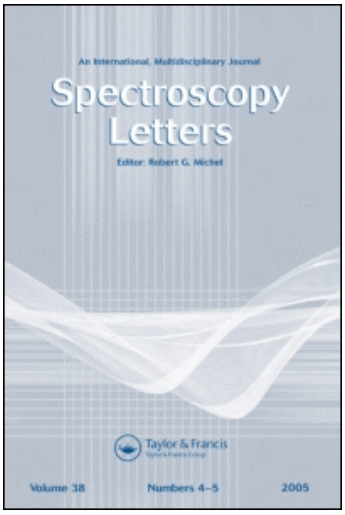

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NMR and Structural and Conformational Features of 2'-Hydroxychalcones and Flavones

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NMR AND STRUCTURAL AND CONFORMATIONAL FEATURES OF 2'-HYDROXYCHALCONES AND FLAVONES

Key Words: 2'-Hydroxychalcones, Flavones, Conformations, NMR Characterization, 1D and 2D NMR Techniques.

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Abstract: New 2'-hydroxychalcone and flavone derivatives have been synthesised. Their [^{1}H] and [^{13}C] NMR spectra were assigned by the application of COSY and HETCOR experiments and allowed the discussion of some structural aspects. It was shown on the basis of NOE experiments some configurational and conformational features of both type of compounds.

INTRODUCTION

2'-Hydroxychalcones and flavones are ubiquitous compounds in plants, where they participate in several vital functions.[1] Moreover

promising pharmacological,[2-5] antioxidant[4-8] and agrochemical[9-12] activities have been found for some of these natural compounds and certain synthetic analogues. The industrial significance of such biological properties point out the need to study the synthesis of new compounds and to establish their structures without any ambiguity, including their stereo- and conformational features. Nuclear magnetic resonance can be a powerful tool to reach such goal. Their biological evaluations can then be made without rational interpretation and the structure-activity and dose-response relationships can be correctly considered.

Following the present interest on the synthesis and new aspects of the structural characterization of 2'-hydroxychalcones and flavones,[13-16] it will be discussed in this communication some structural and conformational features of 2'-hydroxychalcones **1a-j** and flavones **2a-j**.

RESULTS AND DISCUSSION

2'-Hydroxychalcones 1 were synthesized by the base-catalysed aldol condensation of 2'-hydroxyacetophenone and the appropriate benzaldehyde derivatives. The oxidative cyclizations of 2'-hydroxy-chalcones 1 into flavones 2 were performed with catalytic amounts of iodine in DMSO.[16-18] In this publication we now report the physical and spectroscopic NMR data of the new chalcone **1d,f,g** and flavone **2c,d,f,g** derivatives; the other chalcones **1a-c,e,h-j** and flavones **2a,b,e,h-j** have been previously reported,[19-22] although without any NMR spectroscopic data. For this reason their NMR data are now reported (Table 1 and 2).

The most noticeable features in the structural characterization of chalcones 1 are the *trans* configurations of their unsaturated moieties, indicated by the $^{3}J_{H\alpha\text{-}H\beta}$=15-16 Hz values, and the strong hydrogen bonds involving the carbonyl groups and the proton of the 2'-hydroxyl substituents. The resonances of these protons are quite sensitive to the B

Table 1. [^{1}H] Chemical Shifts (ppm, from TMS) of 2'-hydroxychalcones **1 a - j** and flavones **2 a - j**.

