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RESEARCH ARTICLE

L-Ascorbic Acid: A Green and Competent Promoter for Solvent-Free Synthesis of Flavones and Coumarins under Conventional as well as Microwave Heating

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Abstract: ***Background***: An expeditious approach has been developed for the synthesis of two distinct classes of benzopyrones viz. flavones and coumarins under solvent-free conditions. L-Ascorbic acid was found to be an effective promoter under microwave irradiation and conventional heating. Various benzo-α-pyrones and benzo-γ-pyrones were synthesized with overall good yields. The present protocol is highly facile and needs no column chromatography for purification and therefore it would serve as an effective and compatible method under both microwave irradiation and conventional heating.

Results: The catalytic ability of L-ascorbic acid was investigated for the synthesis of flavones and coumarins. For this purpose, cyclodehydration of 1-(2-hydroxyphenyl)-3-aryl-1,3-propanedione and Pechmann coumarin synthesis, reactions were selected. And accordingly, it was observed that one mole of L-ascorbic acid was necessary for the completion of reaction. In all the cases, the desired flavones were smoothly generated with good to excellent yields; indicating its excellent tolerance for various functional groups. However, electron donating groups favors coumarin synthesis under these conditions. All the reaction mixtures were carefully analyzed and NMR indicates high conversions and lack of side products.

Conclusion: We have developed L-ascorbic acid-promoted, solvent-free and simple method for the synthesis of benzo-α-pyrones and benzo-γ-pyrone under microwave irradiation as well as conventional heating in good to excellent yields. The notable advantages of this method are solvent-free conditions, inexpensive and efficient eco-friendly promoter, and shorter reaction time and can be carried out under air. This methodology is highly facile and requires no column chromatography for purification. The resulting flavones and coumarins are versatile building blocks in the construction of heterocyclic architectures, dominant in natural products. Further studies of exploiting the efficiency of L-ascorbic acid as a promoter in synthesis of various heterocyclic compounds are in progress.

ARTICLE HISTORY

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1. INTRODUCTION

Scientists are employing various tools from their "bag of tricks' to achieve rapid, more precise and well-organized ways to accelerate the pace of the natural product synthesis. The quest for novel natural products is everlasting and benzopyrones are no different from them due to their interesting biological activities. The two distinct benzopyrones *viz.* Benzo-α-pyrone (coumarin) and benzo-γ-pyrone (chromone), due to their fascinating structural motif have been extensively used in organic synthesis (Fig. 1).

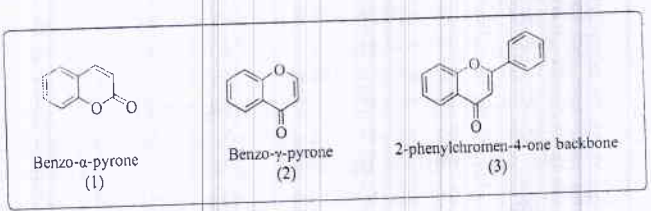

Fig. (1). Various benzopyrone structure.

Flavones are a class of flavonoids with 2-phenylchromen-4-one backbone (Fig. 1). They are a regular part of our diet as they are easily found in fruits, vegetables, nuts, olive oil, tea, and red wine [1]. Flavones have been reported to exhibit a wide spectrum of biological activities [2] such as anti-cancer [3], anti-microbial [4, 5], anti-viral

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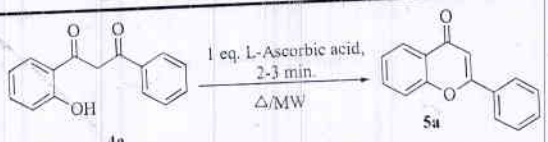
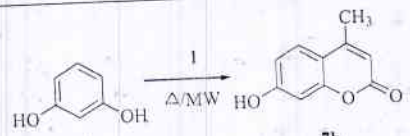
Table 1. Effect of amount of catalyst on the synthesis of flavones[a] and coumarins[b] under solvent-free conditions.



