The Carbon-13 Nuclear Magnetic Resonance Spectra of Flavonoids and Related Compounds

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The ^{13}C n.m.r. spectra of a wide variety of flavonoids and related compounds and vanillin isomers are reported. Particular attention is directed towards features of the spectra which are most useful for structure elucidation, and the principle of additivity of substituent effects in such systems is critically examined. It is shown that the acetylation of phenolic hydroxy-groups can be used to identify the positions of the hydroxy-groups on an aromatic ring, a technique which is particularly useful when both hydroxy- and methoxy-groups are present.

PROTON n.m.r. spectroscopy has been widely used for elucidation of the structures of flavonoids.[1] However there are as yet few published ^{13}C n.m.r. data for flavonoids, although such data promise to be equally valuable. In this paper we report the ^{13}C n.m.r. spectra of a wide variety of flavonoids and related compounds (chalcones, flavanones, flavones, isoflavones, coumarins, isocoumarins, aurones, isoaurones, pterocarpans, *etc.*), and discuss the way in which this information can be used for elucidation of structure. Most of the compounds studied have only one ring A substituent, attached to C-7 (or its equivalent) on the flavonoid nucleus, in order to simplify the spectral interpretation.†

Kingsbury and Looker have recently reported the ^{13}C n.m.r. spectra of a series of monomethoxy-flavones,[2] and Joseph-Nathan *et al.* have used a europium shift reagent to make unequivocal assignments of the signals in the ^{13}C spectrum of flavone itself.[3] In another recent paper, Sojka has reported the ^{13}C spectra of some simple coumarin derivatives in chloroform and in sulphuric acid, and has shown that protonation occurs predominantly at the carbonyl oxygen atom leading to deshielding of C-2 and C-4 by 10 and 20 p.p.m., respectively.[4] The ^{13}C n.m.r. spectra of a series of bromo-, methyl-, hydroxy-, and methoxy-coumarins have also been reported, by Cussans and Huckerby,[5] and Crombie *et al.* have reported ^{13}C spectra of a series of rotenoids.[6] Finally, Wehrli has shown that coupling between ^{13}C and hydrogen-bonded hydroxy-protons can be used as an aid to the interpretation of ^{13}C spectra of 5-hydroxy-flavones and -flavanones.[7]

In the present study, spectra were recorded for solutions in $CDCl_3$ or $CDCl_3-(CD_3)_2SO$, according to solubility. Tests have shown that solvent shifts of *ca.* 0—0.5 p.p.m. can normally be expected on going from $CDCl_3$ to $(CD_3)_2SO$, although some carbon atoms experience slightly larger shifts. Chemical shifts were assigned by comparison with the spectra of simpler model compounds, and by consideration of the known substituent effects

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† The spectra of some 5,7-disubstituted compounds have recently been reported, and may be regarded as complementary to this study (H. Wagner, V. M. Chari, and J. Sonnenbichler, *Tetrahedron Letters*, 1976, 1799; B. Ternai and K. R. Markham, *Tetrahedron*, 1976, **32**, 565).

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[2] C. A. Kingsbury and J. H. Looker, *J. Org. Chem.*, 1975, **40**, 1120.

[3] P. Joseph Nathan, J. Mares, Ma. C. Hernandez, and J. N. Shoolery, *J. Magnetic Resonance*, 1974, **16**, 447.

[4] S. A. Sojka, *J. Org. Chem.*, 1975, **40**, 1175.

[5] N. J. Cussans and T. N. Huckerby, *Tetrahedron*, 1975, **31**, 2587, 2591, 2719; *Tetrahedron Letters*, 1975, 2445; see also R. D Lapper, *ibid.*, 1974, 4293.

[6] L. Crombie, G. W. Kilbee, and D. A. Whiting, *J.C.S. Perkin I*, 1975, 1497.

[7] F. W. Wehrli, *J.C.S. Chem. Comm.*, 1975, 663.

TABLE 1 †

^{13}C N.m.r. spectra of chalcones

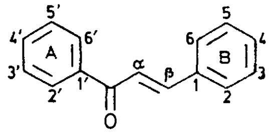
Chalcone	C-1	C-2	C-3	C-4	C-5	C-6	C-β	C-α	C=O	C-1′	C-2′	C-3′	C-4′	C-5′	C-6′	OMe	OAc
(1)	134.45	128.90	128.58	130.80	128.58	128.90	145.25	118.47	193.57	119.93	163.55	118.75	136.25	119.93	129.63		
(2)	134.26	128.75	128.19	130.43	128.19	128.75	144.66	123.35	190.56	132.02	148.65	125.77	132.29	124.96	129.63		169.78 20.63
*							−0.59	+4.88	−3.01	+12.09	−14.90	+7.01	−3.96	+5.03	−0.00		
(3) ‡	121.83	157.90	116.75	132.10	120.17	130.08	142.19	118.35	194.59	119.78	163.46	118.82	136.04	120.29	129.88		
(4)	127.06	149.55	126.22	131.33	123.12	127.39	138.35	126.90	191.07	131.92	148.55	125.81	132.39	123.28	129.70		168.85 169.02 20.82
*	+5.23	−8.35	+9.47	−0.77	+2.95	−2.69	−3.84	+8.55	−3.52	+12.14	−14.91	+6.99	−3.65	+3.01	−0.18		
(5)	123.70	159.11	111.38	132.25	120.84	129.68	141.16	118.56	194.36	120.27	163.65	118.79	136.17	120.84	129.74	55.60	
(6)	123.10	158.55	111.18	132.18	120.61	129.11	140.28	123.31	191.10	132.40	148.66	125.78	131.91	125.45	129.68	55.25	168.89 20.73
*							−0.88	+4.75	−3.26	+12.13	−14.99	+6.99	−4.26	+4.61	−0.06		
(7)	127.42	130.59	114.58	162.12	114.58	130.59	145.40	118.62	193.74	120.20	163.64	118.79	136.17	117.67	129.58	55.45	
(8)	126.93	130.02	114.31	161.59	114.31	130.02	145.03	122.79	191.07	132.34	148.45	125.77	132.01	123.24	129.55	55.21	168.97 20.82
*							−0.37	+4.17	−2.67	+12.14	−15.19	+6.98	−4.16	+5.57	−0.03		
(9)	134.64	128.80	128.36	130.46	128.36	128.80	144.19	120.18	191.57	113.97	166.51	100.98	166.02	107.59	131.06	55.49	
(10)	134.55	128.75	128.36	130.23	128.36	128.75	143.76	128.10	188.90	124.64	150.90	109.13	163.06	111.41	131.66	55.52	168.96 20.93
*							−0.43	+7.92	−2.67	+10.67	−15.61	+8.15	−2.96	+3.82	+0.60		
(11)	122.02	157.70	116.73	131.81	120.42	129.96	141.10	119.77	192.81	114.35	166.51	101.12	166.01	107.39	131.51	55.53	
(12)	127.29	149.50	126.17	131.07	123.08	127.29	136.85	126.47	188.63	124.06	150.97	109.16	163.20	111.40	131.78	55.55	168.86 169.00 20.75 20.87
*	+5.27	−8.20	+9.44	+0.74	+2.66	−2.67	−4.25	+6.70	−4.18	+9.71	−15.54	+8.04	−2.81	+4.01	+0.27		
(13)	122.67	158.71	111.28	131.24	120.74	128.74	137.58	127.86	191.10	124.63	160.44	98.78	164.07	105.29	132.85	55.76 55.53	
(14)	127.23	130.15	114.23	161.54	114.23	130.15	143.93	117.44	191.44	113.97	166.33	100.96	165.73	107.24	130.96	55.32 55.18	
(15) ‡	126.01	130.46	116.13	160.13	116.13	130.46	144.75	116.61	191.79	114.05	165.74	100.99	166.21	107.26	131.05	55.45	
(16) ‡	126.12	130.67	116.25	160.34	116.25	130.67	144.86	116.75	191.95	114.13	166.33	101.13	165.92	107.33	131.28	55.49	
(17)	132.32	129.27	122.07	150.91	122.07	129.27	142.80	124.87	189.00	124.33	152.11	109.14	163.13	111.57	131.67	55.65	168.79 169.79 21.04
*	+6.20	−1.40	+5.82	−9.43	+5.82	−1.40	−2.06	+8.12	−2.95	+10.20	−14.22	+8.01	−2.79	+4.24	−0.39		
(18)	128.41	130.27	114.61	160.69	114.61	130.27	142.31	125.33	190.95	122.69	161.68	98.86	164.46	105.55	132.96	55.48 55.62 55.86	
(19)	135.90	113.48	159.70	116.14	129.72	120.91	143.94	120.24	191.37	113.90	166.43	100.95	165.93	107.39	131.08	55.12 55.32	
(20)	135.94	113.12	159.73	116.07	129.76	120.73	143.73	124.95	188.95	124.25	150.89	109.11	163.08	111.44	131.68	55.15 55.56	168.99 20.94
*							−0.21	+4.71	−2.42	+10.35	−15.54	+8.16	−2.85	+4.05	+0.60		
(21) ‡	135.80	115.08	157.69	118.16	129.77	120.02	144.49	119.83	191.67	113.93	166.32	100.99	165.91	107.26	131.33	55.44	
(22) ‡	127.76	114.94	146.91	150.49	111.67	122.18	144.65	118.12	191.76	114.00	166.09	100.96	165.84	107.17	131.96	55.49	
(23) ‡	127.70	122.42	139.95	153.17	112.52	129.00	143.13	119.32	191.63	113.97	166.19	100.90	165.96	107.21	132.11	55.95 55.51	168.20 20.40

