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The ^{13}C nmr chemical shifts of methoxy and acetoxyaurones are reported. The signals are assigned on the basis of substituent effects and comparison with structurally related compounds. Assignments are also verified by Sford.

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Flavonoid compounds are one of the largest groups of naturally occurring heterocyclic compounds. These include flavones, isoflavones, coumarins, chalcones, rotenoids, pterocarpans and aurones. Except for the naturally occurring aurones a considerable amount of ^{13}C -nmr data has been reported for the flavonoids (1-10). Pelter, *et al.*, have studied 6-methoxy, 6-methoxy-4'-hydroxy and some methyl derivatives of aurones. They assigned chemical shift values to different carbon atoms and differentiated between the *E* and *Z* types of aurones (11).

We now wish to report ^{13}C -nmr spectral data for aurones having the oxygenation pattern of either resorcinol or phloroglucinol in the A-ring and either 4'- or 3',4'-oxygenation in the B-ring, with the view of studying the applicability of the additive rules to this class of compounds. The data obtained from aurones 1-5 is presented in Table I. Two compounds (6 and 7) from Pelter's

work have also been included for comparison purposes. The range of absorption observed for the carbonyl carbon atom is from 178.9 to 185.9 ppm and not from 181.8 to 185.9 ppm as reported by Pelter, *et al.* (11). This discrepancy is attributed to shielding of the carbonyl carbon atom by the methoxy group at the C-4 carbon. Another observation which becomes apparent from study of these compounds is that if the A-ring is of the resorcinol type, the carbonyl carbon atom absorbs in the region 181.7-183.2 ppm, which is slightly downfield when compared with the absorption for the A-ring of the phloroglucinol type (178.9-180.5 ppm). In agreement with the reported values, chemical shifts of C-2 and =C-H lie within closely defined limits (10).

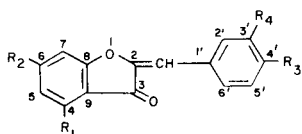
In 4,6-dimethoxyaurone (1) the chemical shifts of C-4, C-5, C-6, C-7 and C-8 follow the additive rules (12). The C-9 carbon atom however, is shifted somewhat less than expected. This agrees with observations made in the case of

Table I

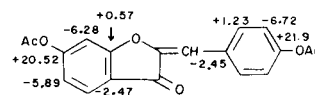
 ^{13}C Chemical Shifts of Aurones (a)

Compound	1	2	3	4	5	6	7
=C-H	109.2	110.9	110.9 (b)	112.1	111.2	112.88	111.63
C-2	147.5	146.7	146.7	147.1	147.4	146.8	147.65
C-3	178.9	180.5	180.3	183.2	183.0	184.57	182.67
C-4	159.0	160.5	159.1	125.5	125.5	124.55	125.59
C-5	94.3	93.8	93.8	117.5	117.7	123.39	112.0
C-6	168.9	168.7	168.7	157.3	157.5	136.78	167.22
C-7	89.1	89.1	89.1	106.6	106.7	112.88	96.54
C-8	168.2	168.7	168.5	166.6	166.6	166.03	168.33
C-9	104.1	105.3	105.2	119.1	118.9	121.57	114.69
C-1'	132.3	125.3	125.4	129.8	130.7	132.25	132.29
C-2'	128.7	132.8	111.0 (b),(c)	132.7	126.0	131.47	131.13
C-3'	130.8	114.3	148.8 (d)	122.1	142.4 (b)	128.82	128.66
C-4'	129.2	159.2	150.2 (d)	151.7	143.3 (b)	129.81	129.4
C-5'	130.8	114.3	113.4 (c)	122.1	123.8	128.82	128.66
C-6'	128.7	132.8	125.2	132.7	129.8	131.47	131.13
OCH ₃ /OAc	56.3	55.2	55.8	168.9	168.2	—	55.91
	56.1	56.0	56.0	168.2	168.0		
				21.1	167.8		
					21.1		
					20.6		

(a) All the above assignments have been verified by taking off-resonance spectra. (b) May be interchanged. (c) May be interchanged. (d) May be interchanged.



