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Solvent Free Microwave-Assisted Knoevenagel Condensation of Dehydroacetic Acid with Benzaldehyde Derivatives

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Synthesis of 3-cinnamoyl-4-hydroxy-6-methyl-2-pyrone (**3**) series *via* Knoevenagel condensation of dehydroacetic acid with benzaldehyde derivatives was dramatically enhanced with respect to conventional heating (CV) by a specific microwave effect when the reaction was performed, under solvent-free conditions, in a microwave reactor. Excellent isolated yields (up to 90 %) were attained within short reaction times (typically 2 to 10 min). Knoevenagel condensation assisted by solvent free microwave procedure (SFMW) was better than conventional procedure in terms of energy saving (20-fold reduction), rapidity (60-fold reduction), yield and cleanliness. Synthesized compounds wera characterized by IR, ^{1}H and ^{13}C NMR spectroscopy.

Key Words: Knoevenagel condensation, Microwave, Solvent free.

INTRODUCTION

Within the past 20 years, there has been a growing interest in new reaction condensations and activation *e.g.*, dry conditions (reactions without solvent), reactions under extreme or non-conventional conditions (high pressure, ultrasound or microwave activation). The effects usually expected are rate enhancement, yield or selectivity improvement, easier work-up or less polluting processes. Microwave heating makes convenient to perform reactions efficiently in the absence of any organic solvents, with the so-called dry media condensations. The advantages of using dry media conditions reach from faster reactions with different selectivity to more economical conditions due to the absence of organic solvents[1].

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Dehydroacetic acid (DHA (**1**) = 3-acetyl-4-hydroxy-6-methyl-2*H*-pyran-2-one) is often investigated compound due to its use in the synthesis of important organic compounds derivatives used as food additives, hypotensions, antimicrobial, insecticidal, cosmetic and promoters for hematocytes production[2-5]. Knoevenagel Condensation of aldehydes with active methylene compounds is one of the most important preparation methods of these substituted and active alkenes. Reaction are generally catalyzed using bases, Lewis acids or surfactant-catalyzed. The reaction preserve the pyronic cycle in the mild base conditions (amines, amino-acids), which is not the case with strong bases as NaOH or KOH. Unfortunately, these procedures require solvents for reaction media, extraction and purification and thus create much wastes[6-10]. Recently, use of microwave dry media technology has been reported as a useful condition for Knoevenagel condensation[11].

In the course of our current interest in organic synthesis under microwave irradiation, we felt that the 'Knoevenagel condensation' could be a good candidate as a model reaction, in order to compare not only the reaction times, yields and 'green' procedures, but also energy consumption for microwave and conventional technologies. The energy consumption should also be considered since it consumes non-renewable resources and produces waste and could also influence in the near future environmental acceptability and economic viability. Energy efficiency of microwave process is rarely discussed in published articles[12].

EXPERIMENTAL

The identity of the synthesized compounds was confirmed by IR, ^{1}H and ^{13}C NMR. Spectra were recorded for each compound and a full signal arrangement for both ^{1}H and ^{13}C was performed. The microwave data, time, temperature and yield were compared to conventional method.

Melting points were determined on a Stuart scientific SPM3 apparatus fitted with a microscope and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded in deuteriochloroform solutions, on a Bruker DRX 300 spectrometer, operating at 300.13 and 75.47 MHz, respectively. The chemical shifts are expressed in δ (ppm) and coupling constants (*J*) in Hertz (Hz). Electron impact mass spectra were obtained at 70 eV electron impact ionization using Nermag R 10-10C quadruple mass spectrometer. Infrared spectra were recorded on Magna-IR 550 series II Nicolet apparatus, using potassium bromide pellets. UV spectra were recorded on Cary 50 Scan UV-Visible spectrometer in chloroform solutions.

Conventional procedure A: To a mixture of DHA **1** (0.084 g) and aldehydes **2** (5 mmol) was added to a solution of chloroform (20 mL) and the catalyst pyridine (0.05 mL) and piperidine (0.05 mL). This mixture was

heated by conventional electrical heated jacket for 6 to 9 h. The reaction mixture was evaporated and the solid material was crystallized in ethanol.

Microwave procedure B: To a mixture of DHA (**1**) (0.084 g) and aldehydes **2** (5 mmol) was added to neutral alumina (1 g) and the catalyst pyridine (0.05 mL) and piperidine (0.05 mL). This mixture was heated by microwaves for 2 to 10 min. The reactions product extracted by chloroform and evaporated, the solid material was crystallized in ethanol.

Microwave procedure C: To a mixture of DHA (**1**) (0.084 g) and aldehydes **2** (5 mmol) was added to neutral alumina (1 g) and the catalyst ammonium acetate (0.1 g). This mixture was heated by microwaves for 2 to 10 min. The reactions product extracted by chloroform and evaporated, the solid material was crystallized in ethanol.

Extraction: Solvent free microwave-assisted Knoevenagel condensation (SFMW) takes 2 to 10 min, whilst 6 to 9 h were required by conventional procedure (CV). For solvent free microwave assisted, the reaction temperature is about 90 to 150 °C depending on the reaction mixture and the reactants. For CV, the reaction temperature is equal to boiling temperature of chloroform at atmospheric pressure (67 °C). A reaction time of 6 min with SFMW provides yields comparable or higher to those obtained after 6 h by means of CV. The ultimate yield obtained was from 60 to 90 % by SFMW and 50 to 80 % by CV. These results mean a substantial saving of time, energy and solvent.