* Shifts induced by acetylation of phenolic hydroxy-groups (+ indicates downfield shift). † Unless otherwise stated spectra in all Tables were taken in $CDCl_3$ solution
‡ Taken in $CDCl_3$-$(CD_3)_2SO$.%$(CD_3)_2SO$: (3) 5, (15) 20, (16) 20, (21) 20, (22) 60, (23) 40.

of hydroxy-, methoxy-, and acetoxy-groups[8,9] (which are commented on in more detail later). All the assignments are supported by off-resonance decoupling experiments, and in some cases by the effect of double irradiation of specific protons in the ^1H n.m.r. spectra. Shifts are reported in p.p.m. downfield from Me_4Si.

Chalcones.—In the ^{13}C n.m.r. spectra of chalcones (Table 1) the carbonyl carbon signals come between 188.6 and 194.6 p.p.m. The presence of a 2′-hydroxy-group moves this signal downfield by *ca.* 3 p.p.m. relative to the corresponding acetoxy- and methoxy-compounds, presumably owing to hydrogen bonding.

The α- and β-carbon signals can in most cases be readily identified by their characteristic appearance as a six-line multiplet (rather than a simple doublet) in the off-resonance decoupled spectrum. The α- and β-carbon atoms give rise to signals at 116.6—128.1 and 136.9—145.4 p.p.m., respectively, in line with values reported for αβ-unsaturated ketones.[8] Comparison of the 2′-hydroxy- and 2′-acetoxy-compounds reveals that the α-carbon atom is also significantly affected (upfield shift) by hydrogen bonding at the carbonyl group. However the magnitude of this shift is less predictable than its direction, because the α- and β-carbon atoms are both noticeably affected by changes in the substitution of ring B.



Chalcone

(1)	2′-HO
(2)	2′-AcO
(3)	2,2′-$(HO)_2$
(4)	2,2′-$(AcO)_2$
(5)	2′-HO-2-MeO
(6)	2′-AcO-2-MeO
(7)	2′-HO-4-MeO
(8)	2′-AcO-4-MeO
(9)	2′-HO-4′-MeO
(10)	2′-AcO-4′-MeO
(11)	2,2′-$(HO)_2$-4′-MeO
(12)	2,2′-$(AcO)_2$-4′-MeO
(13)	2,2′,4′-$(MeO)_3$
(14)	2′-HO-4,4′-$(MeO)_2$
(15)	4-HO-2′,4′-$(MeO)_2$
(16)	2′,4-$(HO)_2$-4′-MeO
(17)	2′,4-$(AcO)_2$-4′-MeO
(18)	2′,4,4′-$(MeO)_3$
(19)	2′-HO-3,4′-$(MeO)_2$
(20)	2′-AcO-3,4′-$(MeO)_2$
(21)	2′,3-$(HO)_2$-4′-MeO
(22)	3-HO-2′,4,4′-$(MeO)_3$
(23)	3-AcO-2′-HO-4,4′-$(MeO)_2$

SCHEME 1 Compounds in Tables 1—3 (chalcones)

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[8] J. B. Stothers, ' Carbon 13 N.M.R. Spectroscopy,' Academic Press, New York, 1972.

[9] G. C. Levy and G. L. Nelson, ' Carbon 13 Nuclear Magnetic Resonance for Organic Chemists,' Wiley–Interscience, New York, 1972.

Table 2 shows the resonances of the ring A carbon atoms of chalcones, and in Table 3 those of the ring B carbon atoms are similarly presented, in such a way that compounds having the same substitution pattern are grouped together.