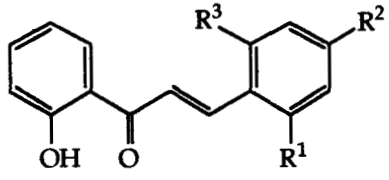
	OH-2'	H-3'	H-4'	H-5'	H-6'	H-α	H-β	H-2	H-3	H-4	H-5	H-6
1 a	12.82	7.03	7.49	6.94	7.92	7.65	7.92	7.65	7.43	7.43	7.43	7.65
1 b	12.70	7.03	7.51	6.94	7.90	7.63	8.30	-	7.76	7.36	7.36	7.36
1 c	12.65	7.04	7.52	6.95	7.88	7.62	8.26	-	7.49	-	7.32	7.70
1 d	12.60	7.03	7.51	6.94	7.84	7.82	7.98	-	7.39	7.21	7.39	-
1 e	12.77	7.02	7.50	6.94	7.89	7.61	7.84	7.58	7.39	-	7.39	7.58
1 f	12.85	7.04	7.50	6.95	7.93	7.59	8.23	-	7.34	7.26	7.26	7.71
1 g	12.85	7.02	7.48	6.91	7.79	7.29	8.09	-	6.93	-	6.93	-
1 h	12.88	7.03	7.49	6.94	7.92	7.62	7.91	7.56	7.24	-	7.24	7.56
1 i	12.95	7.02	7.48	6.93	7.92	7.54	7.90	7.62	6.95	-	6.95	7.62
1 j	12.94	7.02	7.48	6.93	7.91	7.53	7.90	7.62	7.02	-	7.02	7.62

	H-3	H-5	H-6	H-7	H-8	H-2'	H-3'	H-4'	H-5'	H-6'
2 a	6.85	8.23	7.42	7.70	7.57	7.93	7.53	7.53	7.53	7.93
2 b	6.66	8.25	7.46	7.69	7.50	-	7.63	7.46	7.46	7.66
2 c	6.66	8.25	7.45	7.71	7.51	-	7.56	-	7.41	7.60
2 d	6.44	8.28	7.44	7.70	7.45	-	7.41	7.41	7.41	-
2 e	6.78	8.22	7.42	7.71	7.55	7.86	7.50	-	7.50	7.86
2 f	6.47	8.24	7.39	7.65	7.46	-	7.29	7.38	7.29	7.49
2 g	6.34	8.28	7.47	7.69	7.45	-	6.98	-	6.98	-
2 h	6.83	8.22	7.41	7.69	7.55	7.81	7.31	-.	7.31	7.81
2 i	6.77	8.22	7.40	7.68	7.54	7.88	7.01	-	7.01	7.88
2 j	6.81	8.23	7.41	7.69	7.55	7.89	7.10	-	7.10	7.89

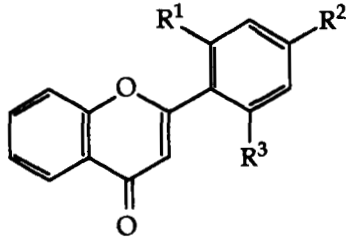
Table 2. [^{13}C] Chemical Shifts (ppm, from TMS) of 2'-hydroxychalcones **1 a - j** and flavones **2 a - j**.

