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CARBON-13 NUCLEAR MAGNETIC RESONANCE SPECTRA OF 2-ARYLIDENE-3(2H)-BENZOFURANONES

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Abstract- ^{13}C-NMR spectra of a variety of 2-arylidene-3(2H)-benzofuranones are reported. Are examined the chemical shifts and is discussed the way in which the substituent effects can be used for elucidation of structure.

In a previous paper[1] we reported some spectroscopic data of ^{13}C-NMR in order to compare the flavonolic compounds and the 2-aryliden-3(2H)-benzofuranones (aurones).

The object of the present paper is to extend the study to the ^{13}C-NMR spectra of aurones, hydroxylated or methoxylated, which are interesting because they can be more frequently found in nature. For this purpose we have prepared two series of compounds (compounds 1 to 6 and 7 to 11). Within each series, the various compounds differ in the substituents (-Cl,-OH,-OCH_3,-OCH_2OCH_3) attached to ring B.

By oxidation from chalcones (14 and 15) we have also obtained two new thienylidene-substituted compounds (12 and 13) (Table I). From table II it appears that the introduction of substituent Cl into the ring B (compounds 1,2,3,4) causes upfield shifts on =CH increasing from para to meta to ortho chloro substituent; it also appears that the effect of this substituent causes a similar effect on C-2 but downfield.

We have noted that when a methoxy-group is introduced at C-7 of the ring A (compounds 6 and 11) the signals of carbon atoms of the ring C are hardly affected. On this basis, it is not unreasonable to compare compounds 2,5 and 7; it can be observed that whenever ortho-substitution is involved we have similar effects on the chemical shifts of the exocyclic olefinic carbon atom (=CH) (compare also compounds 3 and 8). Likewise, inspection of the spectral data of com=

pounds 6,9,10 and 11 shows that because of the effects of the substituent the chemical shift of =CH is moved upfield and that of C-2 is moved downfield, -OH being more effective than $-OCH_2OCH_3$.

Even greater upfield shifts are obtained by introducing a thienyl-ring at =CH (compounds 12 and 13).

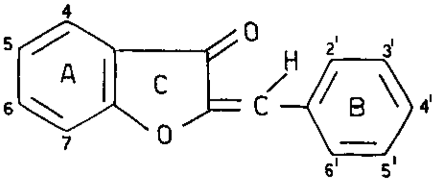
It is known from literature[2,3] that the introduction of a methoxy substituent at C-6 of the ring A has a remarkable effect on the chemical shift of C-3 (signals move from 184.5 to 182.6 ppm). Because of the introduction of a $-OCH_3$ group at C-4 we notice a further change in the chemical shift of the carbonyl carbon in the range 181.25 to 179.91.

The chemical shifts of ^{1}H-NMR are listed in table III.

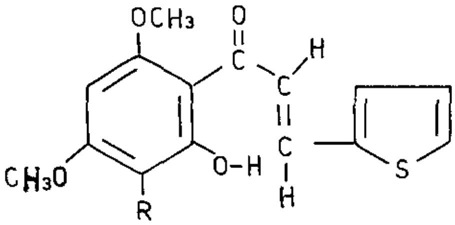
EXPERIMENTAL

The chalcones and aurones reported here were prepared by known methods[4]. Satisfactory elemental analyses for newly synthesised compounds were obtained. The melting points were determined with a Büchi apparatus and are uncorrected.

TABLE I

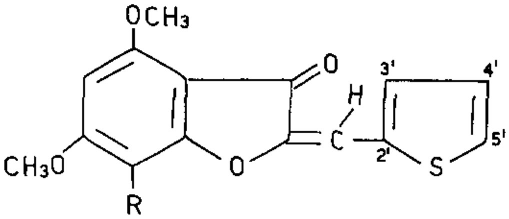


	Substituents	Melting point(°C)	References
1	4,6,7-Tri-OMe	185-186 *	4,6
2	4,6,7-Tri-OMe-2'-Cl	205-206 **	5
3	4,6,7-Tri-OMe-3'-Cl	203-204 **	5
4	4,6,7-Tri-OMe-4'-Cl	245-246 **	5
5	4,6,7,2'-Tetra-OMe	193-194 *	4
6	4,6,7,3',5'-Penta-OMe-4'-OH	214-215 *	7
7	4,6-Di-OMe-2'-OCH_2OCH_3	184-185 *	8
8	4,6-Di-OMe-3'-OCH_2OCH_3	138-140 *	8
9	4,6,3'-Tri-OMe-4'-OCH_2OCH_3	138-140 *	8
10	4,6,3',5'-Tetra-OMe-4'-OCH_2OCH_3	167-168 *	8
11	4,6,3',5'-Tetra-OMe-4'-OH	232-235 *	8



14 R=OCH_3, mp 117-118°C

15 R=H , mp 120-121°C



12 R=OCH_3, mp 176-177°C

13 R=H , mp 193-194°C

* The mps are identical to those reported in literature.