TABLE 2

Chemical shifts of ring A carbon atoms in chalcones

	C-1′	C-2′	C-3′	C-4′	C-5′	C-6′
(a) 2′-Hydroxychalcones						
(1)	119.93	163.55	118.76	136.25	119.93	129.63
(3)	119.78	163.46	118.82	136.04	120.29	129.88
(5)	120.27	163.65	118.79	136.17	120.84	129.74
(7)	120.20	163.64	118.79	136.17	117.67	129.58
(b) 2′-Acetoxychalcones						
(2)	132.02	148.65	125.77	132.29	124.96	129.63
(4)	131.92	148.55	125.81	132.39	123.28	129.70
(6)	132.40	148.66	125.78	131.91	125.45	129.68
(8)	132.34	148.45	125.77	132.01	123.24	129.55
(c) 2′-Hydroxy-4′-methoxychalcones						
(9)	113.97	166.51	100.98	166.02	107.59	131.06
(11)	114.35	166.51	101.12	166.01	107.39	131.51
(14)	113.97	166.33	100.96	165.73	107.24	130.96
(16)	114.13	166.33	101.13	165.92	107.33	131.28
(19)	113.90	166.43	100.95	165.93	107.39	131.08
(21)	113.93	166.32	100.99	165.91	107.26	131.33
(23)	113.97	166.19	100.90	165.96	107.21	131.28
(d) 2′,4′-Dimethoxychalcones						
(13)	124.63	160.44	98.78	164.07	105.29	132.85
(15)	114.05	165.74	100.99	166.21	107.26	131.05
(18)	122.69	161.68	98.86	164.46	105.55	132.96
(22)	114.00	166.09	100.96	165.84	107.17	131.96
(e) 2′-Acetoxy-4′-methoxychalcones						
(10)	124.64	150.90	109.13	163.06	111.41	131.66
(12)	124.06	150.97	109.16	163.20	111.40	131.78
(17)	124.33	152.11	109.14	163.13	111.57	131.67
(20)	124.25	150.89	109.11	163.08	111.44	131.68

Flavanones.—In the ^{13}C n.m.r. spectra of flavanones (Table 4) the carbonyl carbon signals again come in the region 189.5—191.6 p.p.m. (except when a 5-OH group is present), but C-2 and C-3 resonances are now readily identified at 75.0—80.3 and 42.8—44.6 p.p.m., respectively, the latter appearing as a triplet in the off-resonance decoupled spectrum, and the former as a doublet.

When a methoxy-group is introduced at C-7 of the flavanone nucleus the C-7 signal itself is moved downfield by 29.9 p.p.m., whilst the C-6 and C-8 resonances are moved upfield by 11.4 and 17.2 p.p.m., respectively, and that of C-4a is moved upfield by 6.2 p.p.m. The carbon atoms *meta* to the methoxy-group (C-5 and C-8a) are only

TABLE 3

Chemical shifts of ring B carbon atoms in chalcones

	C-1	C-2	C-3	C-4	C-5	C-6
(a) 2-Hydroxychalcones						
(3)	121.83	157.90	116.75	132.10	120.17	130.08
(11)	122.02	157.70	116.73	131.81	120.42	129.96
(b) 2-Methoxychalcones						
(5)	123.70	159.11	111.38	132.25	120.84	129.68
(6)	123.10	158.55	111.18	132.18	120.61	129.11
(13)	122.67	158.71	111.28	131.24	120.74	128.74
(c) 2-Acetoxychalcones						
(4)	127.06	149.55	126.22	131.33	123.12	127.39
(12)	127.29	149.50	126.17	131.07	123.08	127.29
(d) 4-Hydroxychalcones						
(15)	126.01	130.46	116.13	160.13	116.13	130.46
(16)	126.12	130.67	116.25	160.34	116.25	130.67
(e) 4-Methoxychalcones						
(7)	127.42	130.59	114.58	162.12	114.58	130.59
(8)	126.93	130.02	114.31	161.59	114.31	130.02
(14)	127.23	130.15	114.23	161.54	114.23	130.15
(18)	128.41	130.27	114.61	160.69	114.61	130.27
(f) 4-Acetoxychalcones						
(17)	132.32	129.27	122.07	150.91	122.07	129.27
(g) 3-Hydroxychalcones						
(21)	135.80	115.08	157.69	118.16	129.77	120.02
(h) 3-Methoxychalcones						
(19)	135.90	131.48	159.70	116.14	129.72	120.91
(20)	135.94	113.12	159.73	116.07	129.76	120.73
(i) 3-Hydroxy-4-methoxychalcones						
(22)	127.76	114.94	146.91	150.49	111.67	122.18
(j) 3-Acetoxy-4-methoxychalcones						
(23)	127.70	122.42	139.95	153.17	112.52	129.00

TABLE 4

^{13}C N.m.r. spectra of flavanones

Flavanone	C-1′	C-2′	C-3′	C-4′	C-5′	C-6′	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-8a	C-4a	OMe	OAc
(24)	138.63	125.99	128.66	128.66	128.66	125.99	79.49	44.60	191.62	126.90	121.45	135.99	117.98	161.34	120.83		
(25)	138.64	125.94	128.53	128.53	128.53	125.94	79.77	44.17	190.06	128.53	110.02	165.88	100.78	163.23	114.67	55.48	
(26)	127.65	155.96	110.63	129.48	120.98	126.49	75.11	43.40	191.46	128.84	110.14	166.16	101.02	164.12	115.05	55.41 55.67	
(27) †	125.38	154.23	115.57	129.06	119.08	126.53	74.95	42.65	190.34	128.17	109.72	165.67	100.89	163.68	114.57	55.57	
(28)	130.63	147.55	122.87	129.48	127.11	126.36	75.09	43.14	190.01	128.60	110.26	165.98	100.75	163.24	114.58	55.59	20.91 168.87
*	+5.25	−6.68	+7.30	+0.42	+8.03	−0.17	+0.14	+0.49	−0.33								
(29)	140.27	111.78	159.70	113.79	129.67	118.12	79.61	44.15	189.95	128.44	109.96	165.82	100.82	163.14	114.67	55.44 55.10	
(30) †	140.25	113.29	157.69	115.56	129.51	116.82	79.37	43.75	189.72	128.15	109.78	165.79	100.98	163.17	114.63	55.54	
(31)	140.41	121.66	150.80	123.19	129.61	119.23	79.07	44.15	189.71	128.50	110.16	165.92	100.81	163.02	114.63	55.52	21.01 168.94
*	+0.16	+8.37	−6.89	+7.37	+0.10	+2.41	−0.30	+0.40	−0.01								
(32)	130.69	127.54	113.95	159.66	113.95	127.54	79.50	43.92	190.23	128.41	109.87	165.80	100.76	163.28	114.63	55.43 55.14	
(33) †	130.05	128.56	115.88	158.67	115.88	128.56	80.32	44.21	190.45	128.56	110.24	166.43	101.43	164.08	115.28	55.97	
(34)	136.23	127.63	121.73	150.34	121.73	127.63	78.61	43.13	189.51	127.86	109.80	165.49	100.88	162.81	114.33	55.65	20.73 168.83
*	+6.18	−0.93	+5.85	−8.33	+5.85	−0.93	−1.71	−1.08	−0.94								
(35) †	131.28	113.64	146.56	147.88	111.53	117.66	78.61	42.80	195.50	163.99	96.44	166.90	95.44	162.93	102.20	55.87	

* Shifts induced by acetylation of phenolic hydroxy-groups. † Taken in $CDCl_3$–$(CD_3)_2SO$.% $(CD_3)_2SO$: (27) 60, (30) 50, (33) 60, (35) 20.