	C-1'	C-2'	C-3'	C-4'	C-5'	C-6'	C=O	C-α	C-β	C-1	C-2	C-3	C-4	C-5	C-6
1 a	120.0	163.6	118.6	136.4	118.9	129.7	193.7	120.1	145.5	134.6	128.7	129.0	130.9	129.0	128.7
1 b	119.9	166.6	118.7	136.5	118.9	129.7	193.5	122.8	141.1	135.7	133.0	127.9	131.5	127.1	130.4
1 c	119.8	163.7	118.7	136.7	118.9	129.6	193.2	123.1	139.8	131.6	136.3	128.6	136.9	127.6	130.3
1 d	119.9	163.6	118.6	136.7	119.0	129.9	193.6	128.8	138.3	135.3	132.2	128.9	130.1	128.9	132.2
1 e	119.9	163.6	118.7	136.5	119.0	129.6	193.4	120.5	144.0	136.8	129.8	129.3	133.0	129.3	129.8
1 f	120.0	163.6	118.6	136.4	118.9	129.7	193.7	121.1	143.0	133.6	138.6	131.0	130.7	126.4	126.5
1 g	119.9	163.6	118.6	136.3	118.8	129.6	193.8	125.2	143.9	131.1	137.3	129.4	139.0	129.4	137.3
1 h	120.1	163.6	118.6	136.3	118.8	129.6	193.8	119.0	145.6	131.9	128.7	129.8	141.6	129.8	128.7
1 i	120.1	163.6	118.6	136.2	118.8	129.5	193.7	117.6	145.4	127.4	130.6	114.5	162.0	114.5	130.6
1 j	120.1	163.6	118.6	136.2	118.8	129.5	193.7	117.7	145.3	127.6	130.6	115.4	161.2	115.4	130.6
	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-1'	C-2'	C-3'	C-4'	C-5'	C-6'
2 a	163.4	107.5	178.4	125.6	125.2	133.8	118.0	156.2	125.2	131.7	126.3	129.0	131.6	129.0	126.3
2 b	162.6	113.0	178.0	125.7	125.3	133.9	118.2	156.6	123.8	131.9	132.9	130.8	131.8	127.1	130.6
2 c	161.5	111.2	177.9	125.8	125.5	134.0	118.2	156.5	123.9	130.4	133.8	130.8	137.4	127.6	131.4
2 d	159.9	114.5	177.6	125.6	125.3	133.5	118.1	156.7	123.8	131.3	134.8	128.2	131.7	128.2	134.8
2 e	162.1	107.6	178.2	125.7	125.3	133.9	118.0	156.1	123.8	130.1	127.5	129.3	137.8	129.3	127.5
2 f	165.5	111.5	177.7	125.2	124.8	133.4	117.7	155.9	123.3	132.0	136.3	130.9	130.3	125.8	128.7
2 g	165.5	113.6	178.3	125.7	125.2	133.7	118.2	156.9	123.9	130.0	136.6	128.6	140.0	128.6	136.6
2 h	163.7	106.8	178.5	125.6	125.2	133.7	118.0	156.2	123.8	128.8	129.7	126.2	142.3	126.2	129.7
2 i	163.5	106.0	178.3	125.6	125.1	133.6	117.9	156.1	123.8	123.9	128.0	114.4	162.4	114.4	128.0
2 j	163.3	106.2	178.4	125.7	125.1	133.6	118.0	156.2	123.9	124.2	128.0	115.3	161.5	115.3	128.0

ring substituents, which are in conjugation with the carbonyl group; they appear at δ 12.85-12.95 ppm for chalcones **1f-j** and at δ 12.60-12.77 ppm for those **1b-e**. The shifts to lower frequency values relative to that of the unsubstituted 2'-hydroxychalcone **1a**, indicate that the former hydrogen bonds are stronger in chalcones having electron donating substituents **1f-j** than in other ones having electron withdrawing substituents **1b-e**.



1



2

a) $R^1 = R^2 = R^3 = H$
b) $R^1 = Cl$; $R^2 = R^3 = H$
c) $R^1 = R^2 = Cl$; $R^3 = H$
d) $R^1 = R^3 = Cl$; $R^2 = H$
e) $R^1 = R^3 = H$; $R^2 = Cl$
f) $R^1 = CH_3$; $R^2 = R^3 = H$
g) $R^1 = R^2 = R^3 = CH_3$
h) $R^1 = R^3 = H$; $R^2 = CH_3$
i) $R^1 = R^3 = H$; $R^2 = OCH_3$
j) $R^1 = R^3 = H$; $R^2 = OCH_2C_6H_5$

Due to the deshielding mesomeric effect of the carbonyl group, the H-β proton resonance of each chalcone **1a-j** appears at higher frequency than those corresponding to H-α proton. However in the case of each 2-substituted chalcone, **1b-d,f,g**, there is a shift to higher frequency in the resonance of H-β (δ 7.98-8.30 ppm) in comparison with the corresponding protons of the 2-unsubstituted derivatives **1a,e,h-j** (δ 7.84-7.92 ppm). This effect can be explained by the steric interaction between the H-β and the 2-substituent.[23,24] NOE experiments with 2,4-dichloro-2'-hydroxy-

chalcone **1c** have indicated close proximity between H-6' and H-α, and also between H-6 and H-α. No effects were observed upon irradiation of the H-β proton resonance (Figure 1). In the case of 2'-hydroxy-2-methyl-chalcone **1f** NOE experiments have indicated close proximity between 2-methyl group and H-β proton (Figure 1). After these experiments, the conformation of the B ring of these compounds was then assigned as shown in Figure 1.