- 1, $R_1 = R_2 = -OCH_3$; $R_3 = R_4 = H$
 2, $R_1 = R_2 = R_3 = -OCH_3$; $R_4 = H$
 3, $R_1 = R_2 = R_3 = R_4 = -OCH_3$
 4, $R_1 = R_4 = H$; $R_2 = R_3 = -OAc$
 5, $R_1 = H$; $R_2 = R_3 = R_4 = -OAc$
 6, $R_1 = R_2 = R_3 = R_4 = H$
 7, $R_2 = -OCH_3$; $R_1 = R_3 = R_4 = H$



Shifts Introduced by Introduction of the Acetoxy Group in Ring A and B in Aurone

other 6-membered flavonoids where C-10 (*i.e.*, between the carbonyl carbon atom and the C-5 carbon atom) has also been observed to be comparatively shifted to a less extent (effect of the carbonyl group) (10). Introduction of a methoxy group at the C-4' position in the B-ring as in compound **2** shifted the C-1', C-3', C-4' and C-5' carbon atoms as expected based on the additive rules (12). However, the *meta*-carbon atoms are unexpectedly shifted by +4.1 ppm.

Compound **3** contains two methoxy groups which are *ortho* to each other in the B-ring. In such cases, since the additive rules are not applicable, assignments for the B-ring were made as follows. The C-3' and C-4' carbon atoms, being oxygenated, were assigned shift values of 150.2 and 148.8 ppm. Since the C-1' carbon atom is not protonated, it is easily identified as a singlet in the Sford at 125.4 ppm. On the basis of the calculated value (115 ppm) (9), C-5' was assigned a value of 113.4 ppm. The remaining two signals at 111.0 and 125.2 ppm were assigned to C-2' and C-6'. Since these carbon atoms are identical in compound **2**, the introduction of the 3'-methoxy group would be expected to shift the *ortho* related C-2' further upfield than the *para* related C-6'. Therefore, C-2' was assigned to the 111.0 ppm signal, and C-6' was assigned to the 125.2 ppm signal.

Acetoxylation of aurones **4** and **5** results in a shift of the various carbon atoms in accordance with the additive rules (12). However, assignment of the B-ring carbon atoms in compound **5** were made based on its similarity to compound **3**.

It was thus observed that the additive rules are also valid in aurones and can serve as a useful tool for assigning chemical shifts to different carbon atoms of naturally occurring aurones.

EXPERIMENTAL

The ^{13}C nmr spectra were recorded on a JEOL PS-100-PFT-100 instrument. Chemical shifts are recorded as ppm downfield from tetramethylsilane, which was used as an internal standard. Deuteriochloroform was used as a solvent with the exception of compound **1** which was recorded in DMSO-*d*₆. The compounds were prepared as described.

4,6-Dimethoxycoumaran-3-one (13).

To a solution of ω -chlorophloroacetophenone dimethyl ether (4.0 g.) in alcohol, was added a saturated solution of potassium acetate (4.5 g.) in water, and the solution was refluxed for eight hours. The hot solution was filtered and the solid (2.5 g.) crystallised on cooling, m.p. 137-138° (lit. m.p. 135-136°).

General Procedure for the Preparation of Methoxyaurones (1-3) (14).

The above coumaran-3-one (300 mg.) was dissolved in a solution of ethanol (8 ml.) and 4.5% sodium hydroxide (2 ml.). To this mixture was added an alcoholic solution (6 ml.) of the corresponding aldehyde (2 equivalents) containing 4.5% sodium hydroxide (6 ml.). The reaction mixture was allowed to stand overnight and then the solution was diluted with water. The precipitate thus obtained was filtered, washed with water, ether and crystallised from ethanol.

6-Hydroxycoumaran-3-one (15).

