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ORIGINAL ARTICLE

Glutamic Acid as an Environmentally Friendly Catalyst for One-Pot Synthesis of 4*H*-Chromene Derivatives and Biological Activity

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KEYWORDS

Biological activity;
Glutamic acid;
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One-pot

ABSTRACT: In this study, the synthesis of 4*H*-chromenes of biological activity via a multicomponent reaction of dimedone, aromatic aldehydes and malononitrile catalyzed by glutamic acid as a catalyst was investigated. The structural features of the synthesized compounds were characterized by melting point, IR and ^{1}H NMR analysis. The catalyst being reported here is cheap, safe to handle and the whole procedure is eco-friendly, Milder conditions, one-pot, excellent yields, operational simplicity and ecofriendly preparation are some advantages of this protocol. The compounds were screened for antimicrobial activity. The results showed that these compounds reacted against all the tested bacteria and fungi.

INTRODUCTION

The multi-component condensation reactions were an important tool in the organic synthesis as they possess ability of building up the pharmaceuticals. Pharmacies are trying to develop green chemistry reactions. Multi-component reaction as a powerful tool for develops for the synthesis of heterocyclic compounds receives growing interest [1-5].

4*H*-chromenes are an important class of oxygen-containing heterocyclic compounds which have attracted significant synthetic interest due to their reactivity and biological activity. These compounds had shown interesting biological properties including antimicrobial, antiviral, antiproliferative, antitumor cancer therapy and central nervous system activity. These derivations were used in the treatment of hypertension, Alzheimer's disease and Seizures [6-8]. Thus, in recent years several methods were established to improve the use of MgO [9, 10], d,l-proline [11, 12], LiBr [13], $CeCl_3$_H_2O [14], potassium phosphate [15], microwave-irradiation [16, 17] and ultrasonic irradiation [19] and different ways have been reported. Previously, in continuation of our investigations, we have synthesized a number of heterocyclic compounds [19-22]. In this research, herein, we report an innovative, convenient, mild and efficient pro-

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cedure for the synthesis of 4*H*-chromene derivatives. One-pot three component condensations of aldehyde derivatives, dimedone and malononitrile were synthesized of 4*H*-chromene derivatives in the presence of glutamic acid as a catalyst in reflux conditions [23-26] (Figure 1).

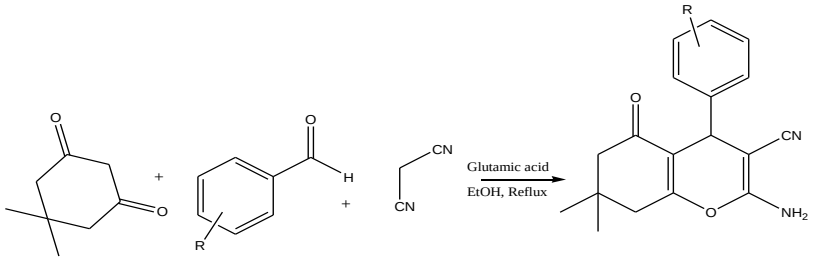


Figure 1. Synthesis of 4*H*-chromene derivatives using glutamic acid as a catalyst

MATERIALS AND METHODS

The materials were purchased from Sigma-Aldrich and Merck chemical companies and were used without any additional purification. Melting points were measured on an Electrothermal 9100 apparatus. Silica gel SILG/UV 254 plates were used for TLC. IR spectra were measured on a Shimadzu IR-470 Spectrophotometer. The ^{1}H NMR spectra were scanned in $CDCl_3$ on a Brucker NMR spectrometer operating at 400.13 MHz. The products were characterized by comparison of their ^{1}H NMR, IR spectra and physical data with those in the literature.

General procedure for the synthesis of 2-amino-7,7-dimethyl-4-phenyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (F1)

A mixture of benzaldehyde (1.0 mmol), dimedone (1.0 mmol), malononitrile (1.0 mmol) and glutamic acid as a catalyst (20 mol%) in ethanol (5 mL) was refluxed for 35 min. The progress of the reaction was monitored by TLC (chloroform/methanol 9:1). After completion of the reaction, the resulting solid (crude product) was filtered and then recrystallized with ethanol–water to obtain pure product. The physical data (mp, IR and ^{1}H NMR) of these known compounds were identical with those reported in the literature.