The observed resonance value for H-β proton of **1d,g** (δ 7.98 and 8.09 ppm) is lower than the corresponding one of **1b,c,f** (δ 8.23-8.30 ppm). This fact is probably due to the 2,6-substituents of **1d,g** which induce non-coplanarity of the B ring with the other part of the molecule and the effect of the 2-substituent on the H-β resonance is minor. Another consequence of this non-coplanarity is the decrease of the double bond anisotropic effect on H-6' protons of **1d,g**, which are shielded relatively to those of others 2'-hydroxychalcones **1a-c,e,f,h-j**.

In the ^{13}C NMR spectra of chalcones **1a-j** (Table 1), the influence of the B ring substituents on the resonances of the C-α and C-β carbon atoms can be observed. In compounds **1b,c**, which have electron withdrawing substituents, there are shifts to higher (+ 2.7 to 3.0 ppm) and to lower (- 4.6 to -5.7 ppm) frequency values of the resonances of C-α and C-β in comparison with the corresponding carbon resonances of unsubstituted 2'-hydroxychalcone **1a**. That situation is due to the electronegativity of the chloro substituents, which decrease the delocalization along the α,β-unsaturated keto part of the molecule, and consequently induce an increase of electron density at the C-β carbon and a decrease at the C-α carbon atom. The effect of the electron donating substituents can be well observed in the resonance of C-α carbon of

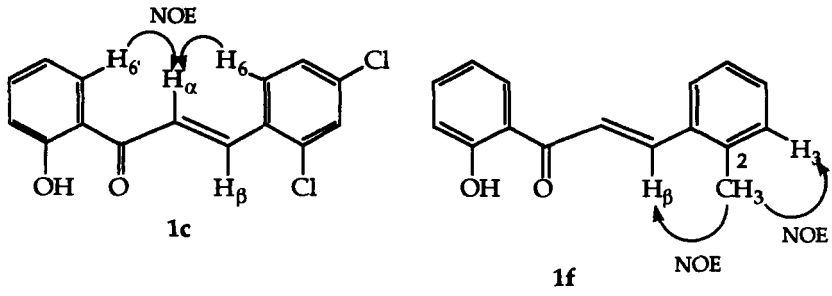


Figure 1. NOE effects observed in 2,4-dichloro-2'-hydroxychalcone **1c** and 2'-hydroxy-2-methylchalcone **1f**

compounds **1h-j**, which is shielded (- 1.1 to -2.5 ppm) relatively to that of the unsubstituted 2'-hydroxychalcone **1a**.

The high frequency value of C-α carbon resonances (δ 125.2-128.8 ppm) of compounds **1d,g**, relatively to those of other chalcones, is indicative of the already refereed non-coplanarity of the B ring with the other part of the molecule.

The main characteristics in the structural characterization of flavones **2a-j** are the resonances of the H-3 proton and C-3 carbon atoms, which appear, respectively, at δ 6.34-6.85 and 106.0-114.5 ppm. The NMR spectra of 2-substituted flavone derivatives **2b-d,f,g** show shifts to lower and to higher frequency resonance values, respectively, of H-3 and C-3 atoms in relation to the resonances of the corresponding atom of the 2-unsubstituted flavones **2a,e,h,i-j**. These effects can be explained by the non-coplanarity of the B ring with the remainder of the molecule. In such a way there is no anisotropic deshielding effect on H-3 proton by the B ring, and there is no conjugation between that aromatic ring and the enone systems yielding a decrease in the electronic density on C-3 carbon and a consequent deshielding effect.

