Molecules **1998**, *3*, 120–131

molecules

ISSN 1420-3049

Evaluation of Effect of Microwave Irradiation on Syntheses and Reactions of Some New 3-Acyl-methylchromones*

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Received: 16 January 1998 / Accepted: 17 February 1998 / Published: 10 March 1998

Abstract: The 3-Acyl-2-R-methylchromones (R = H, ArO, $C_6H_4(CO)_2N$) were prepared in good yields by different methods from 2-hydroxyaroylacetone derivatives. Some subsequent reactions of these compounds with hydroxylamine and 3-formylchromones are described. The effect of microwave irradation on some condensation reactions was studied.

Keywords: Microwave irradiation, aldol reaction, 4-oxo-4*H*-[1]-benzopyran derivatives, rearrengement of chromones, 3-formylchromones.

Introduction

This paper is a continuation of our previous works [1-4] where we reported synthesis, theoretical, spectral and biological studies of chromone derivatives. The present work describes the study and the preparation of some new 3-acylchromones and their reactions by classic or microwave methods.

The 3-Acyl-2-R-methylchromones with their several functional groups are useful building-blocks in organic synthesis. The chromones are possible precursors in forming new nitrogen heterocycles after nucleophilic opening of the γ-pyrone ring [5,6].

Methyl groups at position 2 and at a carbonyl group of the studied compounds can be active in aldol type reactions. Electron-deficit centres at carbonyl groups and carbon at position 2 of the γ-pyrone ring are very effective in reactions with nucleophilic reagents. The synthesized compounds **2, 5, 8 - 11** are useful for further transformations.

Results and Discussions

The composition of the prepared compounds **2-11** were proved by elemental analysis and their structures were determined by NMR and IR spectra.

* This paper was presented at ECSOC-1, http://www.mdpi.org/ecsoc-1.htm, 1-30 September 1997.
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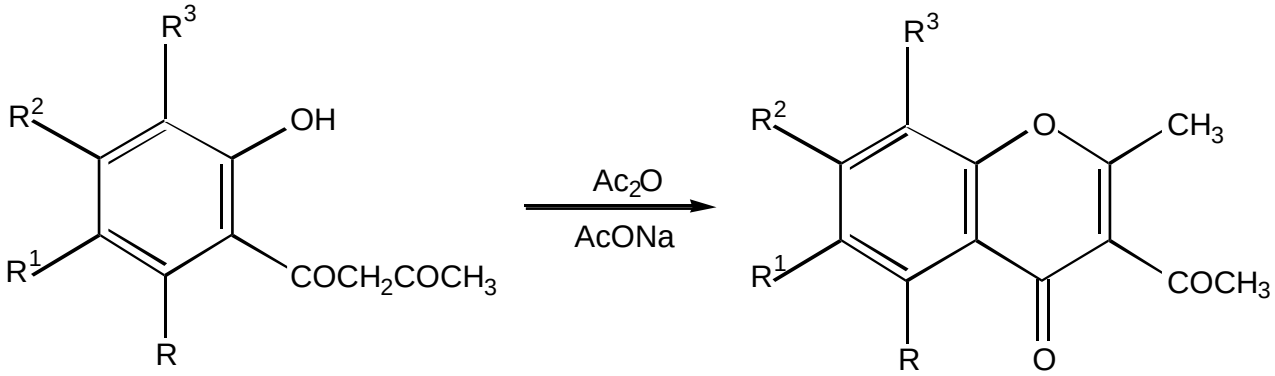
The main goal of this study was the preparation of new 3-acyl-2-R-methylchromones and the comparison of the reaction results obtained by the classical method with microwave irradiation. Structural formulas of prepared compounds are depicted in schemes 1 - 3.

