Chelate Systems. Part III. Infrared Spectra of Flavanones and Flavones.*

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The carbonyl stretching frequencies of a number of flavanones and flavones are recorded. The frequency shifts caused by methoxyl groups and by the hydrogen-bonded systems involving the 3- and the 5-hydroxyl group are discussed.

In Parts I and II * the use of partition chromatography in the study of hydrogen bonding was discussed and chelation of flavones recognised by deviations from characteristic R_M values. Hydrogen bonding has been more generally investigated by infrared spectroscopy (Baker, *Ann. Reports*, 1936, **32**, 285; Gordy, *J. Chem. Phys.*, 1940, **8**, 516; Flett, *J.*, 1948, 1441; Rasmussen, Tunnicliff, and Brattain, *J. Amer. Chem. Soc.*, 1949, **71**, 1068). Hergert and Kurth (*ibid.*, 1953, **75**, 1622) have measured the infrared light-absorption spectra of Nujol and perfluorohexane mulls of several polyhydroxy- and polyacetoxy-flavones and -flavanones, but since it is known that interactions in the solid phase can give rise to significant changes in absorption spectra, the study of simpler compounds of this class in dilute solution seemed desirable.

The infrared absorption spectra of carbon tetrachloride solutions of a number of flavanones and flavones have been measured and the carbonyl stretching frequencies are recorded in Table 1.

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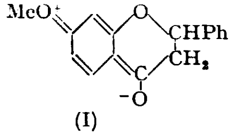
* Parts I and II, *J.*, 1952, 4268, 5027.

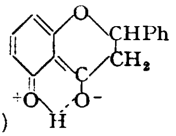
TABLE 1.

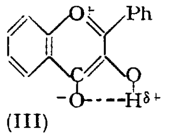
Compound	CO frequency, cm.$^{-1}$	Compound	CO frequency, cm.$^{-1}$
Flavanones		Flavones (*contd.*)	
(Unsubstd.)	1695	3-Hydroxy-	1619
7-Methoxy-	1685	5-Hydroxy-	1652
7 : 4′-Dimethoxy-	1686	3 : 5-Dihydroxy-	1638
5-Hydroxy-	1648	3-Hydroxy-7-methoxy-	1621
		3-Hydroxy-3′-methoxy-	1619
Flavones		3-Hydroxy-3′ : 4′-dimethoxy-	1616
(Unsubstd.)	1649	3-Hydroxy-7 : 3′-dimethoxy-	1616
7-Methoxy-	1640	*3-Hydroxy-7 : 4′-dimethoxy-	1611
3′-Methoxy-	1655	5-Hydroxy-7-methoxy-	1659
4′-Methoxy-	1653	5-Hydroxy-3′-methoxy-	1645
7 : 3′-Dimethoxy-	1638	5-Hydroxy-4′-methoxy-	1649
7 : 4′-Dimethoxy-	1646	5-Hydroxy-7 : 3′-dimethoxy-	1647
3′ : 4′-Dimethoxy-	1647	*7 : 3′ : 4′-Trimethoxy-	1638

* These compounds were not sufficiently soluble to give carbonyl absorption of greater than 20%. The reported frequencies may therefore be inaccurate.

Flavanones. From Table 1 it is seen that introduction of a methoxyl group in the 7-position of the flavanone nucleus causes a frequency shift of —10 cm.$^{-1}$, presumably due to the contribution of (I) to the resonance structure. The introduction of a 4′-methoxyl group, as expected, causes no further change. A hydroxyl group in the 5-position causes a larger frequency decrease (40 cm.$^{-1}$) resulting from the contribution of the chelated structure (II).