Microwave effect

Cost, cleanliness and up-scaling: The reduced cost of extraction is clearly advantageous for the proposed solvent free microwave Knoevenagel condensation in terms of time and energy. Conventional procedure required a reaction time of 8 h. The SFMW method required heating for 6 min only. The energy required to perform the two reaction methods are respectively 0.8 kW h for CV and 0.04 kW h for SFMW. The power consumption has been determined with a Wattmeter at the microwave generator entrance and the electrical heater power supply. The energy efficiency of the solvent free microwave method is considerably higher than the conventional procedure if we take in account short reaction times required, reduction in solvent used and cleanliness of the process.

Regarding environmental impact, the calculated quantity of carbon dioxide rejected in the atmosphere is higher in the case of conventional procedure (640 g CO_2/ experiment, 12800 g CO_2/ mole of product). These calculations have been made according to literature to obtain 1 kW h from coal or fuel, 800 g CO_2 will be rejected in the atmosphere during combustion of fossil fuel[13].

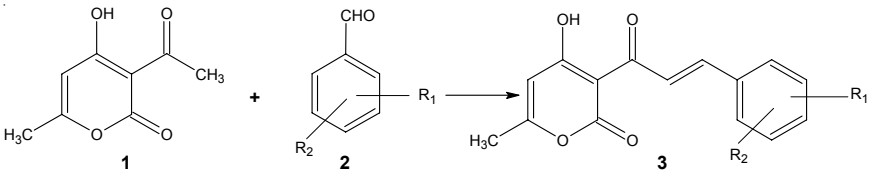
RESULTS AND DISCUSSION

To evaluate the synergy between dry media and microwave irradiation in this reaction, several experiments were tried and many compounds have been synthesized (18 compounds) and all compounds have been tested (Fig. 1). Tables 1 and 2 describe the effect of microwave on the yield and reaction times and the results are compared to the conventional method. Microwave irradiation of DHA (**1**) and benzaldehyde derivatives **2** give higher yields in comparison with conventional procedure. The reaction time are also dramatically reduced by a factor of 50-forl.

TABLE-1
SOLVENT FREE MICROWAVE-ASSISTED KNOEVENAGEL CONDENSATION CARRIED OUT UNDER THE DIFFERENT REACTION CONDITIONS

Product	Conventional procedure (solvent)			Microwave procedure (solvent free)			
	Time (h)	Temp. (ºC)	Yield (%)	Time (h)	Temp. (ºC)	Power (W)	Yield (%)
3a	7	67	54	6	84	200	62
3b	6	67	72	6	83	200	87
3c	9	67	53	8	164	600	60
3d	8	67	50	2	74	600	76
3e	8	67	43	6	145	600	69
3f	7	67	50	6	147	600	75
3g	8	67	51	6	145	600	66
3h	8	67	45	6	86	200	67
3i	9	67	44	6	143	600	55
3j	9	67	62	2	78	600	70
3k	6	67	72	6	84	200	75
3l	6	67	64	8	100	200	72
3m	8	67	50	8	98	200	55
3n	6	67	81	4	130	600	90
3o	9	67	25	10	120	200	35
3p	9	67	43	10	120	200	66
3q	9	67	47	10	180	600	61
3r	8	67	58	8	140	600	67

In this study, we present solvent free microwave assisted Knoevenagel condensation as an 'environmentally friendly' synthesis method suitable for preparation of substituted alkenes. SFMW is a very clean method, which avoids the use of large quantity of solvent and voluminous reactors for large scale applications. SFMW could also be used to produce larger quantities



3a-r:

a; R_1 = H, R_2 = H	**b**; R_1 = H, R_2 = 4-OCH_3	**c**; R_1 = H, R_2 = 4-Cl
d; R_1 = H, R_2 = 4-Br	**e**; R_1 = H, R_2 = 4-F	**f**; R_1 = H, R_2 = 4-$N(C_2H_5)_2$
g; R_1 = H,R_2 = 4-$N(CH_3)_2$	**h**; R_1 = H, R_2 = 4-OH	**i**; R_1 = H, R_2 = 4-NO_2
j; R_1 = H, R_2 =3-CH_3	**k**; R_1 = H, R_2 = 3-OCH_3	**l**; R_1 = H, R_2 = 3-Cl
m; R_1 = H, R_2 = 3-Br	**n**; R_1 = H, R_2 = 2-OCH_3	**o**; R_1 = H, R_2 = 2-OH
p; R_1 = H, R_2 = 2-Br	**q**; R_1 = 2-Cl, R_2 = 4-Cl	**r**; R_1 = 2-Cl, R_2 = 6-Cl

Fig. 1. Knoevenagel condensation of dehydroacetic acid (**1**) with benzaldehyde derivatives (**3a-r**)

TABLE-2
SOLVENT FREE MICROWAVE-ASSISTED KNOEVENAGEL CONDENSATION OF DEHYDROACETIC ACID (**1**) WITH BENZALDEHYDE DERIVATIVES (**3a-r**) CATALYZED BY AMMONIUM ACETATE AND NEUTRAL ALUMINA

Product	Microwave (CH_3COONH_4/Alumina)			
	Time (h)	Temp. (ºC)	Powder (W)	Yield (%)
3a	6	110	450	60
3b	6	110	450	75
3c	12	171	600	50
3d	4	128	600	55
3e	8	140	600	40
3f	6	140	600	65
3g	8	160	600	53
3h	6	112	450	60
3i	8	141	600	40
3j	4	140	600	55
3k	6	111	450	68
3l	6	111	450	55
3m	8	130	450	40
3n	6	135	600	85
3o	8	129	450	22
3p	6	114	450	38
3q	12	181	600	40
3r	12	182	600	43

by using existing big scale microwave reactors suitable for dry media synthesis assisted by microwaves. These microwave reactors are suitable for the dry media synthesis of 10, 20, 100 kg of products per time.