** No value available in literature.

TABLE II. ^{13}C CHEMICAL SHIFTS

Compounds	2	3	4	5	6	7	7a	3a	=CH
1	147.82*	181.25*	158.40*	91.14**	155.05*	130.78*	160.83*	128.30*	110.92**
2	148.68	180.26	158.21	91.35	155.21	130.69	161.04	127.98	105.89
3	148.39	180.41	158.16	91.31	155.14	131.87	161.10	128.05	109.03
4	148.03	180.46	158.18	91.25	155.17	135.39	161.07	128.06	109.44
5	147.82	180.67	158.69	91.16	154.98	131.29	160.53	121.70	105.04
6	146.88	180.44	158.19	91.03	155.04	138.73	160.62	127.84	111.78
7	148.10	180.61	159.51	94.09	169.01	89.33**	168.87	122.50	104.81
8	148.09	180.60	159.57	94.19	169.17	89.43	169.09	129.70	110.46
9	147.91	180.53	159.53	94.08	168.87	89.31	168.87	127.10	110.96
10	147.48	180.47	159.57	94.15	168.96	89.36	168.96	128.48	110.97
11	146.91	180.46	159.52	94.08	168.79	89.31	168.79	127.81	111.58
12	146.20	179.83	157.55	91.24	154.77	135.79*	160.53	128.07	104.88
13	146.42	179.91	159.44	94.24	168.93	89.44**	168.68	127.62	104.79

	1'	2'	3'	4'	5'	6'	OCH_2	OCH_3
1	132.63*	131.16**	128.87**	129.49**	128.87**	131.16**	=	56.54;56.77;61.44 (C-6,4,7).
2	130.76	135.60*	129.98	130.08	127.06	131.85	=	56.64;56.78;61.46 (C-6,4,7).
3	134.42	130.71**	134.81*	129.21	130.04	129.12	=	56.58;56.82;61.40 (C-6,4,7)
4	131.18	132.23	129.18**	135.33*	129.18	132.23	=	56.58;56.78;61.46 (C-6,4,7)
5	131.29	154.98*	110.84	130.92**	120.91	131.60	=	55.67;56.57;56.76 61.35(C-2',6,4,7)
6	124.08	108.39*	147.23*	108.59*	147.23*	108.39	=	56.29;56.52;56.76 61.18(C-3',5',6,4,7)
7	122.50	156.48*	114.62**	130.75**	121.96**	131.59	94.86(T)	56.08;56.24;56.32 ($3-OCH_3$)
8	134.00	118.86**	157.55*	117.30	129.78	124.99	94.67	56.14;56.27($3-OCH_3$)

TABLE II. Continued

	1'	2'	3'	4'	5'	6'	OCH_2	OCH_3
9	127.10*	116.18**	149.79*	147.18*	114.42**	125.07**	95.37	56.25;56.11 (4-OCH_3)
10	128.48	108.71	153.48	108.39	153.48*	108.71	98.37	56.25;57.19 (5-OCH_3)
11	124.10	108.57	147.24	108.80	147.24	108.57	=	56.14;56.25; 56.49(4-OCH_3)
12	=	135.79*	132.11**	127.87**	130.67**	=	=	56.51;56.80; 61.31(C-6,4,7)
13	=	135.84	132.05	127.86	130.57	=	=	56.15;56.26 (C-6,4)

*singlet; ** doublet. The carbon signals of methoxy-groups are quartet. In $CDCl_3$, ppm from TMS. Spectra were determined on a Varian FT-80A spectrometer (20 MHz). All the assignments were confirmed by off-resonance experiments.

TABLE III. ^{1}H-NMR DATA

Compounds	=CH	H-5	H-7	Ar-H	Ar-OR
1	6.78*	6.21*	=	7.35-7.90(m,3H)	3.94 4.04(2s,3-OCH_3)
2	7.27	6.21	=	8.35(H-3',dd 8.0,2.5)	4.0(s,3-OCH_3)
				7.28-7.70(m,3H)	
3	6.75	6.20	=	8.0(H-2',br W 1/2 4.0)	4.02 4.10(2s,3-OCH_3)
				7.28-7.90(m,3H)	
4	6.75	6.20	=	7.45 7.82(2d,8.0,4H)	3.98 4.00(2s,3-OCH_3)
5	7.45	6.27	=	8.38(H-3',dd,8.0,2.0)	3.95 4.0 4.06(3s,4-OCH_3)
				6.85-7.70(m,3H)	
6	6.72	6.20	=	7.23(s,2H)	3.98 4.0 4.02(3s,5-OCH_3)
7	7.40	6.18**	6.42**	8.70(H-3',dd,7.0,1.5)	3.52 5.30(2s,$OC\underline{H}_2OC\underline{H}_3$)
				7.0-7.50(m,3H)	3.90 3.98(2s,2-OCH_3)
8	6.80	6.20	6.42	7.0-7.80(m,4H)	3.52 5.28(2s,$OC\underline{H}_2OC\underline{H}_3$)
					3.92 3.98(2s,2-OCH_3)
9	6.80	6.20	6.42	7.15-7.60(m,3H)	3.55 5.32(2s,$OC\underline{H}_2OC\underline{H}_3$)
					3.96 3.98(2s,3-OCH_3)
10	6.78	6.22	6.42	7.22(s,2H)	3.65 5.28(2s,$OC\underline{H}_2OC\underline{H}_3$)
					3.98 4.02(2s,4-OCH_3)
11	6.78	6.22	6.44	7.22(s,2H)	3.98 4.00(2s,4-OCH_3)
12	7.18	6.27*	=	7.21(H-4',dd,4.2,5.3)	4.02 4.15(2s,3-OCH_3)
				7.40-7.70(m,2H)	
13	7.10	6.10**	6.32	7.15(H-4',dd,4.2,5.3)	3.94 3.97(2s,2-OCH_3)

*singlet; **doublet, J=2.0; δ in $CDCl_3$(J values in Hz).

Spectra were determined on a Varian EM-360 spectrometer (60 MHz).

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