TABLE 5

^{13}C N.m.r. spectra of flavones

Flavone	C-1′	C-2′	C-3′	C-4′	C-5′	C-6′	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-8a	C-4a	OMe	OAc
(36) †	131.5	126.0	128.8	131.3	128.8	126.0	163.0	107.3	178.0	125.4	124.9	133.5	117.9	156.0	123.7		
(37) †	131.6	125.8	128.7	131.1	128.7	125.8	162.6	107.2	177.4	126.7	114.1	163.7	100.2	157.7	117.6	55.9	
(38)	121.06	158.30	112.65	132.28	120.77	129.24	160.53	111.84	178.33	127.05	114.23	164.12	100.37	158.00	121.06	55.71 55.81	
(39)	124.22	127.93	114.50	162.38	114.50	127.93	163.20	106.14	177.97	127.08	114.24	164.16	100.49	158.00	117.86	55.51 55.84	
(40) ‡	121.77	128.13	115.93	160.84	115.93	128.13	162.72	104.66	176.32	126.12	114.26	163.69	100.83	157.38	117.15	55.95	
(41)	129.16	127.24	122.12	152.90	122.12	127.29	161.92	107.30	177.41	126.85	114.31	164.01	100.29	157.71	117.61	55.79	21.11 169.70
•	+7.39	−0.84	+6.19	−7.94	+6.19	−0.84	−0.80	+2.64	+1.09								

* Shifts induced by acetylation of phenolic hydroxy-groups. † Ref. 2. ‡ Taken in $(CD_3)_2SO$ solution.

TABLE 6

^{13}C N.m.r. spectra of isoflavones

Isoflavone	C-1′	C-2′	C-3′	C-4′	C-5′	C-6′	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-8a	C-4a	OMe	OAc
(42)	127.90	128.25	128.80	131.79	128.80	128.25	152.38	125.11	175.31	127.64	114.43	163.81	100.01	157.73	118.32	55.74	
(43)	121.11	157.66	111.37	131.84	120.60	129.74	153.83	122.67	175.49	127.87	114.35	163.96	100.28	158.09	118.61	55.81	
(44)	120.70	156.64	119.64	130.51	120.81	129.71	155.44	152.09	178.62	127.87	115.79	164.94	99.87	157.97	117.15	56.01	
(45)	125.03	149.02	125.82	131.42	122.79	129.38	153.31	122.29	174.46	127.48	114.54	163.92	100.17	157.80	117.96	55.78	20.90 168.96
*	+4.33	−7.62	+6.18	+0.91	+1.98	−0.33	−2.13	−2.80	−4.16								
(46)	124.09	129.92†	113.79	159.36	113.79	129.92 †	151.82 †	124.66	175.53	127.57 †	114.33	163.72	99.96	157.71	118.27	55.72 55.22	
(47) ‡	122.41	129.78	115.16	157.51	115.16	129.78	151.84	124.44	175.20	127.01	114.25	163.54	99.97	157.20	117.92	55.69	
(48)	129.68	130.11	121.67	150.71	121.67	130.11	152.66	124.57	175.55	127.89	114.72	164.22	100.24	158.05	118.49	55.89	21.14 169.45
*	+7.27	+0.33	+6.51	−6.80	+6.51	+0.33	+0.82	+0.13	+035								
(49) ‡	123.87	130.01	113.61	159.20	113.61	130.01	152.22	124.43	175.19	127.24	115.13	162.71	102.30	157.79	117.00	55.09	
(50)	123.68	129.96	113.90	159.55	113.90	129.96	152.38	125.08	175.61	127.71	119.26	154.22	110.76	156.45	122.16	55.28	21.13 168.28
*							+0.16	+0.65	+0.42	+0.47	+4.13	−8.49	+8.46	−1.34	+5.16		
(51)	124.31	130.20	113.60	159.31	113.60	130.20	149.80	125.86	175.30	161.37	96.09	163.71	92.51	159.74	119.69	55.23 55.63 56.27	

* Shifts induced by acetylation of phenolic hydroxy-groups. † Confirmed by double irradiation. ‡ Taken in CDCl$_3$–(CD$_3$)$_2$SO (7 : 3).

slightly affected (+1.6 and +1.9 p.p.m.). Earlier results have indicated that in simple benzene derivatives the carbon atom to which a methoxy-group is attached is deshielded by 30.2 p.p.m., whereas the carbon atoms *ortho* and *para* to the methoxy-group are shielded by 15.5 and 8.9 p.p.m., respectively.[8] It has been further suggested that the shielding effects of substituents on an aromatic nucleus exhibit an additive relationship, provided the groups are not *ortho* to one another.[8,9] Comparison of the values reported here with those for simple benzene derivatives indicates that in more complex systems the actual shifts vary in magnitude (but not in direction). Although there is no doubt that the concept of an additive relationship is useful for predictive purposes, care must clearly be exercised when making assignments solely based on this principle. (Further examples are discussed later.)

TABLE 7

Chemical shifts of ring A carbon atoms in 7-methoxy-flavanones, -flavones, and -isoflavones, and 6-methoxy-aurones

	C-5	C-6	C-7	C-8	C-8a	C-4a
(a) 7-Methoxyflavanones						
(25)	128.53	110.02	165.88	100.78	163.23	114.67
(26)	128·84	110.14	166.16	101.02	164.12	115.05
(27)	128.17	109.72	165.67	100.89	163.68	114.57
(28)	128.60	110.26	165.98	100.75	163.24	114.58
(29)	128.44	109.96	165.82	100.82	163.14	114.67
(30)	128.15	109.78	165.79	100.98	163.17	114.63
(31)	128.50	110.16	165.92	100.81	163.02	114.63
(32)	128.41	109.87	165.80	100.76	163.28	114.63
(33)	128.56	110.24	166.43	101.43	164.08	115.28
(34)	127.86	109.80	165.49	100.88	162.81	114.33
(b) 7-Methoxyflavones						
(37)	126.7	114.1	163.7	100.2	157.7	117.6
(38)	127.05	114.23	164.12	100.37	158.00	121.06
(39)	127.08	114.24	164.16	100.49	158.00	117.86
(40)	126.12	114.26	163.69	100.83	157.38	117.15
(41)	126.85	114.31	164.01	100.29	157.11	117.61
(c) 7-Methoxyisoflavones						
(42)	127.64	114.43	163.81	100.01	157.73	118.32
(43)	127.87	114.35	163.96	100.28	158.09	118.61
(44)	127.87	115.79	164.94	99.87	157.97	117.15
(45)	127.48	114.54	163.92	100.17	157.80	117.96
(46)	127.57	114.33	163.72	99.96	157.71	118.27
(47)	127.01	114.25	163.54	99.97	157.20	117.92
(48)	127.89	114.72	164.22	110.24	158.05	118.49
(d) 6-Methoxyaurones *						
(63)	125.59	112.00	167.22	96.54	168.33	114.69
(64)	125.25	112.78	166.97	96.46	167.82	114.88

* From Table 11.