Solvent free microwave-assisted reactions as Knoevenagel condensation is a combination in form of synergy between microwave and dry media. The apparatus is relatively simple. The reaction, isolation and purification are performed in reduced stages and using less solvent and energy. Fig. 1 presents the general procedure for the formation of 3-cinnamoyl-4-hydroxy-6-methyl-2-pyrone (**3**) by Knoevenagel condensation of DHA (**1**) and benzal-dehyde derivatives (**2**).

As can be shown in Tables 1 and 2 the yields are higher using microwave than in conventional method, as well as the time needed to formation of compounds is less.

The Knoevenagel condensation of an active methylene compound and aldehydes is a convenient route to the synthesis of substituted alkenes. The mechanism of the Knoevenagel condensation is normally carried out in the presence of base (piperidine/pyridine or ammonium acetate) to remove the somewhat acidic or 'active' hydrogen atom, followed by attack of the resulting anion on the carbonyl carbon of the benzaldehyde. Elimination of a molecule of water results in the formation of a system of extended conjugation.

A possible explanation for the favourable effect of solvent free microwave is that it enhances dipole-dipoles interaction. During the reaction, the transition state involves delocalized anion. The mechanism will confer an enhancement in polarity which results on enhancement of molecule-wave interactions due to polarization phenomenon. The microwave activation effect become important due to enhancement in ionic dissociation and the reactants are transformed into more polar compounds in the transition state (Fig. 2).

^{1}H- ^{13}C NMR, Mass Spectra, IR and UV data for synthesized compounds (18 compounds):

All synthesized compounds were subjected to ^{1}H- ^{13}C NMR, mass spectra, IR and UV test and the results confirm the purity of these compounds.

4-Hydroxy-6-methyl-3-[(2E)-3-phenylprop-2-enoyl]-2*H*-pyran-2-one (3a): m.p. 130-132 °C; ^{1}H NMR ($CDCl_3$): δ 2.29 (s, 3H, 7-CH_3), 6.00 (s, 1H, H-5), 7.44 (m, 5H, Ar), 7.97 (d, 1H, H-2', *J* = 13.00 Hz), 8.28 (d, 1H, H-3', *J* = 13.00 Hz), 18.90 (s, 1H, OH); ^{13}C NMR ($CDCl_3$): δ 20.58 (C-7), 99.42 (C-3), 102.33 (C-5), 122.90 (C-2'), 129.10 (C-3",5"), 129.50 (C-2", 6"), 131.00 (C-1"), 134.90 (C-4") 146.10 (C-3'), 161.00 (C-2), 168.60 (C-6), 183.10 (C-4), 192.60 (C1'); MS: m/z 250 (M^+, 30), 255 (12), 241 (12), 228 (11), 212 (13), 199 (25), 195 (13), 185 (19), 166 (14), 152 (11),

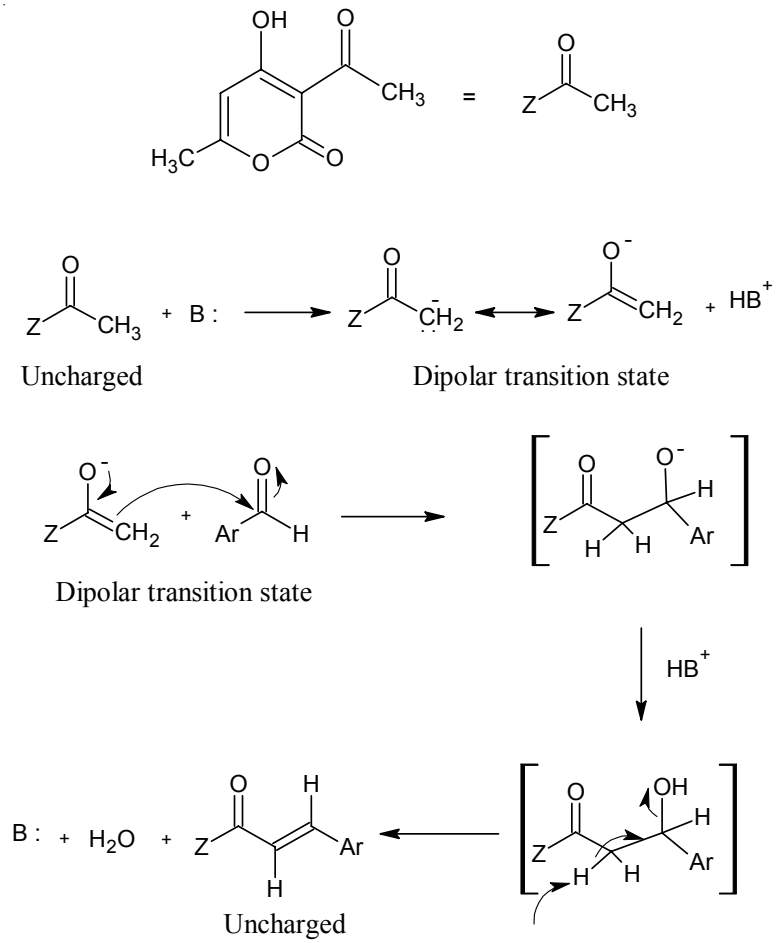


Fig. 2. Microwave effect according to reaction mechanism

151 (32), 135 (33), 131 (8), 129 (22), 125 (8), 111 (55), 110 (45), 103 (24), 97 (68), 96 (42), 83 (86), 77 (24), 73 (100), 69 (90), 55 (85); IR: (ν, cm^{-1}) 3550-3100, 1750-1700, 1660-1600, 1570-1415, 1220, 1010, 988, 895, 760, 700; UV: (λ_{max}, nm) 227 (ε, 4.391), 345 (ε, 4.054).