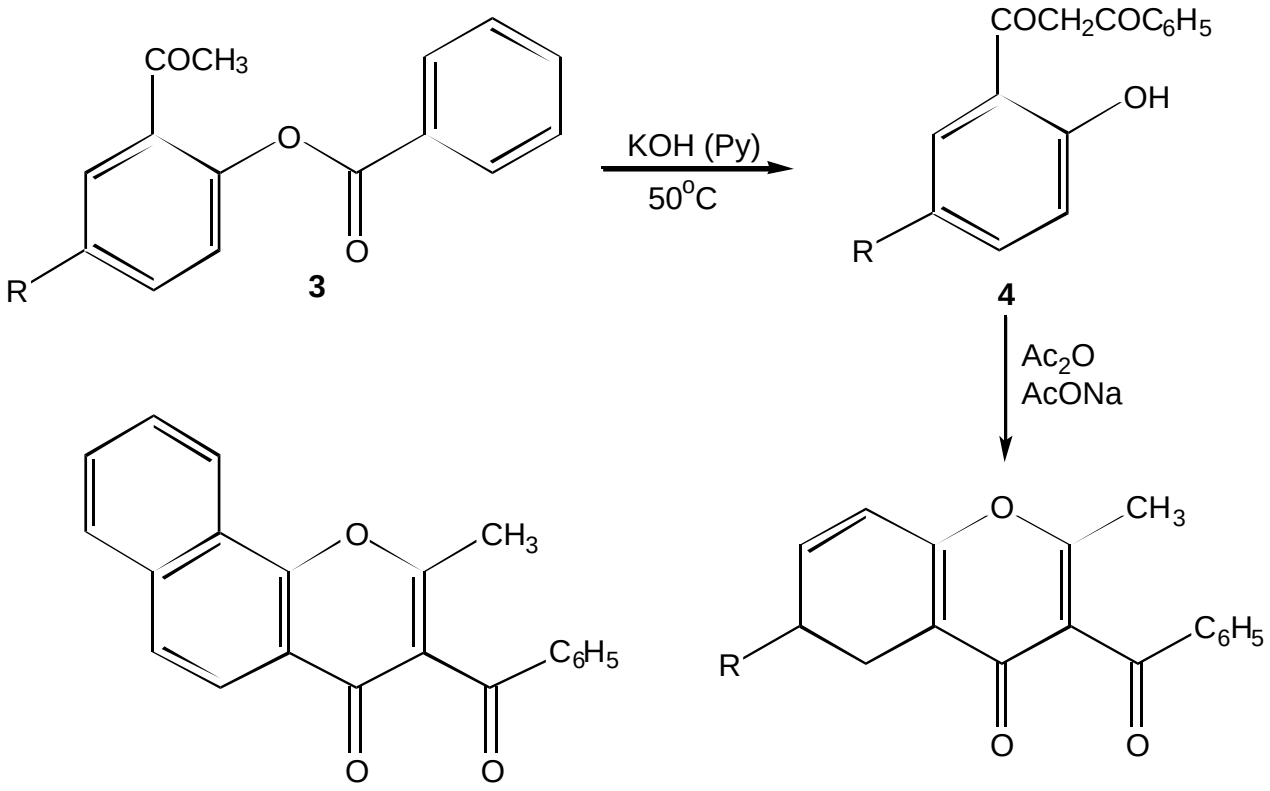
To prepare compounds **2**, two known methods can be used. One of them is the Kostanecki-Robinson acetylation of 2-hydroxyacetophenone derivatives with acetic anhydride and sodium acetate [7-9]. This cyclocondensation reaction is known so far only as a classic modification by heating the reacting mixture. The use of a rearrangement of 2-acyloxy-1-acetoarones by treating with metallic sodium is another, more general method for the preparation of 3-acyl-2-methylchromones. The rearranged intermediates - 2-hydroxyaroylacetones **1**, were formed. Compounds **1** rendered 3-acyl-2-methylchromones or 2-methylchromones by acid-catalyzed cyclization.



1 **2**

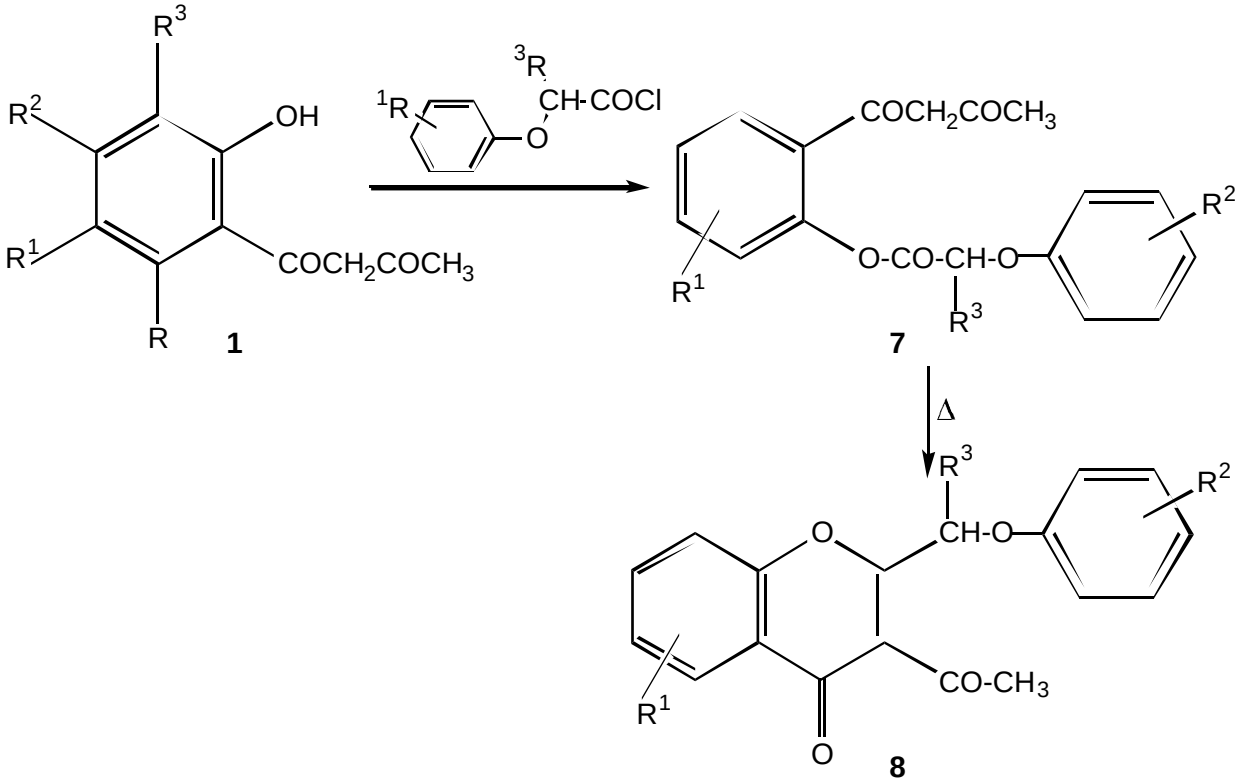
	R	R^1	R^2	R^3
2a	H	H	H	H
2b	H	CH_3	H	H
2c	H	Cl	H	H
2d	H	Br	H	H
2e	H	Cl	H	Cl
2f	H	Cl	CH_3	H
2g	H	CH_3	CH_3	H
2h	-(CH=CH)$_2$-		H	H
2i	H	H	-(CH=CH)$_2$-	

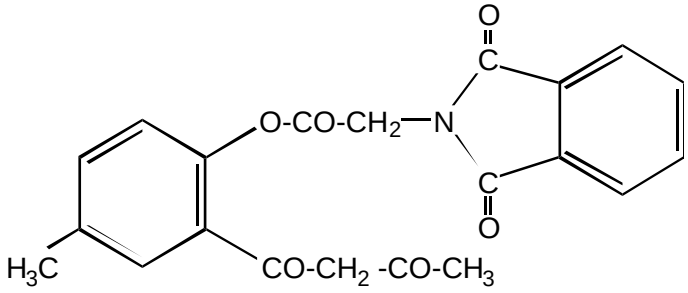
Scheme 1.