Flavones and Isoflavones.—The assignment of chemical shifts in the flavone series (Table 5) was considerably aided by comparison with the data reported by Kingsbury and Looker.[2] In the case of the isoflavones (Table 6) the unequivocal identification and clear separation of the ^{1}H n.m.r. signals made it possible to perform specific irradiation experiments to confirm some of the assignments. The carbonyl carbon signals of both flavones and isoflavones come in the region 174.5—178.6 p.p.m., but C-2 and C-3 are sufficiently different in the two series to permit an immediate distinction. In the flavones the C-2 signal appears as a singlet (in the off-resonance decoupled spectrum) at 160.5—163.2 p.p.m., and that of C-3 as a doublet at 104.7—111.8 p.p.m., whereas in the isoflavones the C-2 resonance is seen as a doublet at 149.8—155.4 and that of C-3 as a singlet at 122.3—125.9 p.p.m.

TABLE 8

Chemical shifts of ring B carbon atoms in flavanones, flavones, isoflavones, and aurones

	C-1′	C-2′	C-3′	C-4′	C-5′	C-6′
(a) 4′-HO						
(33)	130.05	128.56	115.88	158.67	115.88	128.56
(40)	121.77	128.13	115.93	160.84	115.93	128.13
(47)	122.41	129.78	115.16	157.51	115.16	129.78
(64)	123.41	133.23	116.14	159.30	116.14	133.23
(b) 4′-AcO						
(34)	136.23	127.63	121.73	150.34	121.73	127.63
(41)	129.16	127.29	122.12	152.90	122.12	127.29
(48)	129.68	130.11	121.67	150.71	121.67	130.11
(c) 4′-MeO						
(32)	130.69	127.54	113.95	159.66	113.95	127.54
(39)	124.22	127.93	114.50	162.38	114.50	127.93
(46)	124.09	129.92	113.79	159.36	113.79	129.92
(49)	123.87	130.01	113.61	159.20	113.61	130.01
(50)	123.68	129.96	113.90	159.55	113.90	129.96
(51)	124.31	130.20	113.60	159.31	113.60	130.20
(d) 2′-HO						
(27)	125.38	154.23	115.57	129.06	119.08	126.53
(44)	120.70	156.64	119.64	130.51	120.81	129.71
(3) 2′AcO						
(28)	130.63	147.55	122.87	129.48	127.11	126.36
(45)	125.03	149.02	125.82	131.42	122.79	129.38
(f) 2′-MeO						
(26)	127.65	155.96	110.63	129.48	120.98	126.49
(38)	121.06	158.30	112.65	132.28	120.77	129.24
(43)	121.11	157.66	111.37	131.84	120.60	129.74
(g) 3′-HO						
(30)	140.25	113.29	157.69	115.56	129.51	116.82
(h) 3′-AcO						
(31)	140.41	121.66	150.80	123.19	129.61	119.23
(i) 3′MeO						
(29)	140.27	111.78	159.70	113.79	129.67	118.12

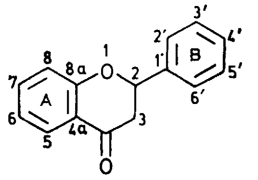
In Table 7 the carbon resonances of the ring A carbon atoms of 7-methoxy-flavanones, -flavones, -isoflavones, and 6-methoxyaurones (see later) are compared. Simi-

TABLE 9

^{13}C N.m.r. spectra of coumarins

Coumarin	C-1′	C-2′	C-3′	C-4′	C-5′	C-6′	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-8a	C-4a	OMe	OAc
(52) †							159.6	115·7	142.7	127.3	123.6	130.9	115.7	153.1	118.1		
(53) ‡							160.7	111.5	144.3	129.5	113.3	161.6	102.5	155.7	111.5		
(54) ‡							160.1	112.3	143.8	129.1	112.0	162.4	100.5	155.3	112.0	55.6	
(55)	134.90	128.26	128.26	128.26	128.26	128.26	160.48	124.68	139.77	128.69	112.61	162.45	100.33	155.15	113.23	55.70	
(56)	135.42	128.20	128.64	129.39	128.64	128.20	160.87	111.73 §	155.84	127.80	112.10	162.61	101.02	155.56	112.39	55.70	
(57)	135.45	128.26	128.67	129.37	128.67	128.26	160.27	110.39	155.76	127.93	113.10	161.58	102.86	155.40	110.82		
(58)	134.86	128.17	128.76	129.62	128.76	128.17	160.08	110.47	154.99	127.69	117.90	153.02	114.28	154.55	116.64		168.40 21.02
							−0.19	+0.06	−0.77	−0.24	+4.80	−8.56	+11.42	−0.85	+5·82		

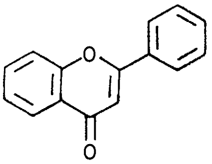
* Shifts induced by acetylation of phenolic hydroxy groups. † Ref. 4. ‡ Ref. 5. § Confirmed by double irradiation. ¶ Taken in $CDCl_3$–$(CD_3)_2SO$ (3: 7).



(24) flavanone

Flavanones

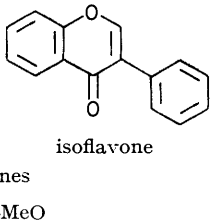
(24)
(25) 7-MeO
(26) 2′,7-$(MeO)_2$
(27) 2′-HO-7-MeO
(28) 2′-AcO-7-MeO
(29) 3′,7-$(MeO)_2$
(30) 3′ HO-7-MeO
(31) 3′-AcO-7-MeO
(32) 4′,7-$(MeO)_2$
(33) 4′-HO-7-MeO
(34) 4′-AcO-7-MeO
(35) 3′,5,7-$(HO)_3$-4′-MeO



(36) flavone

Flavones

(36)
(37) 7-MeO
(38) 2′,7-$(MeO)_2$
(39) 4′,7-$(MeO)_2$
(40) 4′-HO-7-MeO
(41) 4′-AcO-7-MeO



isoflavone

Isoflavones

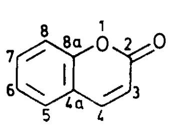
(42) 7-MeO
(43) 2′,7-$(MeO)_2$
(44) 2′-HO-7-MeO
(45) 2′-AcO-7-MeO
(46) 4′,7-$(MeO)_2$
(47) 4′-HO-7-MeO
(48) 4′-AcO-7-MeO
(49) 7-HO-4′-MeO
(50) 7-AcO-4′-MeO
(51) 4′,5,7-$(MeO)_3$

SCHEME 2 Compounds in Tables 4—8 (flavanones, flavones, and isoflavones)

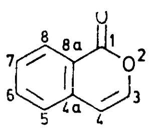
larly in Table 8 the chemical shifts of common ring B part structures are compared. The relatively minor differences which exist indicate that ring A is substantially insulated from changes in the substitution and unsaturation of C-2 and C-3. In contrast, the chemical shifts of the ring B carbon atoms in the four series differ significantly, particularly at the 1′-position. Thus, for example, the chemical shifts of the 1′-carbon atoms of the flavanones occur appreciably downfield from those in the other series.