4-Hydroxy-3-[(2E)-3-(4-methoxyphenyl) prop-2-enoyl]-6-methyl-2*H*-pyran-2-one (3b): m.p. 208-210 °C ; ^{1}H NMR ($CDCl_3$): δ 2.34 (s, 3H, 7-CH_3), 3.97 (s, 3H, 7"-O-CH_3), 6.10 (s, 1H, H-5), 7.88 (m, 4H, Ar), 8.16 (d, 1H, H-2', *J* = 15.00 Hz), 8.49 (d, 1H, H-3', *J* = 15.00 Hz), 18.00 (s, 1H, OH); ^{13}C NMR ($CDCl_3$): δ 20.65 (C-7), 28.90 (C-7"), 99.34 (C-3), 102.67 (C-5), 114.53 (C-3".5"), 120.37 (C-2'), 127.63 (C-1"), 131.28 (C-2".6"), 146.58 (C-3'), 161.14 (C-2), 162.37 (C-4"), 168.31 (C-6), 183.45 (C-4),

192.49 (C-1'), MS: m/z 286(M^+, 49), 285 (12), 271 (21), 258 (13), 256 (2), 241 (53), 179 (13), 174 (100), 162 (96), 153 (56), 125 (2), 107 (4), 101 (4), 102 (92), 85 (14), 77 (30), 69 (18); IR: (ν, cm^{-1}) 3600-3100, 1730-1690, 1650-1580, 1550-1450, 1415, 1365, 1295, 1235, 1005, 730, 700; UV: (λ_{max}, nm) 245.0 (ε, 3.7716), 379.0 (ε, 4.1628).

3-[(2E)-3-(4-Chlorophenyl) prop-2-enoyl]-4-hydroxy-6-methyl-2*H*-pyran-2-one (3c): m.p. 159-160 °C ; ^{1}H NMR ($CDCl_3$): δ 2.33(s, 3H, 7-CH_3), 5.98 (s, 1H, H-5), 7.65 (m, 4H, Ar), 7.92 (d, 1H, H-2', *J* = 15.00 Hz), 8.28 (d, 1H, H-3', *J* = 15.00 Hz), 16.50 (s, 1H, OH). ^{13}C NMR ($CDCl_3$): δ 20.73 (C7), 99.55 (C3), 102.38 (C5), 123.60 (C2'), 129.30 (C-3".5"), 130.32 (C-2",6"), 133.28 (C-4"), 137.09 (C1"), 144.65 (C3'), 161.25 (C2), 168.31 (C6), 183.12 (C4), 192.65 (C1'); MS: m/z 292 (M^+, 10), 291 (76), 290 (100), 289 (52), 277 (10), 275 (12), 247 (13), 179 (16), 167 (10), 165 (17), 153 (4), 139 (10), 137 (10), 113 (4), 111 (15), 102 (12), 101 (12), 97 (13), 85 (23), 69 (22); IR: (ν, cm^{-1}) 3600-3100, 1720-1680, 1625-1590, 1520-1410, 1000; UV: (λ_{max}, nm) 350.0 (ε, 4.261), 259.0 (ε, 4.271).

3-[(2E)-3-(4-Bromophenyl) prop-2-enoyl]-4-hydroxy-6-methyl-2*H*-pyran-2-one (3d): m.p. 170-173 °C ; ^{1}H NMR ($CDCl_3$): δ 2.27 (s, 3H, 7-CH_3), 5.85 (s, 1H, H-5), 7.49 (m, 4H, Ar), 7.76 (d, 1H, H-2', *J* = 14.00 Hz), 8.29 (d, 1H, H-3', *J* = 14.00 Hz), 16.50 (s, 1H, OH); ^{13}C NMR ($CDCl_3$): δ 20.73 (C7), 99.57 (C3), 102.37 (C5), 123.73 (C2'), 125.55 (C-4"), 130.50 (C-2",6"), 132.28 (C-3",5"), 133.70 (C1"), 144.72 (C3'), 161.26 (C2), 168.93 (C6), 183.11 (C4), 192.68 (C1'); MS: m/z 336 (M^+, 40), 335 (29), 334 (40), 333 (22), 321 (2), 319 (2), 308 (2), 306 (2), 293 (4), 291 (7), 289 (4), 211 (45), 209 (46), 183 (15), 181 (15), 179 (67), 157 (2), 155 (2), 153 (10), 125 (7), 115 (21), 102 (100), 85 (56), 83 (39), 69 (46), 43 (59); IR: (ν, cm^{-1}) 3620-3150, 1750-1700, 1675-1615, 1580-1490, 1435, 1010, 990, 820, 735; UV: (λ_{max}, nm) 251.0 (ε, 3.8964), 361.0 (ε, 4.6099).

3-[(2E)-3-(4-Fluorophenyl) prop-2-enoyl]-4-hydroxy-6-methyl-2*H*-pyran-2-one (3e): m.p. 147-149 °C ; ^{1}H NMR ($CDCl_3$): δ 2.35 (s, 3H, 7-CH_3), 5.94 (s, 1H, H-5), 7.56 (m, 4H, Ar), 7.96 (d, 1H, H-2', *J* = 14.00 Hz), 8.37 (d, 1H, H-3', *J* = 14.00 Hz), 16.00 (s, 1H, OH); ^{13}C NMR ($CDCl_3$): δ 20.70 (C7), 99.48 (C3), 102.42 (C5), 116.36 (C3", 5"), 122.80 (C2'), 131.04 (C1"), 131.27 (C2",6"), 144.93 (C3'), 161.30 (C2),162.81 (C-4"), 168.80 (C6), 183.17 (C4), 192.69 (C1'); MS: m/z 274 (M^+, 85), 273 (54), 246 (9), 244 (9), 231 (18), 229 (15), 179 (80), 153 (10), 149 (100), 125 (16), 121 (44), 101 (69), 95 (17), 85 (52), 83 (35), 75 (29), 70 (48), 43 (52); IR: (ν, cm^{-1}) 3550-3150, 1750-1700, 1660-1600, 1570-1415, 1050, 730; UV: (λ_{max}, nm) 357.5 (ε, 4.496), 246.5 (ε, 3.792).