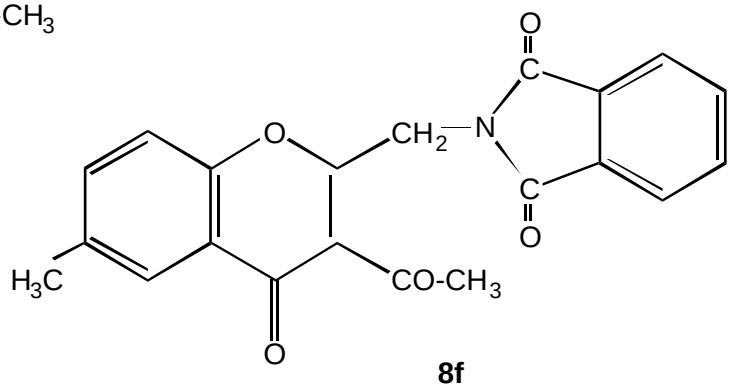
	R
5a	H
5b	CH_3
5c	Br

Scheme 2.





7f



8f

	R^1	R^2	R^3		R^1	R^2	R^3
7a	5-CH_3	2,4-Cl_2	H	**8a**	6-CH_3	2,4-Cl_2	H
7b	5-CH_3	2,4,5-Cl_2	H	**8b**	6-CH_3	2,4,5-Cl_2	H
7c	5-Cl	2-CH_3, 4-Cl	H	**8c**	6-Cl	2-CH_3, 4-Cl	H
				8d	6-CH_3	2,4-Cl_2	CH_3
				8e	6-CH_3	2-CH_3, 4-Cl	H

Scheme 3.

Table 1. Physical data of the prepared compounds.

Comp	Formula	M.P., °C	Calc. / Found				$\nu_{(C=O)}$ [c]	$\nu_{(C=O)}$ [c]	$\nu_{(C=N)}$ [c]	$\nu_{(OH)}$ [c]
Yield, %	M.W.	Solvent	%C	%H	%N	%Cl	pyrone	acetyl		
2a	$C_{12}H_{10}O_3$	86-87	71.28	4.98			1637	1687		
72	202.21	P.Ether[b]	71.56	5.07						
2b	$C_{13}H_{12}O^3$	116-118	72.21	5.59			1639	1691		
85	216.24	Cyclohex[a]	72.45	5.64						
2c	$C_{12}H_9ClO_3$	129-131	60.90	3.83		14.98	1639	1691		
82	236.65	Cyclohex[a]	60.77	3.84		14.98				
2d	$C_{12}H_9BrO_3$	124-125	51.27	3.23		28.42	1640	1692		
82	281.11	Cyclohex[a]	51.31	3.17		28.63				
2e	$C_{12}H_8Cl_2O_3$	132-134	53.17	2.97		26.15	1643	1680		
98	271.10	Cyclohex[a]	53.40	3.01		26.18				
2f	$C_{13}H_{11}ClO_3$	152-153	62.29	4.42		14.14	1637	1687		
91	250.68	Cyclohex[a]	62.56	4.45		14.29				
2g	$C_{14}H_{14}O_3$	112-114	73.03	6.13			1636	1677		
84	230.26	Cyclohex[a]	73.31	6.14						
2h	$C_{16}H_{12}O_3$	154-156	76.18	4.79			1637	1685		
91	252.27	Cyclohex[a]	76.22	4.81						
2i	$C_{16}H_{12}O_3$	136-138	76.18	4.79			1648	1699		
95	252.27	Cyclohex[a]	76.24	4.79						
5a	$C_{17}H_{12}O_3$	113.5-115	77.21	4.54						
73	264.2	Cyclohex[a]	77.38	4.41						
5b	$C_{18}H_{14}O_3$	90-93	77.64	5.03						
26	278.22	Cyclohex[a]	77.52	5.11						
5c	$C_{17}H_{11}BrO_3$	141-143	59.48	3.21						
74	343.2	Cyclohex[a]	59.73	3.29						
5d	$C_{21}H_{16}O_3$	210-212	80.20	4.45						
72	314.2	Dioxane	80.09	4.32						
7a	$C_{19}H_{16}Cl_2O_5$	119-121	57.74	4.08		17.94				
21	395.24	Cyclohex[a]	57.32	4.02		17.77				
7b	$C_{19}H_{15}Cl_3O_5$	94-95	53.11	3.52		24.75				
18	429.68	Cyclohex[a]	53.50	3.45		24.50				
7c	$C_{19}H_{16}Cl_2O_5$	104-105	57.74	4.08		17.94				
25	395.24	Cyclohex[a]	52.85	4.19		17.75				
7f	$C_{24}H_{17}NO_8$	112-114	64.43	3.83		3.13				
18	447.40	Toluene	64.28	3.72		3.15				
8a	$C_{19}H_{14}Cl_2O_4$	150-151	60.80	3.74		18.80				
	377.22	Ethanole	59.96	3.69		18.82				
8b	$C_{19}H_{13}Cl_3O_4$	187-189	55.44	3.18		25.84				
	411.67	Ethanole	55.25	3.18		25.95				
8c	$C_{19}H_{14}Cl_2O_4$	145-148	60.50	3.74		18.89				
	377.20	Ethanole	60.44	3.52		18.01				
8d	$C_{20}H_{16}Cl_2O_4$	127-129	61.40	4.12		18.12				
	391.25	Ethanole	61.28	4.05		18.25				
8e	$C_{20}H_{17}ClO_4$	153-156	67.33	4.80		9.94				
	356.81	Ethanole	67.45	4.92		10.23				
8f	$C_{21}H_{15}NO_5$	241-244								

Table 1 contd.