Introducing a methoxy-substituent at C-7 of flavone has a similar effect to that already noted in the flavanone series. The C-7 signal itself is moved downfield by 30.2 p.p.m., the *ortho-* and *para*-carbon signals (C-6 C-8, and C-4a) are moved upfield by 10.8, 17.7, and 6.1 p.p.m. respectively, and the *meta*-carbon signals (C-5 and C-8a) are only slightly affected (+1.3 and +1.7 p.p.m.).[2] Once again the two *ortho*-carbon atoms are affected by different amounts by the introduction of the 7-methoxy-group.

Coumarins and Isocoumarins.—The assignments in the coumarin series were greatly aided by comparison with the data published by Sojka,[4] and Cussans and Huckerby,[5] for coumarin itself and its simple derivatives. The assignments in both series were also confirmed by specific decoupling experiments. The carbonyl carbon signals come in the same region of the spectrum for both series of compounds, 160.1—160.9 p.p.m. in the coumarins (Table 9) and 160.2—162.6 p.p.m. in the isocoumarins (Table 10). However the chemical shifts of C-3 and C-4 may be used to differentiate between the two series, and also to establish the point of attachment of ring B.



(52) coumarin



isocoumarin

Coumarins

(53) 7-HO
(54) 7 MeO
(55) 7-MeO-3-Ph
(56) 7-MeO-4-Ph
(57) 7-HO-4-Ph
(58) 7-AcO-4-Ph

Isocoumarins

(59) 3-Ph
(60) 3-[2,4-$(MeO)_2C_6H_3$]
(61) 5,7-$(MeO)_2$-4-Ph
(62) 5,7-$(AcO)_2$-4-Ph

SCHEME 3 Compounds in Tables 9 and 10 (coumarins and isocoumarins)

TABLE 10

^{13}C N.m.r. spectra of isocoumarins

Isocoumarin	C-1′	C-2′	C-3′	C-4′	C-5′	C-6′	C-1	C-3	C-4	C-5	C-6	C-7	C-8	C-8a	C-4a	OMe	OAc
(59)	131.81	125.08	128.66	129.78	128.66	125.08	162.00	153.43	101.66	127.94	134.65	129.44	125.83	120.40	137.34		
(60)	113.73	161.98	105.36	158.64	105.07	129.62	162.58	150.60	98.96	127.52	134.67	129.13	126.18	120.18	138.43	55.63 55.45	
(61)	136.67	127.09	129.13	126.86	129.13	127.09	161.89	140.33 †	118.72	156.64	106.31 †	160.30	102.42 †	123.32	120.25	55.70 55.42	
(62)	134.75	128.13	129.81	127.79	129.81	128.13	160.24	143.28	116.97	146.19	120.58	150.02	123.98	123.42	126.66		168.56 168.28 20.91 19.32

† Confirmed by double irradiation.

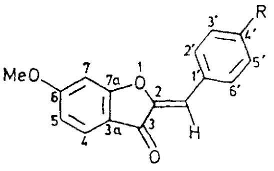
Aurones and Isoaurones.—A limited number of compounds containing a five-membered heterocycle have also been examined (Table 11) and have provided valuable information for identification of an uncharacterized isoaurone.[10] Once again the chemical shifts of the three-carbon unit are particularly useful for determining the type of compound under consideration. The characteristic chemical shifts of the central three carbon atoms in different types of flavonoids and related compounds are listed in Table 12. The carbonyl carbon signal comes at 174—179 p.p.m. in flavones and isoflavones, 189—197 p.p.m. in chalcones and flavanones, and 160—163 p.p.m. in coumarins and isocoumarins. Amongst the five-membered heterocycles the carbonyl carbon

TABLE 11

^{13}C N.m.r. spectra of aurones and isoaurones

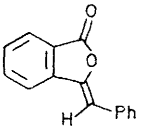
Aurone	C-1′	C-2′	C-3′	C-4′	C-5′	C-6′	=CH–	C-2	C-3	C-4	C-5	C-6	C-7	C-7a	C-3a	OMe
(63)	132.29	128.66	131.13	129.40	131.13	128.66	111.63	147.65	182.67	125.59	112.00	167.22	96.54	168.33	114.69	55.91
(64) *	123.41	133.23	116.14	159.30	116.14	133.23	111.93	146.06	182.49	125.25	112.78	166.97	96.46	167.82	114.88	55.92
Benzylidene-phthalide	C-1′	C-2′	C-3′	C-4′	C-5′	C-6′	=CH–	C-1	C-3	C-4	C-5	C-6	C-7	C-7a	C-3a	
(65)	133.16	128.80	130.17	129.81	130.17	128.80	107.07	167.07	144.62	128.44	134.53	119.86	125.52	123.42	140.62	
Isoaurone	C-1′	C-2′	C-3′	C-4′	C-5′	C-6′	=CH–	C-2	C-3	C-4	C-5	C-6	C-7	C-7a	C-3a	OMe
(66)	133.83	128.65	129.16	130.75	129.16	128.65	140.67	168.62	122.12	123.47	122.61	130.33	111.02	154.29	128.36	
(67)	134.81	129.12	129.59	130.42	129.59	129.12	137.80	169.80	122.30	124.05	110.12	162.63	97.57	156.45	114.83	55.87

* Taken in $CDCl_3$–$(CD_3)_2SO$(4 : 1).



(63) R = H

(64) R = OH



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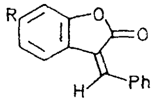


(66) R = H

(67) R = OMe

TABLE 12

Chemical shifts of the central three-carbon unit (in order of increasing value) *

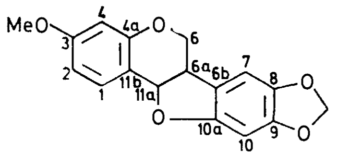
Chalcones	116.6—128.1 (d) † (C-3)	136.9—145.4 (d) † (C-2)	188.6—194.6 (s) (C=O)
Flavanones	42.8—44.6 (t) (C-3)	75.0—80.3 (d) (C-2)	189.5—195.5 (s) (C=O)
Flavones	104.7—111.8 (d) (C-3)	160.5—163.2 (s) (C-2)	176.3—178.3 (s) (C=O)
Isoflavones	122.3—125.9 (s) (C-3)	149.8—155.4 (d) (C-2)	174.5—178.6 (s) (C=O)
3-Ph-coumarins ‡	124.7 (s) (C-3)	139.8 (d) (C-4)	160.5 (s) (C=O)
4-Ph-coumarins	110.2—111.7 (d) (C-3)	155.0—155.8 (s) (C-4)	160.1—160.9 (s) (C=O)
3-Ph-isocoumarins	99.0—101.7 (d) (C-4)	150.6—153.4 (s) (C-3)	162.0—162.6 (s) (C=O)
4-Ph-isocoumarins	117.0—118.7 (s) (C-4)	140.3—143.3 (d) (C-3)	160.2—161.9 (s) (C=O)
Aurones	111.6—111.9 (d) (=CH–)	146.1—147.7 (s) (C-2)	182.5—182.7 (s) (C=O)
Benzylidene-phthalide ‡	107.1 (d) (=CH–)	144.6 (s) (C-3)	161.1 (s) (C=O)
Isoaurones	122.1—122.3 (s) (C-3)	137.8—140.7 (d) (=CH–)	168.6—169.8 (s) (C=O)
Pterocarpans	39.5—40.2 (d) (C-6a)	66.4—66.5 (t) (C-6)	78.4—78.5 (d) (C-11a)

* Multiplicity in off-resonance spectrum also indicated. † Usually observed as double multiplet. ‡ Only one compound examined.