3-{(2E)-3-[4-(Diethylamino)phenyl] prop-2-enoyl}-4-hydroxy-6-methyl-2*H*-pyran-2-one (3f): m.p. 150-151 °C; ^{1}H NMR ($CDCl_3$): δ 1.23 (m, 6H, 8"-CH_3, 10"-CH_3), 3.50 (m, 4H, 7"-N-CH_2, 9"-N-CH_2), 2.26 (s,

3H, 7-CH_3), 5.88 (s, 1H, H-5), 7.15 (m, 4H, Ar), 7.76 (d, 1H, H-2', *J* = 13.00 Hz), 8.16 (d, 1H, H-3', *J* = 13.00 Hz), 18.00 (s, 1H, OH); ^{13}C NMR ($CDCl_3$): δ 20.53 (C7), 28.97 (C-8",10"), 43.26 (C-7",9"), 99.93 (C-3), 103.34 (C-5), 115.67 (C-2'), 111.15 (C-3".5"), 122.04 (C1"), 131.10 (C-2",6"), 148.48 (C3'), 151.92 (C4"), 161.69 (C2), 167.23 (C6), 184.05 (C4), 191.06 (C1'); MS: m/z 327 (M^+, 62), 326 (3), 312 (3), 202 (5), 179 (5), 174 (3), 153 (5), 148 (6), 130 (11), 125 (3), 115 (9), 102 (9), 85 (22), 69 (24), 55 (9); IR: (ν, cm^{-1}) 3650-3150, 1735-1690, 1620-1550, 1535-1420, 1350, 1310, 129, 1260, 1240, 1180, 1150, 1070, 1020, 990, 950, 870, 820, 740; UV: (λ_{max}, nm) 236.0 (ε, 3.2859), 327.5 (ε, 3.2283).

3-{(2E)-3-[4-(Dimethylamino) phenyl] prop-2-enoyl}-4-hydroxy-6-methyl-2*H*-pyran-2-one (3g): m.p. 220-222 °C; ^{1}H NMR ($CDCl_3$): δ 2.28 (s, 3H, 7-CH_3), 2.80 (s, 6H, 7"-N-CH_3, 8"-N-CH_3), 5.89 (s, 1H, H-5), 7.28 (m, 4H, Ar), 7.96 (d, 1H, H-2', *J* = 15.00 Hz), 8.23 (d, 1H, H-3', *J* = 15.00 Hz), 18.16 (s, 1H, OH); ^{13}C NMR ($CDCl_3$): δ 20.56 (C-7), 28.90 (C7",8"), 99.03 (C-3), 103.22 (C-5), 111.87 (C3",5"), 116.48 (C-2'), 122.79 (C-1"), 131.83 (C-2",6"), 148.30 (C-3'), 152.66 (C4"), 161.64 (C-2), 167.44 (C-6), 183.96 (C-4), 191.35 (C-1'); MS: m/z 299(M^+, 100), 298 (15), 284 (2), 271 (3), 256 (6), 254 (1), 179 (3), 174 (27), 153 (3), 146 (10), 134 (27), 125 (3), 120 (3), 115 (4), 102 (8), 85 (20), 83 (24), 77 (7); IR:(ν, cm^{-1}) 3600-3130, 1700-1690, 1620-1570, 1555-1400, 1370, 1355, 1290, 1210, 1190, 1130, 1060, 1020, 990, 940, 850, 820, 800, 710; UV: (λ_{max}, nm) 260.0 (ε, 4.2353), 326.0 (ε, 4.3915).

4-Hydroxy-3-[(2E)-3-(4-hydroxyphenyl) prop-2-enoyl]-6-methyl-2*H*-pyran-2-one (3h): m.p. 234-236 °C; ^{1}H NMR ($CDCl_3$): δ 2.32 (s, 3H, 7-CH_3), 6.28 (s, 1H, H-5), 7.30 (m, 4H, Ar), 7.84 (d, 1H, H-2', *J* = 15.00 Hz), 8.13 (d, 1H, H-3', *J* = 15.00 Hz), 16.45 (s, 1H, OH); ^{13}C NMR ($CDCl_3$): δ 19.94 (C-7), 98.60 (C-3), 101.99 (C-5), 116.16 (C-3", 5"), 118.57 (C-1'), 125.33 (C-1"), 131.34 (C-2", 6"), 146.50 (C-2'), 160.52 (C-4"), 161.05 (C-2), 169.44 (C-6), 182.71 (C4), 191.50 (C1'); MS: m/z 272 (M^+, 100), 271 (49), 257 (2), 244 (2), 229 (25), 185 (24), 179 (28), 160 (15), 153 (11), 147 (90), 125 (10), 119 (24), 107 (20), 93 (11), 91 (84), 85 (41), 69 (43), 43 (55); IR: (ν, cm^{-1}) 3500-3080, 1720-1670, 1630-1590, 1550-1430, 1330, 1280, 1250, 1170, 1020, 1000, 970, 825, 710; UV: (λ_{max}, nm) 254 (ε, 3.8833), 367 (ε, 4.6151).