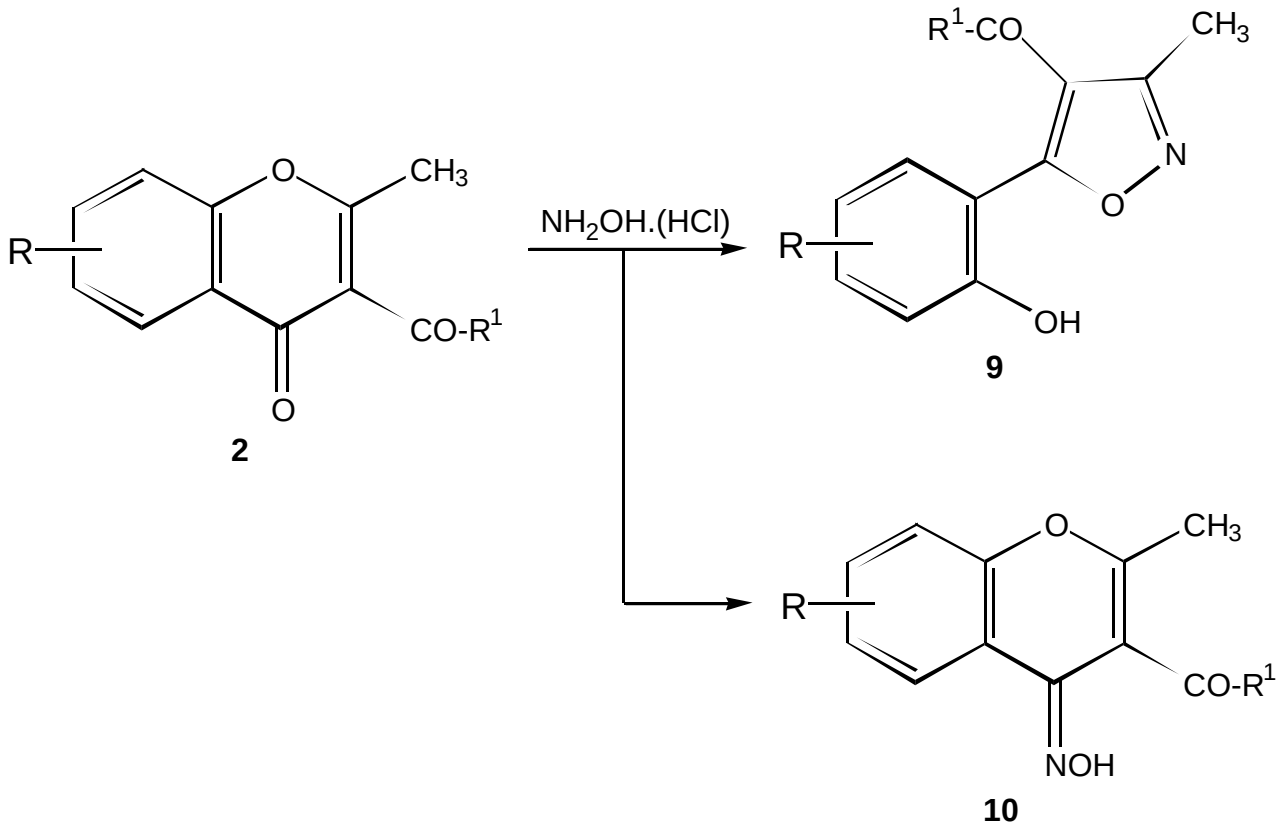
9a	$C_{17}H_{12}ClNO_3$	114-115	58.77	4.55	5.27	13.34		1683	1612	3100
57	265.70	Cyclohex[a]	58.46	4.55	5.06	13.58				(br)
9b	$C_{14}H_{15}NO_3$	119-121	68.56	6.16	5.71			1680	1613	3100
62	245.28	Cyclohex[a]	68.55	6.19	5.52					(br)
9c	$C_{17}H_{13}NO_3$	73-75	73.12	4.66	5.02					
48	279.2	Cyclohex[a]	73.17	4.82	4.88					
9d	$C_{18}H_{15}NO_3$	90-92	73.72	5.12	4.78					
50	293.2	Cyclohex[a]	73.72	5.21	4.79					
9e	$C_{17}H_{12}BrNO_3$	121-123	56.98	3.35	3.91					
52	358.2		57.12	3.38	3.94					
10a	$C_{17}H_{12}ClNO_3$	150-151	58.77	4.55	5.27	13.34		1681	1620	3120
20	265.70	Benzene	58.35	4.60	5.02	13.61				
10b	$C_{14}H_{15}NO_3$	142-144	68.56	6.16	5.71			1675	1620	3127
28	245.28	Benzene	68.61	6.16	5.74					
10c	$C_{14}H_{13}NO_3$	212-214	73.12	4.66	5.02					
33	279.2	Toluene	73.15	4.70	5.06					
10d	$C_{18}H_{15}NO_3$	182-187	73.72	5.12	4.78					
35	293.2	Toluene	73.64	5.20	4.72					
10e	$C_{17}H_{12}BrNO_3$	221-223	56.98	3.35	3.91					
24	358.2	Toluene	57.04	3.34	3.86					
11a	$C_{12}H_{22}O_5$	174-175	73.74	3.94						
	358.35	Ethanol	73.64	3.70						
11b	$C_{23}H_{16}O_5$	289-291	74.19	4.33						
	372.38	Ethanol	73.99	4.23						
11c	$C_{22}H_{13}ClO_5$	270-273	67.27	3.34		9.03				
	392.80	Ethanol	67.17	3.10		8.93				
11d	$C_{23}H_{15}ClO_5$	264-266	67.91	3.72		8.71				
	406.85	Ethanol	67.70	3.52		8.50				
11e	$C_{24}H_{18}O_5$	224-226	74.60	4.70						
	386.40	Ethanol	74.40	4.65						
11f	$C_{22}H_{12}Cl_2O_5$	300-301	61.85	2.83		16.60				
	427.20	DM-Et[c]	61.59	2.73		16.73				
11g	$C_{22}H_{13}Cl_2O_5$	265-267	67.27	3.34		9.03				
	392.8	Ethanol	67.10	3.20		9.09				