4a 5a

Sr. No.	Amount of Catalyst	Conventional heating		Microwave heating	
		Time	% Yield	Time	% Yield
1	0.1	2	5	3	6
2	0.2	2	23	3	22
3	0.4	2	37	3	38
4	0.6	2	56	3	55
5	0.8	2	79	3	80
6	1	2	93	3	94
7	1.2	2	93	3	94



6b 7b

1. Ethyl acetoacetate, 1 eq. L-Ascorbic acid, 10-15 min.

8	0.1	15	5	10	6
9	0.2	15	23	10	22
10	0.4	15	37	10	38
11	0.6	15	56	10	55
12	0.8	15	79	10	80
13	1	15	93	10	94
14	1.2	15	94	10	97

Reagent [a]1-(2-hydroxyphenyl)-3-phenylpropane-1,3-dione [b]Resorcinol (0. 5g).

The above study showed that one mole of L-ascorbic acid was necessary for the completion of reaction. The correlation of amount of catalyst with yield at fixed time and fixed temperature is shown in Fig. (3). The graph (Fig. 3) gives a clear picture of the reaction, which shows that as the amount of L-ascorbic acid increases, there is a gradual increase in the reaction yield. It shows a linear relationship between the amount of L-ascorbic acid and the yield of reaction.

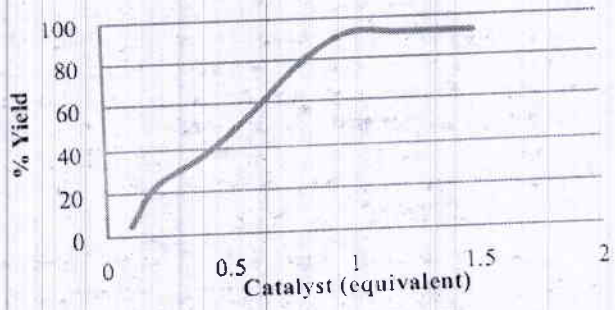


Fig (3). Correlation of % Yield with amount of catalyst.

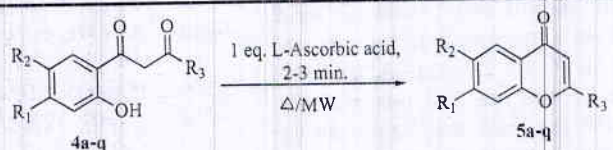
With the optimal reaction conditions in hand, both the reactions were examined to test the scope and limitation of this method. In all cases the desired flavones were smoothly generated with good to excellent yields; indicating its excellent tolerance for various functional groups (Table 2). However, electron donating groups favor coumarin synthesis under these conditions. All reaction mixtures were carefully analyzed and NMR indicates high conversions and lack of side products.

2. EXPERIMENTAL SECTION

2.1. General

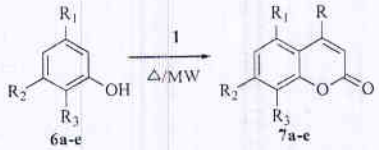
Unless otherwise specified, all reagents and starting materials were purchased from commercial sources and used as received. Analytical thin-layer chromatography (TLC) was performed on precoated Merck silica gel plates (60F-254), visualized with a UV-254 lamp, and stained with $KMnO_4$. The 1-(2-hydroxyphenyl)-3-aryl-1,3-propanediones were purchased from sigma aldrich and were used as it is. ^1H and ^{13}C NMR spectra were obtained as solutions in deuterated

Table 2. L-Ascorbic acid promoted synthesis of flavones and coumarins under solvent-free conditions.[a]



4a-q 5a-q

No	Compd.	R_1	R_2	R_3	Conventional heating[b]	Microwave heating[c]	Mp (°C)	
					(%) Yield[d]	(%) Yield[d]	Found	Reported
1	**5a**	H	H	Phenyl	93	94	96-98	96-97 [34]
2	**5b**	H	H	4-MeO-Phenyl	92	91	156-158	157-158 [34]
3	**5c**	H	H	4-F-Phenyl	87	88	149-151	148-150 [34]
4	**5d**	H	H	3-CF_3O-Phenyl	81	82	155-156	153-156 [34]
5	**5e**	H	H	3-CF_3-Phenyl	87	86	146-148	146-147 [34]
6	**5f**	H	H	Cyclohexyl	84	85	128-129	127-129 [34]
7	**5g**	OMe	H	Phenyl	88	87	108-110	109-110 [34]
8	**5h**	OMe	H	4-MeO-Phenyl	87	86	193-195	194-195 [34]
9	**5i**	OMe	H	4-F-Phenyl	83	84	171-173	172-173 [34]
10	**5j**	OMe	H	Cyclohexyl	82	83	152-153	152-154 [34]
11	**5k**	H	F	Phenyl	85	84	127-128	128-129 [34]
12	**5l**	H	Cl	Phenyl	90	89	182-184	183-184 [34]
13	**5m**	H	OMe	Phenyl	91	90	160-162	160-161 [34]
14	**5n**	H	OMe	4-MeO-Phenyl	86	85	194-195	195-196 [34]
15	**5o**	H	OMe	4-F-Phenyl	87	86	151-152	152-153 [34]
16	**5p**	H	OMe	3-CF_3O-Phenyl	79	80	161-164	161-163 [34]
17	**5q**	H	Me	2-F-4-Br-Phenyl	75	77	151-153	153 [34]