4-Hydroxy-6-methyl-3-[(2E)-3-(4-nitrophenyl) prop-2-enoyl]-2*H*-pyran-2-one (3i): m.p. 243-246 °C ; ^{1}H NMR (CF_3CO_2D): δ 2.44 (s, 3H, 7-CH_3), 6.16 (s, 1H, H-5), 8.03 (m, 4H, Ar), 8.25 (d, 1H, H-2', *J* = 13.00 Hz), 8.41 (d, 1H, H-3', *J* = 13.00 Hz), 17.44 (s, 1H, OH); ^{13}C NMR ($CDCl_3$): δ 20.81 (C7), 99.78 (C3), 102.18 (C5), 124.22 (C-3",5"), 127.39 (C2'), 129.56 (C-2", 6"), 140.86 (C1"), 142.36 (C3'), 148.81 (C-4"), 161.21 (C2), 169.52 (C6), 182.89 (C4), 192.46 (C1'); MS: m/z 301 (M^+, 88), 300 (26),

286 (10), 256 (2), 243 (4), 241 (52), 179 (100), 176 (48), 153 (15), 148 (2), 125 (25), 122 (5), 102 (56), 97 (50), 77 (15); IR: (ν, cm^{-1}) 3640-3100, 1725-1690, 1630-1310, 1530-1412, 1340, 1230, 1170, 1110, 1000, 950, 885, 840, 780, 750, 705; UV: (λ_{max}, nm) 216 (ε, 4.5028), 350.0 (ε, 4.2519).

4-Hydroxy-6-methyl-3-[(2E)-3-(3-methylphenyl) prop-2-enoyl]-2*H*-pyran-2-one (3j): m.p. 140-143 °C ; ^{1}H NMR ($CDCl_3$): δ 2.31 (s, 3H, 7-CH_3), 2.36 (s, 3H,7"-CH_3), 5.97 (s, 1H, H-5), 7.43 (m, 4H, Ar), 7.97 (d, 3H, 7"-CH_3), 8.10 (d, 1H, H-2', *J* = 13.00 Hz), 8.28 (d, 1H, H-3', *J* = 13.00 Hz), 17.00 (s, 1H, OH); ^{13}C NMR ($CDCl_3$): δ 20.70 (C-7), 28.7 (C-7"), 99.48 (C-3), 102.49 (C5), 122.76 (C2'), 128.89 (C-5"), 129.69 (C-2",6"), 132.11 (C-3"), 134.72 (C-4"), 138.71 (C1"), 146.72 (C2'), 161.31 (C2), 168.66 (C6), 183.27 (C4), 192.84 (C1'); MS: m/z 270 (M^+, 68), 269 (51), 255 (21), 242 (42), 227 (19), 225 (14), 200 (20), 186 (18), 185 (56), 184 (46), 179 (97), 171 (14), 153 (16), 145 (89), 125 (11), 117 (28), 116 (22), 115 (100), 91 (72), 85 (4261), 77 (13), 69 (33), 65 (24), 43 (52); IR: (ν, cm^{-1}) 3600-3200, 1755-1705, 1650-1620, 1550-1500, 1380, 1260, 1000, 950, 800, 710; UV: (λ_{max}, nm) 227.0 (ε, 3.371), 364.5 (ε, 4.054).

4-Hydroxy-3-[(2E)-3-(3-methoxyphenyl) prop-2-enoyl]-6-methyl-2*H*-pyran-2-one (3k): m.p. 148-150 °C; ^{1}H NMR ($CDCl_3$): δ 2.29 (s, 3H, 7-CH_3), 3.76 (s, 3H, 7"-OCH_3), 5.95 (s, 1H, H-5), 7.88 (m, 4H, Ar), 7.98 (d, 1H, H-2', *J* = 14.00 Hz), 8.30 (d, 1H, H-3', *J* = 14.00 Hz), 17.00 (s, 1H, OH); ^{13}C NMR ($CDCl_3$): δ 20.69 (C7), 29.74 (C-7"), 99.54 (C3), 102.42 (C-5), 113.80 (C-2"), 117.24 (C-4"), 121.98 (C2'), 123.35 (C-6"), 129.97 (C-5"), 136.16 (C-1"), 146.27 (C-3'), 159.99 (C-3"), 161.25 (C-2), 168.76 (C-6), 183.19 (C-4), 192.81 (C-1'); MS: m/z 286 (M^+, 55), 285 (12), 271 (2), 258 (34), 243 (14), 241 (18), 179 (36), 161 (69), 153 (8), 133 (15), 125 (7), 102 (24), 90 (37), 85 (33), 77 (48), 43 (38); IR: (ν, cm^{-1}) 3620-3110, 1750-1700, 1655-1620, 1540-1500, 1480, 1450, 1385, 1355, 1250, 1200, 1160, 1040,1000, 980, 930, 890, 830, 790, 720; UV: (λ_{max}, nm) 213 (ε, 3.7368), 363 (ε, 3.8375).

3-[(2E)-3-(3-Chlorophenyl) prop-2-enoyl]-4-hydroxy-6-methyl-2*H*-pyran-2-one (3l): m.p. 154-156 °C; ^{1}H NMR ($CDCl_3$): δ 2.32 (s, 3H, 7-CH_3), 6.05 (s, 1H, H-5), 7.59 (m, 4H, Ar), 8.04 (d, 1H, H-2', *J* = 15.00 Hz), 8.32 (d, 1H, H-3', *J* = 15.00 Hz), 17.06 (s, 1H, OH); ^{13}C NMR ($CDCl_3$): δ 20.75 (C-7), 99.61 (C-3), 102.32 (C-5), 124.52 (C-2'), 127.22 (C-6"), 128.82 (C-2"), 130.21 (C-5"), 130.86 (C-4"), 135.05 (C-3"), 136.61 (C-1"), 144.35 (C-3'), 161.22 (C-2), 169.05 (C-6), 183.05 (C-4), 192.69 (C-1'); MS: m/z 292 (M^+, 20), 291 (25), 290 (36), 283 (20), 264 (7), 262 (12), 249 (8), 247 (21), 245 (12), 179 (100), 167 (22), 165 (71), 153 (14), 139 (12), 137 (24), 125 (17), 113 (14), 111 (10), 102 (98), 101 (77), 85 (73), 75 (50), 69 (55). IR: (ν, cm^{-1}) 3620-3130, 1750-1700, 1665-1620, 1560-1520, 1465, 1360, 1200, 990-1080, 910, 860, 830, 760; UV: (λ_{max}, nm) 250.0 (ε, 3.506), 354.0 (ε, 4.287).