Spectral data for the synthesis of 4H-Chromene derivatives

2-amino-7,7-dimethyl-4-phenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (F1):

m.p. 228-229 ^{o}C; FT-IR (V_{max}/cm^{-1}) (KBr disc): 3420, 3300 (NH_2 Str.); 3010 (CH_{arom} Str.); 1600 ($C{=}C_{arom}$ Str.); 1643 ($C{=}C_{Aliph}$ Str.); 1680 (C=O Str.); 1210 (C-O Str.). ^{1}H NMR (400.13 MHz, $CDCl_3$): 1.05(3H, s, CH_3); 1.13(3H, s, CH_3); 2.24(2H, AB q, ^3J = 16.4, 9.4 Hz, CH_2); 2.47(2H, m, CH_2); 4.42(H, s, CH); 4.57(2H, s, NH_2); 7.19-7.32(5H, m, CHarom). Spectra of compound F1 is below (Figure 2).

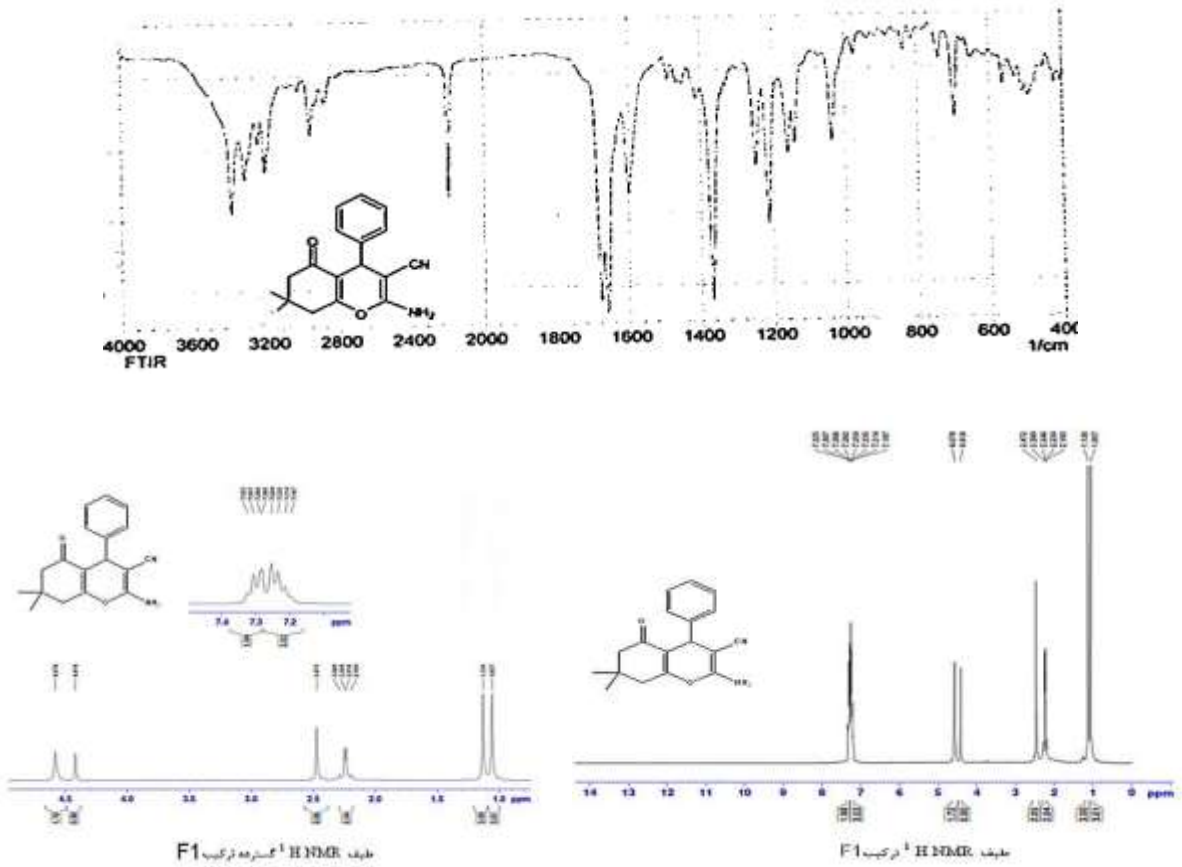


Figure 2. Spectral of F1 compound.