The non-coplanarity mentionated above was confirmed by NOE experiments. On irradiation of the H-3 proton resonance of the

2',4'-dichloroflavone **2d** no NOE effects were observed, whereas upon irradiation of 2'-CH_3 protons resonance of 2'-methylflavone **2f** NOE effects were observed on H-3' and H-3 protons (Figure 2). This means that there is some proximity between H-3 and the 2'-Cl and 2'-CH_3 substituents. As a consequence of this situation and due to the steric hindrance between the H-3 and 2'-substituent, there is some degree of non-coplanarity between the B ring and the chromone moiety.

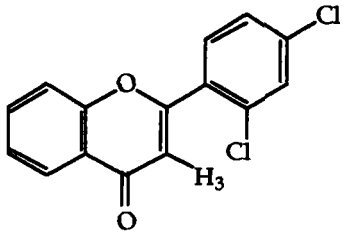
EXPERIMENTAL

Organic solvents were of reagent grade and were purified by standard procedures. Thin layer chromatography was carried out on plastic sheets of Merck silica gel 60 F_{254}. Column chromatography was carried out by using Merck silica gel (70-230 mesh ASTM). Nuclear magnetic resonance spectra, in deuteriochloroform, were recorded on a Brucker AMX 300 spectrometer, using tetramethylsilane as internal reference. All the ^1H and ^{13}C assignments were obtained through 2D COSY and HETCOR experiments, with standard Brucker microprograms, using 1 s and 1.5 s, respectively, for the relaxation delays. In homonuclear NOE difference experiments 2 s for the irradiation time and 3 s for the relaxation delay were utilized. Electron impact (EI) mass spectra were run on a Autospec Q VG 7070C. Melting points are uncorrected and were determined on a Reichert-Termovar hot-plate instrument. Elemental analyses were performed at the Chemistry Department, University of Coimbra, Portugal.

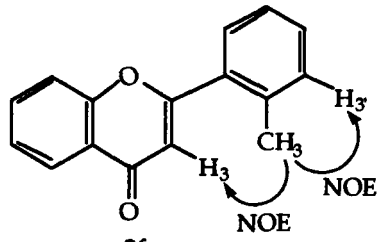
2.2. Synthesis of 2'-hydroxychalcones 1

2.2.1. 2'-hydroxychalcone 1d,f,g

To a methanolic solution (160 ml) of 2'-hydroxyacetophenone (4 ml, 33 mmol), an aqueous solution of sodium hydroxide (60 %, 160 ml) was



2d



2f

Irradiation of H-3 ---> NOE effect
not observed

Figure 2. Structure of 2',4'-dichloroflavone **2d** and NOE effects observed in 2'-methylflavone **2f**

slowly added. After cooling the solution to room temperature, the appropriate benzaldehyde (40 mmol) was added. The reaction mixture was stirred at room temperature during 4 hours, and after this period it was poured into a mixture of ice (300 g) and commercial hydrochloric acid (pH was adjusted to 2). The solid which was formed was filtered, dissolved in chloroform (300 ml), and washed with a 5 % aqueous solution of sodium hydrogen carbonate (2 x 200 ml). The organic layer was collected, dried over anhydrous sodium sulfate and the solvent evaporated to dryness. The residue, in each case, was crystallized from ethanol.

2,6-dichloro-2'-hydroxychalcone 1d (74%): mp 100-101°C. EIMS m/z (int. rel.) 296 ($M^{+\cdot}$, ^{37}Cl x 2; 3), 292 ($M^{+\cdot}$, ^{35}Cl x 2; 23), 291 (8), 275 (3), 257 (100), 199 (4), 194 (5), 171 (6), 165 (9), 147 (55), 135 (11), 121 (41), 120 (13), 99 (11), 93 (12), 92 (7). Anal. calcd. for $C_{15}H_{10}O_2Cl_2$: C, 61.46; H, 3.44%; Found: C, 61.51; H, 3.51%.

2'-Hydroxy-2-methylchalcone 1f (85 %): mp 76-78 °C. EIMS m/z (int. rel.) 238 ($M^{+\cdot}$, 98), 237 (50), 223 (100), 221 (32), 220 (74), 219 (59), 147 (74),

121 (60), 118 (38), 115 (46), 91 (30). Anal. calcd. for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92%; Found: C, 80.91; H, 6.19%.