[a] solvent is cyclohexane, [b] 40-60, [c] in cm^{-1}, [c]solvent DMSO-ethanol

In our study we prepared 3-acetyl-2-methylchromone derivatives **2** in high yield (72-98%) using 2-(hydroxyaroyl) acetone derivatives **1** with freshly prepared sodium acetate and acetic anhydride under classic reaction conditions by refluxing for 2 hours. Using microwave irradiation the preparation times of products **2** from the same components were shortened to only 3 - 8 minutes.

The structure of compounds **2** (R=H) was confirmed by IR, ^{1}H-NMR, and ^{13}C-NMR spectra. IR-spectra (in nujol) showed acetyl carbonyl stretching frequencies as a strong band at 1699-1677 cm^{-1} and γ- pyrone at 1648 - 1636 cm^{-1}. In the ^{1}H-NMR spectra the CH_3 acetyl signals occurred at δ 2.70 - 2.62 ppm, while the signals of CH_2-CH_3 occurred at δ 2.66 - 2.52 ppm . Other proton signals and the ^{13}C-NMR spectra are listed in Tables 2 and 3.

3-Benzoyl-2-methylchromone derivatives **5** were prepared by treatment of 2-hydroxybenzoyl-acetophenones with acetic anhydride and sodium acetate at 110º C for 3 hours. On the other hand compounds **5** were produced after 3 - 6 minutes in a yield of 80% by focused microwave irradiation.

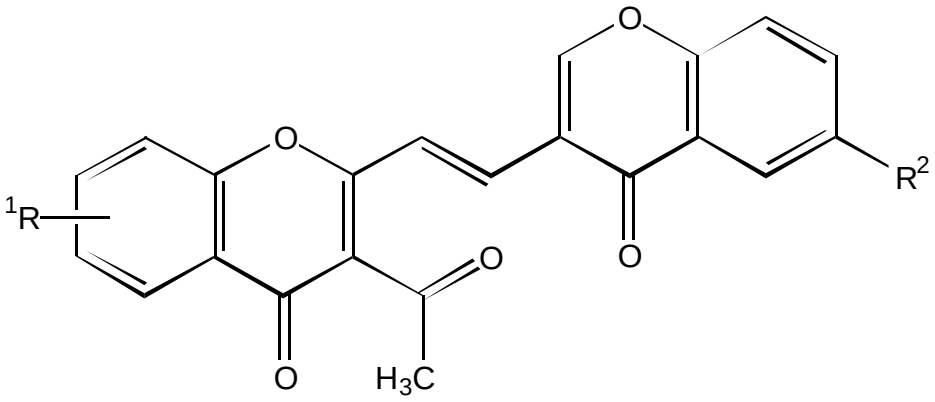


	R	R^1		R	R^1
9a	4-Cl, 5-CH_3	CH_3	**10a**	5-Cl, 6-CH_3	CH_3
9b	4,5-$(CH_3)_2$	CH_3	**10b**	4,5-$(CH_3)_2$	CH_3
9c	H	C_6H_5	**10c**	H	C_6H_5
9d	5-CH_3	C_6H_5	**10d**	6-CH_3	C_6H_5
9e	5-Br	C_6H_5	**10e**	6-Br	C_6H_5

Scheme 4.

The preparation of compounds **7** and **8** paved a new route to synthesis of the title compounds. Reaction of compounds **1** with acid chlorides and potassium carbonate in acetone under reflux for 3 hours yielded 3-acetyl-2-aryloxymethylchromone derivatives **3** in about 47% yields. Intermediates **7** could be isolated from a cold water-hydrogen carbonate solution after gentle acidification with CH_3COOH in about 27-30% yields. The cyclocondensation of intermediates **7** with compounds **8** is very easy to affect by heating in toluene. Furthermore, by heating the starting compounds under reflux in dry toluene for 3 hrs, only cyclic products **8** were isolated (80% yields). In the microwave oven the condensation reaction of components **1** with acylchlorides, potassium carbonate and acetone took only 2 minutes to achieve 85 % yield of compounds **8.** No intermediates **7** were isolated.

Compounds **2** contain two active CH_3 groups which can react by aldol reaction. The aldol condensation product **11** was obtained by the reaction of **2** with 3-formyl chromones in an acetyl anhydride medium by both classic and microwave irradiation methods. In both cases, the reaction occured only at the methyl group position 2 of the γ-pyrone ring. Again, the classic method required heating at about 120−130 °C for 2−3 hrs. The microwave irradiation shortened the reaction time to 40 sec to 2 min.