ω -Chloroacetophenone was refluxed with aqueous potassium acetate (5 g. in 50 ml.) for 15 minutes. On cooling, 6-hydroxy coumaran-3-one (5 g.) separated, m.p. 241-243° (lit. m.p. 241-242°).

General Method for the Preparation of Acetoxyaurones (4,5) (16).

A mixture of 6-hydroxycoumaran-3-one (500 mg.) and the corresponding hydroxybenzaldehyde (2 equivalents) in acetic anhydride (4.5 ml.) was refluxed in an oil bath at 140-150° for 4 hours. The reaction mixture was then poured over crushed ice and kept overnight. The pale yellow solid that separated was filtered and crystallised from ethanol.

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Table II

Aurone	R ₁	R ₂	R ₃	R ₄	M.p.°C	% Yield	Molecular Weight Calcd.	Molecular Weight Found	Molecular Formula Calculated from Computerised Mass Spectrometer	Analyses			
										Calcd. C	Calcd. H	Found C	Found H
1	OCH ₃	OCH ₃	H	H	152-154	58	282.0892	282.0916	C ₁₇ H ₁₄ O ₄	72.34	5.0	72.2	5.1
2	OCH ₃	OCH ₃	OCH ₃	H	192-194	62	312.0998	312.0974	C ₁₈ H ₁₆ O ₅	69.4	5.17	69.5	5.1
3	OCH ₃	OCH ₃	OCH ₃	OCH ₃	169-170	57	342.1103	342.1112	C ₁₉ H ₁₈ O ₆	66.69	5.3	66.4	5.2
4	H	OAc	OAc	H	160-162	44	338.0790	338.0791	C ₁₉ H ₁₄ O ₆	67.8	4.18	67.6	4.4
5	H	OAc	OAc	OAc	164-165	45	396.0845	396.0857	C ₂₁ H ₁₆ O ₆	63.63	4.07	63.8	4.2

REFERENCES AND NOTES

- (1) P. J. Nathan, J. Mares, M. C. Hernandez and J. N. Shoolery, *J. Magn. Reson.*, **16**, 447 (1974).
- (2) S. A. Sojka, *J. Org. Chem.*, **40**, 1175 (1975).
- (3) N. J. Cussans and T. N. Huckerby, *Tetrahedron*, **31**, 2587, 2591, 2719 (1975).
- (4) N. J. Cussans and T. N. Huckerby, *Tetrahedron Letters*, 2445 (1975).
- (5) K. R. Markham and B. Ternai, *Tetrahedron*, **32**, 2607 (1976).
- (6) B. Ternai and K. R. Markham, *ibid.*, **32**, 565 (1976).
- (7) H. Wagner, V. M. Chari and J. Sonnenbichler, *Tetrahedron Letters*, 1799 (1976).
- (8) E. Wenkert and H. E. Gottlieb, *Phytochemistry*, **16**, 1811 (1977).
- (9) C. A. Kingsbury and J. H. Looker, *J. Org. Chem.*, **40**, 1120 (1975).
- (10) A. Pelter, R. S. Ward and T. K. Gray, *J. Chem. Soc., Perkin Trans. I*, 2475 (1976).
- (11) A. Pelter, R. S. Ward and H. G. Heller, *ibid.*, 328 (1979).
- (12a) G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists", Wiley-Interscience, New York, N. Y., 1972; (b) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Vol. 24 of Organic Chemistry, A series of Monographs, Academic Press, New York, N. Y., 1972.
- (13) P. Friedlaender and L. C. Schnell, *Ber.*, **30**, 2153 (1897).
- (14) V. D. Vittorio, *Rend. Ist. Super. Sanita*, **21**, 418 (1958).
- (15) E. C. Horning and D. B. Reimer, *J. Am. Chem. Soc.*, **70**, 3619 (1948).
- (16) H. Wagner and L. Farkas in "The Flavonoids", J. B. Harborne, T. J. Mabry and H. Mabry, Eds., Chapman and Hall, 1975, p. 183.