6a-e 7a-e

1) Ethyl acetoacetate (**6a-d, R = CH_3**) OR ethyl 3-oxo-3-phenylpropanoate (6e, R = Ph), 1 eq. L-Ascorbic acid, 10-15 min.

18	**7a**	OH	OH	H	94	97	282-284	280-281 [35]
19	**7b**	H	OH	H	88	92	185	184-185 [35]
20	**7c**	H	OMe	H	90	94	108-110	108-109 [36]
21	**7d**	H	OH	OH	84	89	236	234-237 [37]
22	**7e**	OH	OH	H	93	95	207-209	208-210 [36]

[a] Reagents: 1 (0.5 g.) various 1-(2-hydroxyphenyl)-3-aryl-1,3-propanediones (1.0 eq.), L-ascorbic acid-LAA (1.0 eq.). 2. Phenols (1.0 eq.), Ethyl acetoacetate (1.0 eq.), ethyl 3-oxo-3-pheny propanoate (1.0 eq.), L-ascorbic acid-LAA (1.0 eq.). [b] preheated oil bath. [c] in microwave reactor [d] Isolated yields.

solvents. Standard ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) were recorded on a Varian Mercury spectrometer in $CDCl_3$ or DMSO-d_6 solution and with tetramethylsilane as an internal standard. Chemical shifts (δ) in parts per million are reported relative to the residual signals of chloroform (7.25 ppm for ^{1}H and 77.16 ppm for ^{13}C). Multiplicities are described as s (singlet), d (doublet), t (triplet), q (quartet), or m (multiplet), and the coupling constants (J) are reported in hertz. IR spectra were recorded on Perkin Elmer Model 1600 series FTIR instrument. Mass spectra were recorded on LC/MS (ES-API) instrument. High-resolution mass spectra (HRMS) were performed with a QTOF Micromass Mass Spectrometer in electro spray ionization mode. All the compounds synthesized are previously reported, physical and spectroscopic data is in agreement with reported values.

(OCH_3); 55.7 (OCH_3); 100.2 (C-8); 105.9 (C-3); 114.0 (C-6); 114.2 (C-13,15); 117.6 (C-10); 126.7 (C-12,16); 127.6 (C-5); 157.7 (C-9); 162.1 (C-14); 162.8 (C-2); 163.9 (C-7); 177.6 (C-4). LCMS (ES-API) *m/z*: 283 $[M+H]^+$ $C_{17}H_{15}O_4$.

2.2.1.9. 7-Methoxy-2-(4-fluoro-phenyl)-chromen-4-one 5i

(Table **2**, entry **9**): white solid, mp 171-173 °C. IR (KBr), *v*, cm^{-1}: 781 (aromatic C=C), 841 (aromatic C=C), 1022, 1294, 1514, 1456, 1608, 1660. ^1H NMR (300 MHz, $CDCl_3$) δ: 3.84 (3H, s, OCH_3); 6.48-6.41 (2H, m, H-6,8); 6.64 (1H, s, H-3); 7.15 (2H, t, *J* = 8.7 Hz, H-13,15); 7.89 (1H, m, H-5); 7.90 (2H, m, H-12,16).^{13}C NMR (75 MHz, $CDCl_3$) δ : 55.6 (OCH_3); 101.3 (C-3); 108.0 (C-8); 110.0 (C-6); 115.7 (C-5,13); 116.0 (C-10); 128.9 (C-11); 128.9 (C-12,16); 130.1 (C-5); 163.4 (C-9); 165.3 (C-14); 165.9 (C-2); 166.7 (C-7); 174.8 (C-4). LCMS (ES-API) *m/z*: 271 $(M+H)^+$ $C_{16}H_{12}FO_3$.