2'-Hydroxy-2,4,6-trimethylchalcone 1g (80 %): mp 75-77 °C. EIMS m/z (int. rel.) 266 ($M^{+\bullet}$, 40), 252 (28), 251 (100), 249 (26), 248 (82), 247 (22), 233 (20), 147 (14), 129 (21), 128 (18), 121 (46), 115 (18), 93 (14). Anal. calcd. for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81%; Found: C, 81.51; H, 6.51%.

2.2.2. 2'-Hydroxychalcones 1a-c,e,h-j

The synthesis of these compounds were carried out using the procedure described for the synthesis of chalcone **1d,f,g** and their physical data agree with the literature.[19-22]

2.3. Synthesis of flavones 2

Iodine (50 mg, 0.2 mmol) was added to a 10 mmol solution of 2'-hydroxychalcones **1a-j**, in DMSO (10 ml). The mixture was heated at reflux for 30 minutes, then was poured into ice (150 g) and water (150 ml) with some crystals of sodium thiosulfate. The solid which was formed was removed by filtration, dissolved in chloroform (150 ml), and washed with a 20 % aqueous solution of sodium thiosulfate (2 x 150 ml). The organic layer was passed through anhydrous sodium sulfate and the solvent evaporated to dryness. The residue was purified by column chromatography, using chloroform as eluent. Finally the compound, in each case, was crystallized from ethanol. The obtained yields were as follows: flavone **2a** (2.16 g, 97 %); 2'-chloroflavone **2b** (2.26 g, 88 %); 2',4'-dichloroflavone **2c** (2.85 g, 98 %); 2',6'-dichloroflavone **2d** (2.80 g, 96 %); 4'-chloroflavone **2e** (2.41 g, 94 %); 2'-methylflavone **2f** (2.24 g, 95 %); 2',4',6'-trimethylflavone **2g** (2.38 g, 90 %); 4'-methylflavone **2h** (2.34 g, 99 %); 4'-methoxyflavone **2i** (2.45 g, 97 %); 4'-benzyloxyflavone **2j** (3.02 g, 92 %).[19,25-28]

2',4'-Dichloroflavone 2c: mp 123-126°C. EIMS m/z (int. rel.) 294 ($M^{+\bullet}$, ^{37}Cl x 2; 14), 290 ($M^{+\bullet}$, ^{35}Cl x 2; 86), 262 (37), 255 (51), 199 (10), 170 (11), 163 (9), 131 (16), 121 (13), 120 (100), 99 (17), 92 (61). Anal. calcd. for $C_{15}H_8O_2Cl_2$: C, 61.88; H, 2.77%; Found: C, 61.60; H, 2.99%.

2',6'-Dichloroflavone 2d: mp 122-123°C. EIMS m/z (int. rel.) 294 ($M^{+\bullet}$, ^{37}Cl x 2; 15), 290 ($M^{+\bullet}$, ^{35}Cl x 2; 80), 262 (25), 255 (37), 199 (10), 170 (12), 163 (10), 121 (19), 120 (100), 99 (20), 92 (85). Anal. calcd. for $C_{15}H_8O_2Cl_2$: C, 61.88; H, 2.77%; Found: C, 61.77; H, 3.07%.

2'-Methylflavone 2f: Yellowish oil. EIMS m/z (int. rel.) 236 ($M^{+\bullet}$, 100), 235 (36), 221 (19), 219 (17), 208 (14), 207 (14), 194 (9), 178 (9), 165 (5), 121 (10), 120 (14), 118 (7), 116 (7), 115 (9), 92 (8).

2',4',,6'-Trimethylflavone 2g: mp 112-114 °C. EIMS m/z (int. rel.) 264 ($M^{+\bullet}$, 100), 263 (20), 249 (20), 247 (16), 144 (50), 129 (38), 128 (30), 121 (68), 92 (16). Anal. calcd. for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10%; Found: C, 62.21; H, 5.81%.

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