3-[(2E)-3-(3-Bromophenyl) prop-2-enoyl]-4-hydroxy-6-methyl-2*H*-pyran-2-one (3m): m.p. 164-166 °C; ^{1}H NMR ($CDCl_3$): δ 2.31 (s, 3H, 7-CH_3), 5.99 (s, 1H, H-5), 7.46 (m, 4H, Ar), 7.99 (d, 1H, H-2', *J* = 14.00 Hz), 8.21 (d, 1H, H-3', *J* = 14.00 Hz), 16.45 (s, 1H, OH); ^{13}C NMR ($CDCl_3$): δ 20.76 (C7), 99.61 (C3), 102.33 (C5), 123.13 (C-3"), 124.52 (C2'), 127 (C-6"), 128.68 (C-5"), 131.90 (C-2"), 133.54 (C-4"), 134.54 (C1"), 144.28 (C-3'), 161.24 (C-2), 169.06 (C-6), 183.06 (C-4), 192.67 (C-1'); MS: m/z 336 (M^+, 7), 335 (42), 334 (33), 333 (41), 308 (3), 306 (5), 304 (3), 293 (3), 291 (6), 289 (5), 211 (4), 209 (3), 208 (27), 183 (2), 181 (2), 179 (6), 125 (4), 102 (100), 101 (19), 85 (65), 69 (35), 43 (54); IR: (ν, cm^{-1}) 3610-3260, 1750-1700, 1670-1620, 1555-1510, 1455, 1410,1355, 1235, 1200, 1020, 1000, 980, 950, 900, 855, 830, 720, cm^{-1}; UV: (λ_{max}, nm) 241.5 (ε, 1.949), 356.5 (ε, 3.538).

4-Hydroxy-3-[(2E)-3-(2-methoxyphenyl) prop-2-enoyl]-6-methyl-2*H*-pyran-2-one (3n): m.p. 165-167 °C; ^{1}H NMR ($CDCl_3$): δ 2.32 (s, 3H, 7-CH_3), 3.90 (s, 3H, 7"-OCH_3), 5.98 (s, 1H, H-5), 7.41 (m, 3H, Ar), 8.10 (d, 1H, H-2', *J* = 13.00 Hz), 8.55 (d, 1H, H-3', *J* = 13.00 Hz), 17.00 (s, 1H, OH); ^{13}C NMR ($CDCl_3$): δ 20.69 (C7), 24.71 (C-7"), 99.48 (C3), 102.58 (C5), 11.25 (C-3"), 120.85 (C2'), 122.99 (C-5"), 123.77 (C1"), 129.55 (C-6"), 132.66 (C-4"), 159.14 (C-2"), 141.71 (C3'), 161.30 (C2), 168.42 (C6), 183.39 (C4), 192.96 (C1'); MS: m/z 286 (M^+, 100), 285 (19), 271 (9), 258 (7), 256 (14), 243 (16), 241 (12), 179 (25), 161 (69), 153 (26), 133 (5), 125 (9), 107 (7), 102 (11), 89 (26), 85 (52), 77 (46), 69 (31), 43 (37); IR: (ν, cm^{-1}) 3620-3200, 1740-1690, 1635-1605, 1540-1480, 1460, 1430, 1380, 1300, 1250, 1230, 1190, 1110, 1025, 1000, 950, 870, 850, 810, 790, 750; UV: (λ_{max}, nm) 253 (ε, 3.5635), 364 (ε, 4.2671).

4-Hydroxy-3-[(2E)-3-(2-hydroxyphenyl) prop-2-enoyl]-6-methyl-2*H*-pyran-2-one (3o): m.p. 207-210 °C; ^{1}H NMR ($CDCl_3$): δ 2.33 (s, 3H, 7-CH_3), 6.32 (s, 1H, H-5), 7.28 (m, 4H, Ar), 7.98 (d, 1H, H-2', *J* = 16.00 Hz), 8.43 (d, 1H, H-3', *J* = 16.00 Hz), 16.55 (s, 1H, OH); ^{13}C NMR ($CDCl_3$): δ 20.05 (C-7), 98.92 (C-3), 101.99 (C-5), 116.46 (C-3"), 119.67 (C-5"), 121.15 (C-1"), 121.91 (C-2'), 129.35 (C-6"), 132.91 (C-4"), 141.64 (C-3'), 157.88 (C-2"), 160.50 (C-2), 169.68 (C-6), 182.73 (C-4), 192.23 (C-1'); MS: m/z 272 (M^+, 44), 271 (6), 257 (2), 244 (2), 229 (3), 179 (6), 153 (18), 147 (24), 125 (8), 119 (6), 93 (11), 91 (100), 90 (16), 85 (29), 69 (28), 43 (39); IR: (ν, cm^{-1}) 3400-3010, 1710-1670, 1635-1608, 1535-1500, 1450, 1355, 1240, 1020, 1000, 850, 750; UV: (λ_{max}, nm) 256 (ε, 3.991) 352 (ε, 4.699).