11

	R^1	R^2		R^1	R^2
11a	H	H	**11e**	6-Cl	H
11b	CH_3	CH_3	**11f**	6, 7-$(CH_3)_2$	H
11c	H	CH_3	**11g**	Cl	Cl
11d	6-Cl	CH_3			

Scheme 5.

Table 2. ^{1}H-NMR spectra of the prepared compounds.

Compound	^{1}H-NMR spectrum[a] (solvent $CDCl_3$ or DMSO[x]) δ (ppm)
2a	8.14(1H, dd, ^{3}J=8.4 and 1.6, H-5), 7.64(1H, ddd, ^{3}J=7.1, 8.2 and 1.6, H-7), 7.39(1H, dd, ^{4}J=8.2 and 1.1, H-8), 7.37(1H, ddd, J=8.4, 7.1 and 1.1, H-6), 2.63(3H, s, CH_3 acetyl), and 2.52(3H, s, C_2-CH_3).
2b	7.99(1H, d, ^{4}J=2.3, H-5), 7.50(1H, dd, ^{4}J=8.7 and ^{4}J=2.3, H-7), 7.34(1H, d, ^{3}J=8.7, H-8), 2.67(3H, s, CH_3 acetyl), 2.55(3H, s, C_2-CH_3), and 2.45(3H, s, C_6-CH_3).
2c	8.14(1H, d, ^{4}J=2.6, H-5), 7.60(1H, dd, ^{3}J=8.8 and ^{4}J=2.6, H-7), 7.38(1H, d, ^{3}J=8.8, H-8), 2.64(3H, s, CH_3 acetyl), and 2.54(3H, s, C_2-CH_3).
2d	8.30(1H, d, ^{4}J=2.4, H-5), 7.76(1H, dd, ^{3}J=8.8 and ^{4}J=2.4, H-7), 7.33(1H, d, ^{3}J=8.8, H-8), 2.64(3H, s, CH_3 acetyl), and 2.53(3H, s, C_2-CH_3).
2e	8.04(1H, d, ^{4}J=2.2, H-5), 7.70(1H, d, ^{4}J=2.2, H-7), 2.62(3H, s, CH_3 acetyl), and 2.60(3H, s, C_2-CH_3).
2f	8.12(1H, s, H-5), 7.33(1H, s, H-8), 2.65(3H, s, CH_3 acetyl), 2.52(3H, s, C_2-CH_3), and 2.49(3H, s, C_7-CH_3).
2g	7.89(1H, s, H-5), 7.18(1H, s, H-8), 2.66(3H, s, CH_3 acetyl), 2.52(3H, s, C_2-CH_3), 2.42(3H, s, C_7-CH_3), and 2.35(3H, s, C_6-CH_3).
2h	9.97(1H, d, ^{3}J=8.6, H-9), 8.06(1H, d, ^{3}J=8.9, H-7), 7.85(1H, d, ^{3}J=9.5, H-12), 7.68(1H, dd, ^{3}J=8.6 and 6.9, H-10), 7.61(1H, dd, ^{3}J=6.9 and 9.5, H-11), 7.45(1H, d, ^{3}J=8.9, H-8), 2.70(3H, s, CH_3 acetyl), and 2.52(3H, s, C_2-CH_3).

Table 2. Continued.