2.2.1.10. 7-Methoxy-2-Cyclohexyl-chromen-4-one 5j

(Table **2**, entry **10**): white solid, mp 152-153 °C. IR (KBr), *v*, cm^{-1}: 831 (aromatic C=C), 923 (aromatic C=C), 1026 (C-O-C), 1238, 1384, 1442, 1502, 1572, 1606 (C=C), 1641 (C=O). ^1H NMR (300 MHz, $CDCl_3$) δ: 8.06 (1H, d, *J* = 8.7 Hz, H-5), 6.95-6.83 (2H, m, H-6,8), 6.09 (1H, s, H-3); 3.88 (3H, s, OCH_3); 2.47 (1H, m, H-11); 1.86-1.45 (10H, m, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 25.6 (C-13,15); 25.7 (C-12,16); 30.3 (C-14); 42.5 (C-11); 55.6 (OCH_3); 99.9 (C-8); 107.5 (C-3); 113.9 (C-6); 117.5 (C-10); 126.7 (C-5); 158.0 (C-9); 163.7 (C-7); 172.7 (C-2); 177.9(C-4). LCMS (ES-API) *m/z*: 259 $[M+H]^+$ $C_{16}H_{19}O_3$.

2.2.1.11. 6-Fluoro-2-phenyl-chromen-4-one 5k

(Table **2**, entry **11**): white solid, mp 127-128°C. IR (KBr), *v*, cm^{-1}: 767 (aromatic C=C), 835 (aromatic C=C), 1176 (C-O-C), 1359, 1570, 1624 (C=C), 1660 (C=O). ^1H NMR (300 MHz, $CDCl_3$) δ: 6.82 (1H, s, H-3); 7.46-7.39 (1H, m, H-8); 7.61-7.50 (4H, m, H-7,13,14,15); 7.93- 7.85 (3H, m, H-5,12,16), ^{13}C NMR (75 MHz, $CDCl_3$) δ: 106.7 (C-3), 110.7 (C-5); 120.2 (C-8); 121.7 (C-7); 122.0 (C-10); 126.2 (C-12,16); 129.0 (C-13,15); 131.3 (C-14); 131.7 (C-11); 152.3 (C-9); 161.1 (C-6); 163.1 (C-2); 177.5 (C-4). LCMS (ES-API) *m/z*: 241 $[M+H]^+$ $C_{15}H_{10}FO_2$.

2.2.1.12. 6-Chloro-2-phenyl-chromen-4-one 5l

(Table **2**, entry **12**): white solid, mp 182-184 °C. IR (KBr), *v*, cm^{-1}: 682 (aromatic C=C), 908 (aromatic C=C), 1132, 1307, 1438, 1457, 1567, 1601, 1651. ^1H NMR (300 MHz, $CDCl_3$) δ: 6.82 (1H, s, H-3); 7.56-7.50 (4H, m, H-8,13,14,15); 7.65-7.61 (1H, m, H-7); 7.90-7.88 (2H, m, H-12,16); 8.17 (d, 1H, *J* = 2.3 Hz, H-5). ^{13}C NMR (75 MHz, $CDCl_3$) δ : 107.3 (C-3); 119.7 (C-8); 124.7 (C-10); 125.1 (C-12,16); 126.3 (C-14); 129.1 (C-13,15); 131.1 (C-6); 131.2 (C-11); 131.8 (C-5); 133.0 (C-7); 154.4 (C-9); 163.7 (C-2); 177.1 (C-4). LCMS (ES-API) *m/z*: 257 $[M+H]^+$ $C_{15}H_{10}ClO_2$.

2.2.1.13. 6-Methoxy-2-phenyl-chromen-4-one 5m

(Table **2**, entry **13**): white solid, mp 160-162 °C. IR (KBr), *v* cm^{-1}: 658 (aromatic C=C), 1641, 846 (aromatic C=C), 1030, 1255, 1361, 1488, 1618. ^1H NMR (300 MHz, $CDCl_3$) δ: 3.89 (3H, s, OCH_3); 6.79 (1H, s, H-3); 7.28 (1H, dd, *J* = 6.7 & *J* = 3.5 Hz, H-8); 7.91-7.88 (2H, m, H-12,16); 7.57 (1H, d, *J* = 2.7 Hz, H-5); 7.51-7.46 (4H, m, H-7,13,14,15). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 55.8 (OCH_3); 104.7 (C-3); 106.7 (C-5); 119.4 (C-8); 123.6 (C-7); 124.4 (C-10); 126.1 (C-12,16); 128.8 (C-14); 131.4 (C-13,15); 131.7 (C-11); 150.8 (C-9); 156.9 (C-6); 163.0 (C-2); 178.2 (C-4). LCMS (ES-API) *m/z*: 253 $[M+H]^+$ $C_{16}H_{13}O_3$.