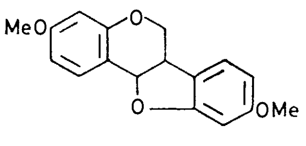
TABLE 13

^{13}C N.m.r. spectra of pterocarpans

	C-11b	C-1	C-2	C-3	C-4	C-4a	C-6	C-6a	C-11a	C-6b	C-7	C-8	C-9	C-10	C-10a	OCH_2O	OMe
(68)	112.26	131.58	108.98	160.85	101.54	156.41	66.42	40.21	78.40	117.79	104.55	141.53	147.93	93.67	154.11	101.14	55.26
(69)	112.25	131.66	108.98	160.83	101.52	156.45	66.51	39.54	78.48	118.98	124.54	106.23	160.93	96.77	160.54		55.39 55.25



68) pterocarpin



(69) homopterocarpin

signals come at 183 p.p.m. in aurones, 161 p.p.m. in benzylidenephthalide, and 169 p.p.m. in isoaurones. The aliphatic carbon signals of flavanones are easily identified and the characteristic chemical shifts of C-2 and C-3 or C-3 and C-4 in other flavonoid compounds can be used to distinguish between flavones and isoflavones, for example, or between 3- and 4-phenyl-coumarins and -isocoumarins.

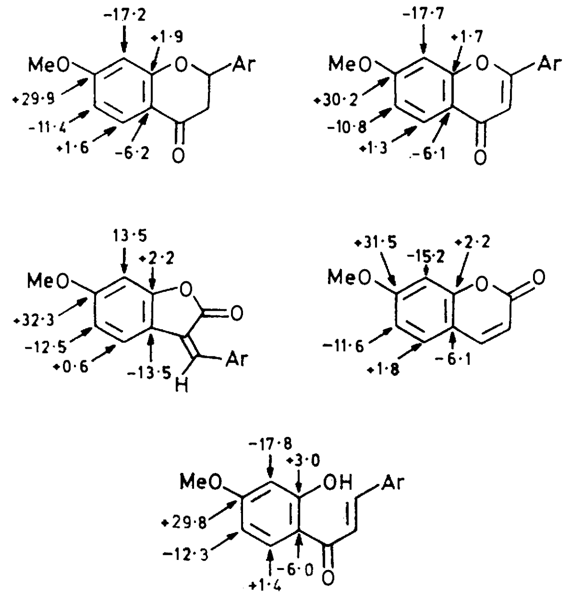


FIGURE 1 Shifts induced by introduction of methoxy group in ring A

Introducing a methoxy-substituent into ring A of isoaurone has a different effect from that in the flavanone, flavone, or indeed coumarin[5] series. The four cases are compared, along with the typical values for a 2′-hydroxychalcone, in Figure 1, which shows that introducing a methoxy-substituent at C-6 in isoaurone has a remarkable effect on the chemical shift of C-3a. The C-6 signal is moved downfield by 32.3 p.p.m., and those of C-5 and C-7 are moved upfield by 12.5 and 13.5 p.p.m., but that of C-3a (*para* to the methoxy-group) is moved upfield by 13.5 p.p.m., a much greater shift than observed in the other compounds.

Pterocarpans.—The aromatic carbon signals in the spectra of pterocarpin and homopterocarpin were easily assigned owing to the fact that ring A is the same in each (Table 13). The spectra contain three readily identifiable signals due to aliphatic carbon atoms and no signals attributable to a carbonyl group. The only low field signals are those due to the aromatic carbon atoms directly attached to ether oxygen atoms.

DISCUSSION

The resonances due to the aromatic carbon atoms of flavonoids cannot be used to differentiate between the various types of compound, but can be used to establish the pattern of substitution present. Thus Tables 2 and 7 demonstrate that the chemical shifts of the ring A carbon atoms are remarkably constant and determined by the effect of the 7-methoxy- or -hydroxy-substituent.

In a similar way the resonance of the ring B carbon atoms can be used to determine the pattern of substitution present. Indeed the effect of introducing a substituent into ring B follows more closely the substituent effects reported for simple benzene derivatives, except where *ortho*-substitution is involved (Figure 2).

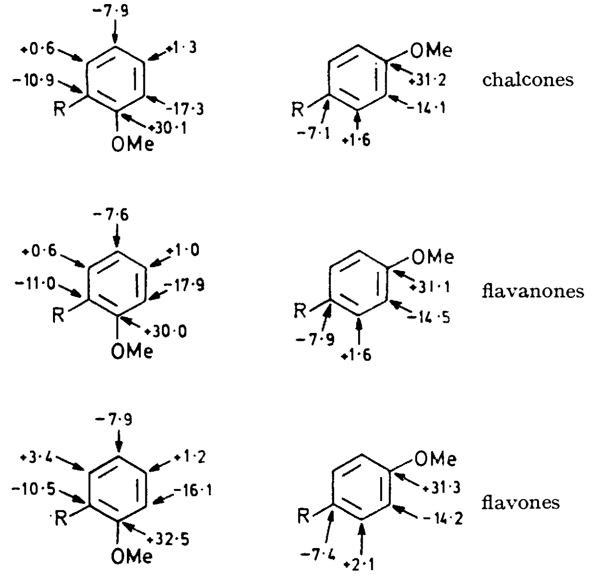


FIGURE 2 Shifts induced by introduction of a methoxy group in ring B

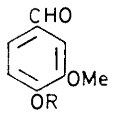
Hydroxy- and methoxy-groups exert a similar effect on the resonances of the aromatic carbon atoms. How-

TABLE 14

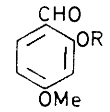
^{13}C N.m.r. spectra of vanillin and related compounds