2-amino-7,7-dimethyl-4-(2-fluorophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (F2):

m.p. 233-235 ^{o}C; FT-IR (V_{max}/cm^{-1}) (KBr disc): 3400, 3310 (NH_2 Str.); 2191 (C≡N Str.); 1602 (C=C_{arom} Str.); 1638 (C=C_{Aliph} Str.); 1658 (C=O Str.); 1197 (C-O Str.).

2-amino-7,7-dimethyl-4-(4-methylphenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (F3):

m.p. 218-220 ^{o}C; FT-IR (V_{max}/cm^{-1}) (KBr disc): 3360, 3318 (NH_2 Str.); 2272 (C≡N Str.); 1600 (C=C_{arom} Str.); 1632 (C=C_{Aliph} Str.); 1691 (C=O Str.); 1231 (C-O Str.).

2-amino-7,7-dimethyl-4-(2-chlorophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (F4):

m.p. 203-205 ^{o}C; FT-IR (V_{max}/cm^{-1}) (KBr disc): 3385, 3327 (NH_2 Str.); 2225 (C≡N Str.); 1600 (C=C_{arom} Str.); 1650 (C=C_{Aliph} Str.); 1683 (C=O Str.); 1209 (C-O Str.).

2-amino-7,7-dimethyl-4-(4-chlorophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (F5):

m.p. 213-216 ^{o}C; FT-IR (V_{max}/cm^{-1}) (KBr disc): 3368, 3315 (NH_2 Str.); 2205 (C≡N Str.); 1610 (C=C_{arom} Str.); 1660 (C=C_{Aliph} Str.); 1678 (C=O Str.); 1222 (C-O Str.).

2-amino-7,7-dimethyl-4-(3-methoxyphenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile(F6):

m.p. 192-195 ^{o}C; FT-IR (V_{max}/cm^{-1}) (KBr disc): 3405, 3327 (NH_2 Str.); 2212 (C≡N Str.); 1601 (C=C_{arom} Str.); 1648 (C=C_{Aliph} Str.); 1688 (C=O Str.); 1202 (C-O Str.).

Antimicrobial activity

The compounds F1-6 were screened by disc diffusion method [27-28], for their antibacterial activity *Escherichia coli, Bacillus subtilis, Staphylococcus aureus* and *Vibreo cholerae* and their fungi activity, *Trichoderma species, Chrysosporium* species, *Aspergillus niger and Asterophora parasitica* by comparing with standard bactericide Ciprofloxacin and standard fungicide Clomatrimazole at 100 µgmL^{-1}. The tubes were incubated aerobically at 37 ºC for 18-24 h. The experiments were run in triplicates and the average results are included in Table 1 and Table 2.

Table 1. Antibacterial activity of compounds

Compound	*E. coli*	*B. subtillus*	*S. aureus*	*V. cholerae*
F1	17	15	16	23
F2	17	8	10	31
F3	18	19	14	23
F4	16	16	26	13
F5	26	15	14	13
F6	28	17	16	-
Ciprofloxacin	28	22	25	33

Table 2. Antifungal activity of compounds

Compound	*Trichoderma* **sp.**	*Chrysosporium* **sp.**	*A. niger*	*A. parasitica*
F1	11	16	14	18
F2	-	10	11	9
F3	12	25	18	21
F4	16	16	23	17
F5	21	21	25	17
F6	16	16	27	19
Clomatrimazole	28	26	25	28

RESULTS AND DISCUSSION

Nowadays, glutamic acid is used as a catalyst in the synthesis of organic compounds. Features of this catalyst that are of interest include: easy separation, environmentally friendly, clean, and economical [23-26]. The mechanism of formation of 4*H*-chromenes using glutamic acid as a catalyst is shown in Figure 3.