2.2.1.14. 6-Methoxy-2-(4-methoxy-phenyl)-chromen-4-one 5n

(Table **2**, entry **14**): white solid, mp 194-196 °C. IR (KBr), *v*, cm^{-1}: 558, 817 (aromatic C=C), 1014, 1196 (C-O-C), 1268, 1454, 1584, 1607 (C=C), 1647 (C=O). ^1H NMR (300 MHz, $CDCl_3$) δ: 3.88 (3H, s, OCH_3); 3.90 (3H, s, OCH_3); 6.73 (1H, s, H-3); 7.01 (2H, d, *J* = 9.0 Hz, H-13,15); 7.27 (1H, m, H-8); 7.58 (1H, d, *J* = 3.0 Hz, H-7); 7.60 (1H, d, *J* = 9.0 Hz, H-5); 7.86 (2H, d, *J* = 9.0 Hz, H-12,16). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 55.4 (OCH_3); 55.9 (OCH_3); 104.8 (C-3); 105.4 (C-5); 114.4 (C-13,15); 119.3 (C-8); 123.5 (C-7); 124.1 (C-11); 124.4 (C-10); 127.8 (C-12,16); 150.9 (C-9); 156.8 (C-6); 162.3 (C-14); 163.1 (C-2); 178.2 (C-4). LCMS (ES-API) *m/z*: 283 $[M+H]^+$ $C_{17}H_{15}O_4$.

2.2.1.15. 2-(4-Fluoro-phenyl)-6-methoxy-chromen-4-one 5o

(Table **2**, entry 15): white solid, mp 151-152°C. IR (KBr), v, cm^{-1}: 719 (aromatic C=C), 910 (aromatic C=C), 1024 (C-O-C), 1168 (C-O-C), 1488, 1620 (C=C), 1661 (C=C), 1727 (C=O). ^1H NMR (300 MHz, $CDCl_3$) δ: 3.90 (3H, s, OCH_3); 6.76 (1H, s, H-3); 7.18-7.31 (3H, m, H-8,13,14); 7.48 (1H, d, *J* = 9.3 Hz, H-7); 7.58 (1H, d, *J* = 2.4 Hz, H-5); 7.92 (2H, d, *J* = 9Hz, H-11,16). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 55.9 (OCH_3); 104.8 (C-3); 116.1 (C-5); 116.4 (C-13,15); 119.4 (C-8); 123.8 (C-7); 124.4 (C-11); 128.3 (C-10); 128.4 (C-12,16); 150.9 (C-9); 157.0 (C-6); 162.1 (C-14); 166.3 (C-2); 178.1 (C-4). LCMS (ES-API) m/z: 271 $[M+H]^+$ $C_{16}H_{12}FO_3$.

2.2.1.16. 6-Methoxy-2-(3-trifluoromethoxy-phenyl)-chromen-4-one 5p

(Table **2**, entry **16**): white solid mp 161-164°C. IR (KBr), *v*, cm^{-1}: 693, 713, 842 (aromatic C=C), 869 (aromatic C=C), 1263, 1490, 1577 (C=C), 1637 (C=O). ^1H NMR (300 MHz, $CDCl_3$) δ: 3.92 (3H, s, OCH_3); 6.81 (1H, s, H-3); 7.30 (1H, dd, *J* = 4.2 & 2.7 Hz, H-16); 7.39 (1H, d, *J* = 8.1 Hz, H-14); 7.50 - 7.58 (3H, m, H-6,7,12); 7.76 (1H, s, H-15); 7.83 (1H, d, *J* = 8.1 Hz, H-5). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 55.9 (OCH_3); 104.8 (C-3); 107.5 (C-12); 118.7 (C-14); 119.5 (C-5); 122.1 (C-8); 123.6 (C-16); 123.9 (C-7); 124.4 (OCF_3); 124.5 (C-10); 130.5 (C-15); 133.9 (C-11); 149.7 (C-9); 150.9 (C-6); 157.1 (C-13); 161.2 (C-2); 177.9 (C-4). HRMS (ESI) : calcd. for $C_{17}H_{12}F_3O_4$ $[M+H]^+$ 337.0681, found 337.0688.

