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

Aurora Bellino, Maria Luisa Marino, and Pietro Venturella*
Istituto di Chimica Organica dell'Università, Via Archirafi, 20
90123-Palermo, Italy

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.

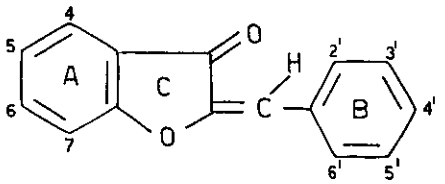
EXPERIMENTAL

The chalcones and aurones reported here were prepared by known methods[4].

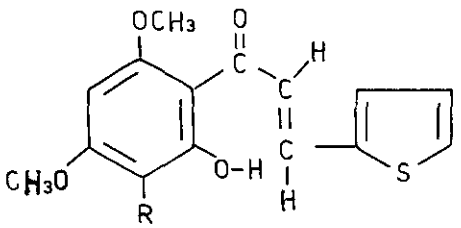
Satisfactory elemental analyses for newly synthesised compounds were obtained.

The melting points were determined with a Büchi apparatus and are uncorrected.

TABLE I

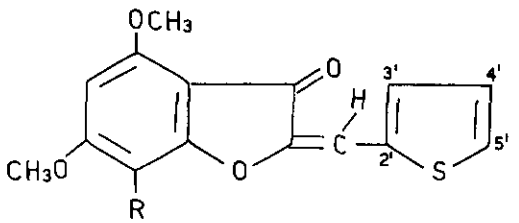


	Substituents	Melting point(°C)	References
1	4,6,7-Tri-OMe	185-186 *	4,6
2	4,6,7-Tri-OMe-2'-Cl	205-206 **	5
3	4,6,7-Tri-OMe-3'-Cl	203-204 **	5
4	4,6,7-Tri-OMe-4'-Cl	245-246 **	5
5	4,6,7,2'-Tetra-OMe	193-194 *	4
6	4,6,7,3',5'-Penta-OMe-4'-OH	214-215 *	7
7	4,6-Di-OMe-2'-OCH_2OCH_3	184-185 *	8
8	4,6-Di-OMe-3'-OCH_2OCH_3	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 ($3\text{-}OCH_3$)
8	134.00	118.86**	157.55*	117.30	129.78	124.99	94.67	56.14;56.27($3\text{-}OCH_3$)

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 ($4\text{-}OCH_3$)
10	128.48	108.71	153.48	108.39	153.48*	108.71	98.37	56.25;57.19 ($5\text{-}OCH_3$)
11	124.10	108.57	147.24	108.80	147.24	108.57	=	56.14;56.25; 56.49($4\text{-}OCH_3$)
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,OCH$_2$OCH$_3$)
				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,OCH$_2$OCH$_3$)
					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,OCH$_2$OCH$_3$)
					3.96 3.98(2s,3-OCH$_3$)
10	6.78	6.22	6.42	7.22(s,2H)	3.65 5.28(2s,OCH$_2$OCH$_3$)
					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).

ACKNOWLEDGEMENT

Financial support of this work by Ministero Pubblica Istruzione,Roma, is greatly appreciated.

REFERENCES

1. A.Bellino,M.L.Marino,and P.Venturella, Chim.and Ind.(Milano),1981,63,697.
2. P.K.Agrawal and R.P.Rastogi,Heterocycles,1981,16,2181.
3. A.Pelter,R.Ward,and T.Ian Gray,J.Chem.Soc.,1976,2475.
4. P.Venturella and A.Bellino,Ann.Chim.,1960,50,202.
5. A.Bellino and P.Venturella,Atti Accad.Sci.Lettere.Arti Palermo,1962,21,17.
6. B.Cummins,E.M.Philbin,J.F.Eades,H.Fletcher,and R.K.Wilson,Tetrahedron, 1963,19,499.
7. A.Arcoleo,A.Bellino,and P.Venturella,Ann.Chim.,1957,47,66.
8. P.Venturella and A.Bellino,Ann.Chim.,1960,50,1510.

Received, 2nd May, 1983