3-[(2E)-3-(2-Bromophenyl) prop-2-enoyl]-4-hydroxy-6-methyl-2*H*-pyran-2-one (3p): m.p. 160-164 °C; ^{1}H NMR ($CDCl_3$): δ 2.28 (s, 3H, 7-CH_3), 5.98 (s, 1H, H-5), 7.56 (m, 3H, Ar), 8.10 (d, 1H, H-2', *J* = 14.00 Hz), 8.50 (d, 1H, H-3', *J* = 14.00 Hz), 17.60 (s, 1H, OH); ^{13}C NMR ($CDCl_3$): δ

20.75 (C-7), 99.63 (C-3), 102.34 (C-5), 125.65 (C-2'),126.50 (C-2''), 127.87 (C-5''), 128.69 (C-6''), 131.90 (C-3''), 133.54 (C-4''), 134.67 (C-1''), 144.16 (C-3'), 161.24 (C2), 169.02 (C6), 183.06 (C4), 192.65 (C1'); MS: m/z 336 (M^+, 2), 335 (4), 334 (4), 333 (5), 308 (2), 306 (2), 289 (2), 255 (18), 254 (100), 211 (2), 209 (2), 183 (2), 181 (2), 179 (2), 153 (2), 125 (2), 102 (51), 101 (21), 85 (82), 69 (17), 43 (21). IR: (ν, cm^{-1}) 3610-3205, 1750-1695, 1660-1610, 1560-1490, 1460, 1430, 1360, 1260, 1240, 1200, 1160, 1020, 1000, 970, 930, 850, 790, 720; UV: (λ_{max}, nm) 245 (ε, 3.363), 360 (ε, 4.419).

3-[(2E)-3-(2,4-Dichlorophenyl)prop-2-enoyl]-4-hydroxy-6-methyl-2*H*-pyran-2-one (3q): m.p. 168-170 °C; ^{1}H NMR ($CDCl_3$): δ 2.28 (s, 3H, 7-CH_3), 5.94 (s, 1H, H-5), 7.71 (d, 1H, H-2', *J* = 15.00 Hz), 7.33 (m, 3H, Ar), 8.04 (d, 1H, H-3', *J* = 15.00 Hz), 17.50 (s, 1H, OH); ^{13}C NMR ($CDCl_3$): δ 20.76 (C7), 99.64 (C3), 102.30 (C5), 125.78 (C2'), 127.72 (C5''), 129.18 (C-3''), 130.07 (C-6''), 131.55 (C-1''), 136.47 (C-2''), 137.09 (C-4''), 140.10 (C-3'), 161.24 (C-2), 169.14 (C-6), 182.99 (C4), 192.50 (C1'); MS: m/z 328 (M^+, 5), 327 (4), 326 (4), 325 (6), 324 (6), 323 (8), 290 (34), 289 (18), 288 (100), 260 (4), 200 (4), 179 (3), 173 (3), 171 (3), 153 (4), 149 (3), 125 (6), 111 (6), 99 (10), 85 (45), 69 (27); IR: (ν, cm^{-1}) 3650-3240, 1760-1700, 1655-1615, 1555-1500, 1380, 1360, 1210, 1140, 1100, 1050, 1000, 940, 830, 700; UV: (λ_{max}, nm) 253 (ε, 43.859), 364 (ε, 4.517).

3-[(2E)-3-(2,6-Dichlorophenyl)prop-2-enoyl]-4-hydroxy-6-methyl-2*H*-pyran-2-one (3r): m.p. 182-185 °C; ^{1}H NMR ($CDCl_3$): δ 2.27 (s, 3H, 7-CH_3), 5.96 (s, 1H, H-5), 7.39 (m, 3H, Ar), 8.14 (d, 1H, H-2', *J* = 15.00 Hz), 8.45 (d, 1H, H-3', *J* = 15.00 Hz), 16.45 (s, 1H, OH); ^{13}C NMR ($CDCl_3$): δ 20.77(C-7), 99.93 (C-3), 102.08 (C-5), 128.90 (C-2'), 129.00 (C-5''), 130.19 (C-3''), 131.42 (C-4''), 132.36 (C-2'', 6''), 135.60 (C-1''), 138.87 (C-3'), 160.99 (C-2), 169.35 (C-6), 182.80 (C-4), 192.95 (C-1'); MS: m/z 328 (M^+, 4), 327 (4), 326 (4), 325 (7), 324 (4), 323 (9), 290 (35), 289 (18), 288 (100), 260 (4), 203 (8), 201 (4), 199 (5), 179 (4), 173 (4), 171 (4), 153 (4), 149 (4), 145 (5), 125 (6), 99 (13), 85 (53), 83 (18), 69 (26), 43 (47). IR: (ν, cm^{-1}) 3630-3220, 1760-1690, 1650-1620, 1580-1500, 1430, 1370, 1240, 1000, 980, 850, 780, 710; UV: (λ_{max}, nm) 259 (ε, 4.271), 350 (ε, 4.261).

Conclusion

Solvent free microwave 'green' procedure has been compared with the conventional procedure method, for the synthesis of substituted alkenes from dehydroacetic acid (**1**) and benzaldehyde derivatives by Knoevenagel condensation, in addition to microwave effect causing specific bond activation, the microwave method offers important advantages over conventional procedure, namely; solvent free process, shorter reaction times (2 to 10 min against 2 to 10 h); better yields (55 to 90 % against 41 to 81 % for conventional procedure); environmentally friendly and lower cost. The results

indicate a significant gain in energy efficiency using microwave: 20-fold reduction in energy demand on switching from electrical heater power supply to microwave reactor. Microwave provides highly focused energy, enabling rapid reaction, substantial saving of energy consumption and a reduced environmental burden (less CO_2 rejected in the atmosphere).

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