2.2.1.17. 2-(4-Bromo-2-fluoro-phenyl)-6-methyl-chromen-4-one 5q

(Table **2**, entry **17**): white solid, mp 151-153°C. IR (KBr), *v*, cm^{-1}: 613, 760 (aromatic C=C), 1071 (C-O-C), 1192, 1257, 1480, 1571, 1679 (C=C), 1753 (C=O). ^1H NMR (300 MHz, $CDCl_3$) δ : 8.02 (1H, t, *J* = 8.1 Hz, H-5); 7.88 (1H, d, *J* = 7.8 Hz, H-7); 7.58 (1H, m, H-16); 7.25-7.45 (3H, m, H-8,13,15); 7.23 (1H, s, H-3); 2.55 (3H, s, CH_3). ^{13}C NMR

(75 MHz, $CDCl_3$) δ : 29.2 (CH_3); 106.9 (C-3); 120.7 (C-8); 121.7 (C-13); 123.8 (C-11); 126.4 (C-10); 127.7 (C-14); 128.9 (C-15); 130.5 (C-16); 130.5 (C-5); 133.6 (C-6); 133.6 (C-7); 148.7 (C-9); 160.1 (C-12); 163.7 (C-2); 197.3 (C-4). LCMS (ES-API) *m/z*: 333 $[M+H]^+$ $C_{16}H_{11}BrFO_2$.

2.2. General Procedure for the Synthesis of Coumarins

Mixture of phenols **6a-d** (0.5g, 4.55 mmol), ethyl acetoacetate (0.60mL, 4.77 mmol) and L-ascorbic acid (3.7g, 4.55 mmol) was heated either on a preheated oil bath or under microwave irradiation, at 180°C for 10-15 min. After completion of reaction (TLC check), the reaction mixture was cooled to room temperature and the flask was sonicated by adding water (10 mL). The crude product was filtered over suction-pump and washed with excess of water (3 × 10 mL) to remove L-ascorbic acid. The solid obtained was dried and crystallized by using ethanol to give the corresponding coumarins in high yield. The purity of products was confirmed by satisfactory spectroscopic data. Similarly, phenol **6e** (0.5mL, 4.77 mmol), ethyl 3-oxo-phenylpropanoate (0.82mL, 4.77 mmol) and L-ascorbic acid (3.7g, 4.55 mmol) was used for the synthesis of 5,7-dihydroxy-4-phenyl-chromen-2-one **8e**.

2.2.1. 5,7-Dihydroxy-4-methyl-chromen-2-one 7a

(Table **3**, entry **18**): pale yellow solid, mp 282-284 °C. IR (KBr), ν, cm^{-1}: 713 (aromatic C=C), 853 (aromatic C=C), 1152 (C-C-C), 1292, 1366, 1459, 1600, 1648, 1705, 2352, 2912, 3392. ^{1}H NMR (300 MHz, DMSO) δ: 2.38 (s, 3H, CH_3), 5.85 (s, 1H, H-3), 6.19 (s, 1H, H-6), 6.27 (s, 1H, H-8), 10.42 (bs, 2H, Ar-OH). ^{13}C NMR (75 MHz, DMSO) δ: 23.4 (CH_3), 94.5 (C-6), 99.1 (C-8), 102.1 (C-9), 110.8 (C-3), 154.9 (C-4), 156.5 (C-10), 157.9 (C-7), 160.1 (C-5), 161.0 (C-2).

2.2.2. 7-Hydroxy-4-methyl-chromen-2-one 7b

(Table **3**, entry **19**): pale yellow solid; mp 185°C. IR spectrum (KBr), ν, cm^{-1}: 846 (aromatic C=C), 1068 (C-O-C), 1273, 1390, 1601, 3135. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.38 (s, 3H, CH_3); 6.05 (s, 1H, H-3); 6.82 (m, 2H, H-6, H-8); 7.44 (d, *J* = 8.5 Hz, 1H, H-5); 9.90 (bs, 1H, Ar- OH). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 18.2 (CH_3); 102.5 (C-8); 110.2 (C-3); 112.0 (C-6); 112.7 (C-9); 125.3 (C-5); 152.7 (C-10); 154.7 (C-4); 160.8 (C-7); 161.2 (C-2).