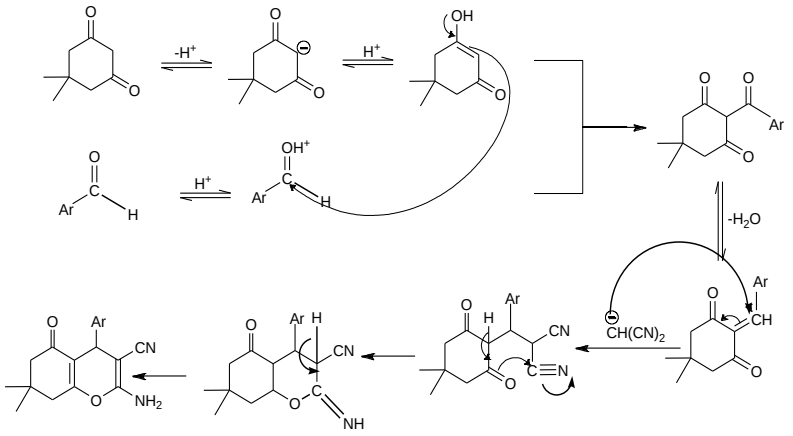


Figure 3. Mechanism of formation of 4*H*-chromenes.

At first, for the optimization of the reaction conditions, the condensation of benzaldehyde, dimedone and malononitrile was investigated. Then, we decided to examine the effect of the various solvents with amount of catalyst on the reaction. As shown in Table 3, the best results in terms of yield and time were obtained 20 mol% of glutamic acid in refluxing ethanol (entry 14). After pursuing the best solvent with catalyst, we evaluated the scope of glutamic acid-catalyzed 4*H*-chromenes reaction using a variety of aldehydes. Aromatic aldehydes bearing both electron-donating and electron withdrawing groups were employed in 4*H*-chromenes reactions and the expected products were obtained in high yields. The results for the preparation of substituted 4*H*-chromene derivatives are summarized in Table 4. Comparison of reaction conditions and product yield between previously reported methods and the present method are shown in Table 5.

All products were known and characterized through comparison of their FT-IR and physical properties with those reported in the literature.

Table 3. Solvent effect with amount catalyst in the synthesis of 4*H*-chromenes[a]

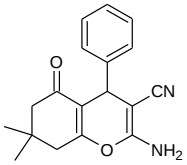
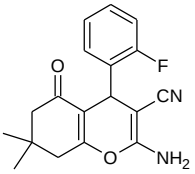
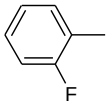
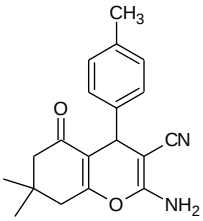
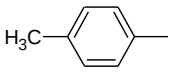
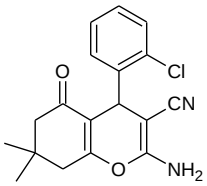
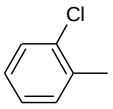
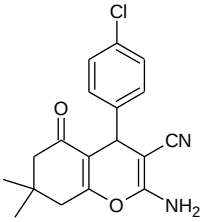
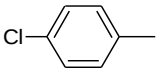
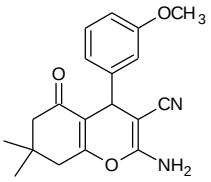
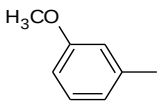
Entry	Catalyst (mol%)	Solvent	Condition	Time (min)	Yield (%)[b]
1	---	Ethanol	R.T.	140	35
2	---	Water	R.T.	140	30
3	---	Dichloromethane	R.T.	140	NP
4	---	Acetonitrile	R.T.	140	NP
5	---	Ethanol-water	Reflux	100	40
6	---	Ethanol	Reflux	100	41
7	---	Water	Reflux	100	42
8	---	Dichloromethane	Reflux	100	NP
9	---	Acetonitrile	Reflux	100	27
10	15	Solvent-free	Reflux	100	70
11	20	Solvent-free	Reflux	100	75
12	25	Solvent-free	Reflux	100	77
13	15	Ethanol	Reflux	35	81
14	20	Ethanol	Reflux	35	91
15	25	Ethanol	Reflux	35	91
16	20	Ethanol-water	Reflux	40	73

Table 3. Continued

17	20	Water	Reflux	40	70
18	20	Dichloromethane	Reflux	40	42
19	20	Acetonitrile	Reflux	40	59

Reaction condition: [a] benzaldehyde (1 mmol), dimedone (1 mmol), malononitrile (1 mmol), glutamic acid (20 mol%), ethanol (5 mL); [b] Isolated yield.

