, Der Chemica Sinica. 2014, 5(5), 67-70.

[20] Omprakash S. Chavan, S. B. Chavan, M. A. Baseer, An efficient synthesis of formyl coumarins by microwave irradiation method-duff Formylation, Der Pharma Chemica. 2015, 7(1), 197-200.

[21] Omprakash S. Chavan, S. A. Jadhav, M. G. Shioorkar, S. B. Chavan, M. A. Baseer, Y. M. Pawar, Perchloric acid modified cellulose: Solid acid catalyst for Pechmann condensation using grinding technic under solvent free condition, J. Chem. Pharm. Res. 2015, 7(5), 899-902.

[22] Omprakash S. Chavan, Santosh A. Jadhav, Mahesh G. Shioorkar, Shivaji B. Chavan, Mohmmad A. Baseer, Devanand B. Shinde, Microwave assisted solvent free synthesis of coumarins using Zn [(L)-Proline]2 catalyst, Rasayan J. Chem. 2015, 8 (2), 194 -197.
[23] Omprakash S. Chavan, S. B. Chavan, S. A. Jadhav, M. G. Shioorkar, M. A. Baseer, A solvent free synthesis of coumarins via Pechmann condensation using PMA:Silica supported BF3:OEt2 catalyst, Der Chemica Sinica. 2015, 6(4), 96-99.
[24] Key-Young Lee, Kwang-Youn Ko, Envirocat EPZ 10: A Recyclable Solid Acid Catalyst for the Synthesis of Biginelli-type 3,4-Dihydropyrimidin-2(1H)-ones, Bull. Korean Chem. Soc. 2004, 25(12), 929.
[25] Babasaheb P. Bandgar, Suhas P. Kasture, Envirocats, as Novel Solid-Supported Catalysts for Friedel-Crafts Acylation, J. Chinese Chem. Soc. 2000, 47, 1243-1246.
[26] T. S. Shaikh, K. A. Undale, D. S. Gaikwad, D. M. Pore , Envirocat EPZ-10: An efficient catalyst for the synthesis of 3-acetoacetylcoumarins, Comptes Rendus Chimie. 2011, 14(11), 987-990.
[27] D. M. Pore, T. S. Shaikh, N. G. Patil, S. B. Dongare, U. V. Desai, Envirocat EPZ-10: A Solid Acid Catalyst for the Synthesis of 1,8-Dioxo-octahydroxanthenes in Aqueous Medium, Syn. Comm. 2010, 40(15), 2215-2219.
[28] H. Mehrabi, H. Abusaidi, Synthesis of Biscoumarin and 3,4-Dihydropyrano[c]chromene Derivatives Catalysed by Sodium Dodecyl Sulfate (SDS) in Neat Water, J. Iran. Chem. Soc., 2010, 7(4) 890-894.

Publication History
Received 04th Aug 2015
Revised 08th Sep 2015
Accepted 25th Sep 2015
Online 30th Oct 2015