2.2.3. 7-Methoxy-4-methyl-chromen-2-one 7c

(Table **3**, entry **20**): sky blue solid, mp 162-164°C. IR spectrum (KBr), ν, cm^{-1}: 795 (aromatic C=C), 809 (aromatic C=C), 1026 (C-O-C), 1155, 1374, 1563, 1763 (C=O), 3027. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.39 (s, 3H, CH_3), 3.87 (s, 3H, OCH_3), 6.12 (s, 1H, H-3), 6.79 (d, *J* = 2.5 Hz, 1H, H-8), 6.86 (dd, *J* = 2.4 & 8.9 Hz, 1H, H-6), 7.49 (d, *J* = 8.9 Hz, 1H, H-5). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 18.6 (CH_3), 55.6 (OCH_3), 100.7 (C-8), 111.8 (C-6), 112.1 (C-3), 113.5 (C-9), 125.5 (C-5), 152.5 (C-10), 155.2 (C-4), 161.2 (C-7), 162.6 (C-2).

2.2.4. 7,8-Dihydroxy-4-methyl-chromen-2-one 7d

(Table **3**, entry **21**): yellow solid; mp 236°C. IR spectrum (KBr), ν, cm^{-1}: 713 (aromatic C=C), 762 (aromatic C=C), 1020 (C-O-C), 1062, 1366, 1452, 1580, 1641, 1651, 1702 (C=O), 2928, 3312. ^{1}H NMR (300 MHz, DMSO) δ: 2.39 (s, 3H, CH_3), 6.08 (s, 1H, H-3), 6.78 (d, *J* = 8.4 Hz, 1H, H-6), 7.04 (d, *J* = 8.4 Hz, 1H, H-5), 9.35 (bs, 1H, Ar-OH), 9.97 (bs, 1H). ^{13}C NMR (75 MHz, DMSO) δ: 18.2 (CH_3), 110.9 (C-3), 112.1(C-6), 112.8 (C-9), 115.5 (C-5), 132.2 (C-8), 143.3 (C-10), 149.4 (C-7), 153.9 (C-4), 160.2 (C-2).

2.2.5. 5,7-Dihydroxy-4-phenyl-chromen-2-one 7e

(Table **3**, entry **22**): pale yellow solid, mp 207-209°C. IR spectrum (KBr), ν, cm^{-1}: 712 (aromatic C=C), 765 (aromatic C=C), 1369, 1452, 1542, 1606, 1702(C=O), 2928, 3376. ^{1}H NMR spectrum (300 MHz, DMSO) δ: 5.75 (s, 1H, H-3); 6.17 (d, *J* = 2.4 Hz, 1H, H-8); 6.28 (d, *J* = 2.4 Hz, 1H, H-6), 7.35 (m, 5H, Ar-H), 10.16 (bs, 1H, Ar-OH), 10.38 (bs, 1H, Ar-OH). ^{13}C NMR spectrum (75 MHz, DMSO) δ: 94.6 (C-6); 99.1 (C-8), 100.5 (C-9), 110.1 (C-3), 127.2 (C-2',C-6'), 127.3 (C-4'), 127.7 (C-3', C-5'), 139.5 (C-1'), 155.9 (C-10), 156.7 (C-4), 157.0 (C-7), 159.8 (C-5), 161.6 (C-2).

3. CONCLUSION

In conclusion, we have developed L-ascorbic acid-promoted, solvent-free and simple method for the synthesis of benzo-α-pyrones and benzo-γ-pyrone under microwave irradiation as well as conventional heating in good to excellent yields. The notable advantages of this method are the solvent-free conditions, inexpensive and efficient eco-friendly promoter, shorter reaction time. This methodology is highly facile and requires no column chromatography for purification. The resulting flavones and coumarins synthesized are versatile building blocks in the construction of heterocyclic architectures dominant in natural products. Further studies of exploiting the efficiency of L-ascorbic acid as a promoter in synthesis of various heterocyclic compounds are in progress.

CONFLICT OF INTEREST

The author(s) confirm that this article content has no conflict of interest.

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