	C-1	C-2	C-3	C-4	C-5	C-6	OMe	OAc	CHO	$COCH_3$
(70)	129.5	109.4	147.5	152.3	114.8 *	127.4	56.0		191.3	
Calc.	129.8	116.2	147.5	146.1	117.3	122.8				
(71)	135.16	110.87	151.85	144.85	123.29	124.42	55.98	168.05, 20.52	190.73	
Calc.	135.4	115.7	153.7	142.2	123.5	122.3				
(72)	130.13	114.04	146.55	152.67	110.48 *	124.39	55.93		190.93	
Calc.	130.6	117.3	141.3	152.3	116.2	122.0				
(73)	129.97	123.16	140.14	156.17	111.95	129.83	56.15	168.38, 20.46	189.73	
Calc.	130.1	123.5	137.4	158.5	115.7	127.6				
(74)	120.72	151.48	148.14	117.97	119.49	124.42	56.21		200.2	
Calc.	125.1	141.3	147.5	121.0	122.0	122.8				
(75)	128.34	140.66	150.97	116.97	125.86	120.33	55.21	167.83, 19.18	187.83	
Calc.	131.3	137.4	153.7	120.5	127.6	122.3				
(76)	115.57	164.99	101.03	167.34	108.68	135.66	55.89		194.92	
Calc.	116.2	156.8	101.8	166.7	106.5	131.7				
(77)	121.54	153.05	108.80	164.99	112.07	133.08	55.78	168.85, 20.75	187.23	
Calc.	122.4	152.9	108.0	166.2	112.1	131.1				
(78)	120.02	152.58	118.41	124.96	155.75	115.11	55.69		195.97	
Calc.	125.1	147.9	117.3	121.0	152.2	116.2				
(79)	128.34	145.44	124.37	121.66	157.36	112.98	55.63	169.35, 20.58	188.08	
Calc.	131.3	144.0	123.5	120.5	157.8	115.7				
(80)	113.80	165.06	100.77	165.92	107.41	132.13	55.46			202.26, 26.10
Calc.	115.1	155.3	100.3	163.6	105.0	130.2				
(81)	122.86	151.23	109.25	163.57	111.46	132.36	55.64	169.18, 21.17		195.37, 28.94
Calc.	121.3	151.4	106.5	163.1	110.6	129.7				

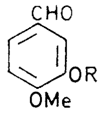
* Confirmed by double irradiation.



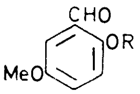
(70) R = H
(71) R = Ac



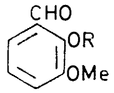
(76) R = H
(77) R = Ac



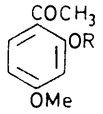
(72) R = H
(73) R = Ac



(78) R = H
(79) R = Ac



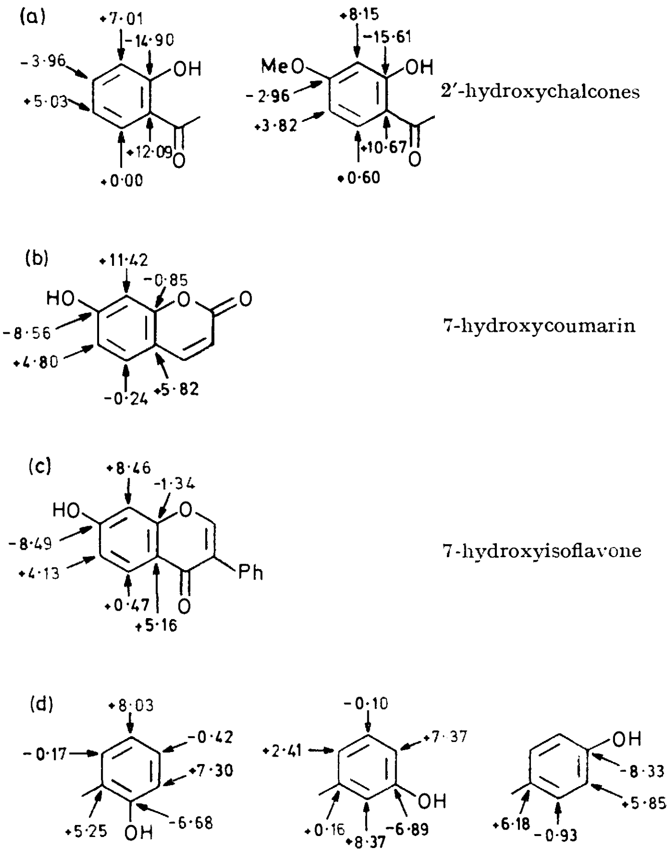
(74) R = H
(75) R = Ac



(80) R = H
(81) R = Ac

ever acetylation of a phenolic hydroxy-group causes a significant shift in the resonances of the aromatic carbon atoms and can be used to determine the arrangement of hydroxy- and methoxy-groups present. Thus the signal due to the carbon atom directly attached to the OH group is moved upfield by 6.6—15.6 p.p.m. upon acetylation, whereas those of the *ortho*- and *para*-carbon atoms are moved downfield by 4.1—12.1 and 2.0—7.9 p.p.m., respectively (see Figure 3). The *meta*-carbon signals are only slightly shifted upon acetylation (+0.9 to —4.3 p.p.m.). The shifts are particularly large for 2′-hydroxychalcones and much narrower limits can be specified for the shifts induced by acetylation of other flavonoid hydroxy-groups. Thus in 2′-hydroxychalcones the signal of the carbon atom to which the hydroxy-group is attached is shifted upfield by 12.9—15.6 p.p.m. upon acetylation, whereas in other flavonoids it is only shifted by 6.6—10.2 p.p.m. The effect of acetylation of 2′-hydroxychalcones on the chemical shift of the carbonyl and α-carbon atoms has already been mentioned.

Vanillin and Related Compounds.—The effect of acetylation has also been studied for a series of simpler benzene derivatives. The observed and calculated chemical shifts (based on reported substituent effects) for a series of vanillin isomers are listed in Table 14. Although in some cases good agreement is observed between the calculated and observed values, in other cases this is not so. It is also interesting that in the compounds which have a carbonyl group *ortho* to the hydroxy-group [compounds (74), (76), (78), and (80)] an appreciable upfield shift of the carbonyl carbon signal is observed on acetylation, almost certainly due to hydrogen bonding in the unacetylated compounds.



2′-hydroxychalcones

7-hydroxycoumarin

7-hydroxyisoflavone

ring B of flavanones

FIGURE 3 Examples of shifts induced by acetylation of phenolic hydroxy groups

In conclusion, the following points emerge. (i) The carbon resonances of the central three-carbon unit can be used to identify the particular type of flavonoid under investigation. (ii) The shifts brought about by introducing a methoxy-group into ring A correlate poorly with values calculated on the basis of reported substituent effects of the methoxy-group. For ring-B-substituted derivatives agreement is much better, except when *ortho*-substituents are involved. (iii) Acetylation of phenolic hydroxy-groups can be used to identify the position of the hydroxy-group on the aromatic ring and can be particularly useful when both hydroxy- and methoxy-groups are present. For complex molecules, the models must be chosen with care, as shown by the frequent lack of agreement between calculated and observed values for vanillin derivatives and related compounds.

EXPERIMENTAL

The ^{13}C spectra were determined with a Varian XL-100 instrument and 620L-100 computer. Chemical shifts are recorded as p.p.m. downfield from Me_4Si, which was used as internal standard. The samples were dissolved in $CDCl_3$, or $CDCl_3$–$(CD_3)_2SO$, according to solubility. The known compounds were all prepared by standard methods. The preparation of compounds reported here for the first time will be published elsewhere.[10]

We thank Dr. M. Balasubramanian and Mr. D. H. J. Ashdown for preparing some of the compounds used.

[6/597 *Received*, 29*th March*, 1976]

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[10] R. S. Ward, T. I. Gray, and A. Pelter, unpublished work.