Compound	^{1}H-NMR spectrum[a] (solvent $CDCl_3$ or DMSO[x]) δ (ppm)
2i[b]	8.45(1H, d, ^{3}J=7.5, H-9), 8.12(1H, d, ^{3}J=8.7, H-5), 7.92(1H, d, ^{3}J=6.8, H-12), 7.76(1H, d, ^{3}J=8.7, H-6), 7.72(1H, d, ^{3}J=7.5, H-10), 7.67(1H, d, ^{3}J=6.8, H-11), 2.70(3H, s, CH_3 acetyl), and 2.66(3H, s, C_2-CH_3).
3c	8,23-7.07(8H, m, arH); 2.52(3H, s)
4b	15.57(1H, s, 1OH); 11.87(1H, s, 2OH); 7.98-6.70(9H, m)
4c	15.48(1H, s, 1OH); 12.01(1H, s, 2OH); 8.02-7.44(9H, m)
5a	7.40-7.96(9H, m); 2.37(3H)
5b[x]	7.95-7.85(3H, m); 7.53-7.40(5H, s); 2.44(3H, s); 2.36(3H, s)
5d	8.56-7.43(11H, m); 2.20(3H, s)
7a	7.92(1H, s, OH); 7.45-6.76(7H, m); 4.71(2H, s, CH_2-O-); 2.44(3H, CH_3-); 2.39(3H, CH_3)
7b	7.98(1H, s, OH); 7.48-7.26(5H, m); 6.99(1H, s); 7.74(2H, s, CH_2-O); 2.44(3H, s); 2.40(3H, s)
7c	10.55(1H, s, OH); 8.44(1H, d, ^{3}J 8.2 Hz); 6.99(1H, s); 7.64-6.60(7H, m); 4.66(2H, s, CH_2O); 2.40(3H, s); 2.39(3H, s)
8a	7.97(1H, s, H-5); 7.49-6.95(5H, Ar-H); 5.40(2H, s, CH_2O); 2.60(3H, s); 2.47(3H, s)
8b insoluble	
8c	8.19(1H, s, H-5); 7.74-6.63(5H, m); 5.26(2H, s); 2.57(3H, s); 2.20(3H, s)
8d	7.95(1H, s); 7.48-7.15(5H, m); 5.99-5.90(1H, q, CH-O); 2.50(3H, s); 2.46(3H, s); 1.6(3H, d ^{3}J=6.8 Hz)
8e	7.99(1H, s, H-5); 7.59-6.60(5H, m); 5.29(2H, s, CH_2-O); 2.56(3H, s); 2.46(3H, s); 2.21(3H, s)
8f	8.03(1H, s, H-5); 7.87-7.46(6H, m); 5.19(2H, s, CH_2-N); 2.62(3H, s); 2.49(3H, s)
9a	11.58(1H, s, OH), 7.38(1H, s, H-6), 6.96(1H, s, H-3), 2.44(3H, s, CH_3), 2.41(3H, s, CH_3), and 2.32(3H, s, CH_3).
9b	11.63(1H, s, OH), 7.19(1H, s, H-6), 6.86(1H, s, H-3), 2.32(3H, s, CH_3), 2.30(3H, s, CH_3), 2.28(3H, s, CH_3), and 2.24(3H, s, CH_3).
9c	11.95(14, s, OH); 7.65-6.55(9H, m); 2.33(3H, s)
9d	11.77(1H, s OH); 7.68-7.30(8H, m); 2.34(3H, s); 2.01(3H, s)
9e	11.81(1H, s OH); 7.62-6.9(8H, m); 2.33(3H, s)
10a	7.43(1H, s, H-5), 6.98(1H, s, H-8), 2.54(3H, s, CH_3 acetyl), and 2.41(6H, brs, C_2-CH_3 and C_7-CH_3).
10b	7.18(1H, s, H-5), 6.85(1H, s, H-8), 2.50(3H, s, CH3 acetyl), 2.32(3H, s, C_2-CH_3), 2.27(3H, s, C_7-CH_3), and 2.22(3H, s, C_6-CH_3).
10c[x]	10.10(1H, s, OH); 7.72-6.60(9H, m); 2.26(3H,s)
10d[x]	9.87(1H, s, OH); 7.62-6.60(8H, m); 2.25(3H, s); 2.20(3H, s)
10c[x]	10.49(1H, s, OH); 7.68-6.53(8H, m); 2.25(3H, s)
11a	8.25(1H, s, H-2); 7.18-7.50(5H, m); 2.70(3H, s)
11b	8.25(1H, s, H-2); 8.50-8.10(2H, m); 7.78-7.39(7H, m); 2.69(3H, s); 2.65(3H, s)
11c	8.22(1H, s, H-2); 8.10-7.78(2H, m); 7.66-7.45(6H, m); 2.68(3H, s); 2.46(3H, s)
11d	8.23(1H, s, H-2); 8.32-8.03(2H, m); 7.80-7.42(7H, m); 2.68(3H, s);
11e	8.22(1H, s, H-2); 8.25-7.96(2H, m); 7.81-7.39(6H, m); 2.38(3H, s); 2.30(3H, s); 2.24(3H, s)
11f	8.24(1H, s, H-2); 8.32-7.40(7H, m); 2.69(3H, s); 2.39(3H, s); 2.34(3H, s)

[a] J in Hz, [b] $J_{10,11}$ not resolved

Table 3. ^{13}C-NMR spectra of the compound **2a - 2i.**

Comp.	C-2	C-3	C-4	C-4a	C-5	C-6	C-7	C-8	C-8a	CO acetyl	CH_3 acetyl	CH_3
2a	168.5	123.6[a]	175.7	123.8[a]	125.5	125.8	133.9	117.6	155.2	200.3	32.1	19.7
2b	168.3	123.3[a]	175.9	123.4[a]	125.1	135.5	135.2	117.4	153.5	200.5	32.1	20.9 19.7
2c	168.8	123.6	174.7	124.7	125.3	131.5	134.2	119.5	153.6	200.0	32.2	19.8
2d	168.7	123.6	174.4	125.0	128.5	118.9	136.9	119.6	154.0	199.8	32.0	19.7
2e	168.9	124.0[a]	174.0	125.6	124.0	131.2	134.0	123.6[a]	149.7	199.3	32.0	19.7
2f	168.6	123.4	174.6	122.7	125.5	132.2	143.3	119.5	153.5	200.1	32.1	20.8 19.8
2g	168.0	123.3	175.7	121.4	125.3	134.7	144.4	117.7	153.7	200.7	32.1	20.3 19.7 19.2
2h[b]	164.7	126.4	177.8	117.0	130.2	130.6	135.8	117.0	156.6	201.1	32.0	19.0
2i[c]	167.4	124.6	175.7	123.5	120.5	125.6	135.9	120.1	152.7	200.5	32.2	19.7

[a] The assignment can be interchanged.
[b] values C-9 126.8, C-10 129.4, C-11 126.7, C-12 128.3.
[c] values C-9 122.0, C-10 127.3, C-11 129.4, C-12 128.1.

It is known that the reaction of 3-acetyl-2,6-dimethylchromone with hydroxylamine in acetic acid gave monoxime and dioxime [10]. Reaction of 3-acetyl-2-methylchromone with hydroxylamine hydrochloride and sodium acetate in ethanol gave 4-acetyl-5-(2-hydroxyphenyl)-3-methylisoxazole [11]. However in the present study we found that 3-acetyl-2-methylchromones reacted with hydroxylamine hydrochloride in pyridine at boiling point and resulted in a mixture of two different products. They were separated by fractional crystallisation from cyclohexane (Scheme 4**).**

The first product gave a deep red colour with alcoholic ferric chloride, and was soluble in aqueous sodium hydroxide, confirming the presence of a phenolic hydroxyl group. Their IR spectra showed a broad band centered at 3100 cm^{-1} for the OH group and a band at 1683 - 1680 cm^{-1} for the C=O acetyl group. These products were thus identified as isoxazole derivatives **9a - 9e**. Additionally, the structure of these isoxazoles was confirmed by ^{1}H-NMR spectra (Table 2).