Table 4. Glutamic acid catalyzed synthesis of 4*H*-chromene derivatives[a]

Entry	product	Ar	Time (min)	Yield (%)[b]	M.P. °C (Found)	M.P. °C (Reported in Lit.)
F1			35	91	228-229	229-231 [29]
F2			55	87	233-235	235-237 [30]
F3			35	95	218-220	219-221 [30]
F4			40	90	201-203	201-205 [30]
F5			40	91	213-214	212-214 [29]
F6			35	94	192-195	192-194 [29]

Reaction condition: [a] benzaldehyde (1 mmol), dimedone (1 mmol), malononitrile (1 mmol), glutamic acid (20 mol%), ethanol (5 mL); [b] Isolated yield.

Table 5. Comparison of reaction conditions and yield of product with reported methods versus the present method

Catalyst	Condition	Yield (%)	Ref.
$SnCl_2$ (10 mol%)	Reflux, Ethanol	94	[31]
Trisodium Citrate	Reflux, Ethanol-Water	80	[31]
$Ni(NO_3)_2 . 6H_2O$ (10 mol%)	Reflux, Ethanol	95	[32]
$Pb(NO_3)_2$ (10 mol%)	Reflux, Ethanol	81	[32]
$AlCl_3$ (10 mol%)	Reflux, Ethanol	69	[32]
$Ni(NO_3)_2 . 6H_2O$ (10 mol%)	CH_3CN	73	[32]
NaBr	MW,70-80 °C	85	[33]
PPA – SiO_2	Reflux, Water	77	[34]
Na_2SeO_4	Reflux, Ethanol-Water	85	[35]
Caro's acid – SiO_2	Reflux, Ethanol-Water	92	[36]
Nano-SnO_2	Reflux, Ethanol	93	[37]
Glutamic acid	Reflux, Ethanol	91	In this Rresearch

Antibacterial screening

The bacterial zones of inhibition values (mm) are given in Table 1. The antimicrobial activities of compounds *V. cholerae, E. coli, B. subtillus, S. aureus* were screened. Ciprofloxacin were used as a standard at 100 μgmL^{-1}. Compounds F1-6 was screened. *E. coli* for compound F6 was highly active, on the other hand for compound F1-5 had low activity compared with the standard ciprofloxacin. *B. subtillus* for compound F3 was highly active compared with the ciprofloxacin. On the other hand for F1, F2, F4, F5 and F6 had low activity compared with the ciprofloxacin. *S. aureus* for compound F4 was highly active compared with ciprofloxacin on the other hand for compound F1, F2, F4, F5; F6 had low activity compared with the ciprofloxacin. *V. cholerae* for compound F2 was highly active compared with the standard ciprofloxacin. On the other hand, for compound F1, F3, F4, had low activity compared with the ciprofloxacin. For F6 no activity was shown.

Antifungal screening

The fungal zones of inhibition values (mm) are given in Table 2. The antifungal activity of compounds *Chrysosporium* sp., *Trichoderma* sp., *A. niger, A. parasitica* were screened. Clomatrimazole were used as a standard at a 100 μgmL^{-1}.Compound F1-6 were screened. *Trichoderma* sp. for compound F5 was highly active for compound F1, F3, F4 and F6 had low activity compared with standard Clomatrimazole. While for compound 1b had no activity with Clomatrimazole. *Chrysosporium* sp. for compound F3 was highly active compared with Clomatrimazole while on the other hand for compound F1, F2, F4, F5 and F6 had low activity compared with standard Clomatrimazole. *A. niger* for compound 1e was highly active compared with standard Clomatrimazole. On the other hand for F1, F2, F3, F4 and F6 had low activity compared with standard Clomatrimazole. *A. parasitica* for compound 1c was highly active compared with standard Clomatrimazole. On the other hand for F1, F2, F4, F5 and F6 had low activity compared with Clomatrimazole.

CONCLUSIONS

We have demonstrated an efficient catalyst for the synthesis of substituted 4*H*-chromenes catalyzed by glutam-

ic acid. The advantages of this method using Glutamic acid include high yields, available time, one-pot, experimental simplicity, environmentally friendly and easy separation of this catalyst. The majority of the compounds (F1-6) exhibited significant activity against selective bacteria and fungi and the zone of inhibition of these title compounds was almost comparable to that of the standard drugs. Thus some of compounds with comparable antimicrobial potency to the presently on used commercial bactericides have been discovered.

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