The second product gave no colouration with alcoholic ferric chloride and their IR spectra (Table 1), indicated the absence of a pyrone CO group of the 3-acetyl-2-methylchromones. The observed IR bands at 1681 - 1675 cm^{-1} showed the presence of a CO acetyl group and 3127 - 3120 cm^{-1} of an OH group. The second products were identifited as oxime derivatives **10** of compounds **2**. their structure was confirmed by ^{1}H NMR spectra (Table 2).

Isoxazoles turned out to be the preferred compounds with 50 - 70 % yields. Yields of oximes **10** were less, about 20 - 30 %.

Experimental Section

General

Infrared spectra were recorded on a Specord IR 75 spectrometer (Zeiss, Jena), in 400 - 4000 cm^{-1} region in nujol. ^{1}H-NMR spectra (δ, ppm) for compounds **3a**, **3b** and **4a**, **4b** were measured with Tesla BS 487 A (80 MHz). ^{1}H-NMR (300 MHz) and ^{13}C-NMR (75 MHz) spectra for compounds **2a - 2i** were measured with a FT NMR spectrometer Bruker AM 300 at 300º K in solution of $CDCl_3$ with TMS as internal standard. ^{13}C NMR was obtained with a 40º flip angle and relaxation delays, CCOSY using a chemical-shift-selective filter as well as a semiselective INEPT optimalized for the value of long range coupling constant $^nJ_{CH}$ = 6 Hz, used for assignment

of 1D H signals. The melting points were determined with a Kofler apparatus.

All microwave assisted reactions were carried out in a Lavis-1000 multi Quant microwave oven. The apparatus has been adapted for laboratory application with an external reflux condenser.

3-*Acetyl-2-methylchromone derivatives* ***2a - 2i***

Method A (classic)

A mixture of 2-hydroxyaroylacetones **1a - 1i** (1g), acetic anhydride (8 ml) and freshly prepared sodium acetate (1g) was refluxed for 6hrs and allowed to cool down. The mixture was diluted with cold water (50 ml) and stirred at room temperature for 30 min. The solid products, which separated, were filtered, washed with water and recrystallized from an appropriate solvent to give **2a - 2i** (Table 1).

Method B (microwave irradiation)

The same mixture as used in the procedure A was irradiated in microwave oven at 270 W for 8 minutes. The isolation procedure is the same as above. The compounds are given in Table 1.

4-Acetyl-5-(2-hydroxyaryl)-3-methylisoxazoles ***9a - 9e*** *and 4-(3-acetyl-2, 7-dimethylchromone)-oximes* ***10a - 10e***

A mixture of **2** (0.0022 mol) in pyridine (3 ml) and hydroxylamine hydrochloride (0.15 g, 0.0022 mol) in water (1 ml) was refluxed for 4 hr. The cooled mixture was poured onto crushed ice and acidified with acetic acid, and the solid separated from the liquid was filtered and recrystallized from cyclohexane to give **9a - 9e**. The unsoluble product in cyclohexane was recrystallized from benzene to give **10a - 10e**.

2-Aryloxymethyl-3-acetylchromone derivatives ***8a - 8e*** *and intermediates* ***7a - 7c***

Method A

To a mixture of 2-hydroxyaroylacetones **1** (1g), K_2CO_3 (0.5g) in dry acetone (20 ml), after 2 hrs stirring at reflux, the aryloxyacetyl chlorides were added. The reaction mixture was stirred and heated under reflux for 2 h and left overnight at room temperature. The mixture was poured onto crushed ice (50g) and the solid product was separated. The product was diluted with 5 % cold $NaHCO_3$. The insoluble fraction (compounds **8a - 8e**) was separated and recrystallized from ethanol. The compounds **7** dissolved in aq. $NaHCO_3$ were separated after acetic acid acidification and recrystallized from cyclohexane.

Method B

The mixture of the same components for preparation of the salt of compounds **1** and dry toluene (20 ml) were stirred at reflux for 2 hrs. After cooling the aryloxyacetyl chloride was slowly added (dropwise). The stirring continued at room temperature for 1 hr and then for an additonal 2 hrs at reflux. Toluene was removed by water vacuum distillation, thereafter the mixture was dried and then dissolved in a 1 % aq. solution of $NaHCO_3$. The solid part was isolated and recrystallized from ethanol. The yield of compound **8** was 87%. No products **7** were isolated from the $NaHCO_3$ solution.

Method C

The mixture of the same reaction components as above (*Method B*) was stirred and irradiated *viz*. microwave at 270 W for 3 minutes (the preparation of the salt) and then, after addition of components **6,** the stirring continued for an additional 6 minutes.

Condensation products ***11*** *of* ***2*** *with 3-formylchromones* ***6***

Method A (classic)

A mixture of compounds **2** (0.01mol), 3-formylchromones (0.01 mol), acetic anhydride (5 ml) and freshly fused potassium acetate (0.5g) was heated at 120 - 130° C for 2h. The cooled mixture was diluted with cooled water and the solid was separated and recrystallized from acetic acid.

Method B

A mixture of the same composition as in method A was irradiated in microwave oven for 40 sec to 2 min. The isolation of the compounds proceeded along the same lines as described in Method A.

Acknowledgement: Financial support for this research by the Slovak Grant Agency (grant No. 1/2178/95) is gratefully acknowledged.

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Sample Availability: Available from the MDPI.