(I)


(II)


(III)

Flavones. Table 2 lists the differences between the carbonyl stretching frequencies of substituted flavones and the corresponding flavanones. The unchelated compounds show the expected frequency decrease resulting from the increased conjugation of the carbonyl group. The small difference between the carbonyl frequencies of 5-hydroxyflavone and 5-hydroxyflavanone is due to the unusual properties of the former chelated system (see below). All the 3-hydroxyflavones examined showed only feeble absorption bands at about 3360 cm.$^{-1}$, suggesting partial suppression of hydroxylic character by internal hydrogen bonding. The shifts in carbonyl stretching frequency caused by the introduction of a hydroxyl group at the 3-position of the flavone nucleus are listed in Table 3.

TABLE 2.

Flavone substituent	None	7-MeO	7 : 4′-Di-OMe	5-OH
Frequency diff. (cm.$^{-1}$), flavone — flavanone	—36	—35	—40	+4

TABLE 3.

Flavone substituents	Frequency shift (cm.$^{-1}$) on addition of 3-OH group	Flavone substituents	Frequency shift (cm.$^{-1}$) on addition of 3-OH group
None	—30	7 : 4′-Di-OMe-	—35
3′-OMe-	—36	7-OMe	—19
3′ : 4′-Di-OMe-	—31	7 : 3′-Di-OMe	—22

These again indicate chelation between the carbonyl and the 3-hydroxyl groups and are interpreted as in Part I (*loc. cit.*) by the stabilisation of ionic structure (III) (and similar forms) by hydrogen bonding (Rasmussen *et al.*, *loc. cit.*).

Chemical evidence, chromatographic data (Part I, *loc. cit.*), and the small depressions of melting point on admixture with water (Gallagher, Hughes, O'Donnell, Philbin, and Wheeler, *J.*, 1953, 3770) clearly establish 5-hydroxyflavones as chelated compounds. Moreover, these compounds show no absorption in the region 3200—3700 cm.$^{-1}$. It is found, however (Table 4), that introduction of a 5-hydroxyl group into flavone *increases* or at most only slightly decreases the carbonyl stretching frequency (cf. Hergert and Kurth (*loc. cit.*). In this respect, 5-hydroxyflavones differ from other *peri*-hydroxy-carbonyl compounds; indeed, Flett (*J.*, 1948, 1441) suggests that the hydrogen bond strengths in 1-hydroxyanthraquinones can be calculated from the carbonyl frequency *decrease*. No adequate interpretation of these effects can be offered.

TABLE 4.

Flavone substituent	Frequency shift (cm.$^{-1}$) on addition of 5-OH group	Flavone substituent	Frequency shift (cm.$^{-1}$) on addition of 5-OH group
None	+3	4′-OMe	−4
7-OMe	+19	7 : 3′-Di-OMe	+9
3′-OMe	−10		

Introduction of a 5-hydroxyl group into 3-hydroxyflavone causes the absorption due to O–H stretching to be intensified and shifted to 3395 cm.$^{-1}$, indicating a decrease in overall hydrogen bonding. These observations are in agreement with the conclusion from chromatographic evidence (Part I, *loc. cit.*) that the two chelate systems are opposed. Table 5 shows the changes in carbonyl stretching frequencies caused by introduction of a 7-methoxyl group into unchelated flavones. As with flavanones, these decreases are ascribed to conjugation of methoxyl and carbonyl groups. Addition of the less conjugated 4′-methoxyl or the unconjugated 3′-methoxyl groups causes the expected small changes in carbonyl frequency, but these are of the same order as the expected errors in measurement.

TABLE 5.

Flavone substituent	Frequency shift (cm.$^{-1}$) on addition of 7-OMe group	Flavone substituent	Frequency shift (cm.$^{-1}$) on addition of 7-OMe group
None	−7	4′-OMe	−17
3′-OMe	−9	3′ : 4′-Di-OMe	−11

Many of the compounds required for this investigation were already available to us, two were generously given by Professor T. R. Seshadri, and the remainder were synthesised by established methods.

EXPERIMENTAL

(a) *Infrared Light-absorption Spectra.*—Spectra were measured on the double-beam recording spectrometer with a rock-salt prism, described by Hales (*J. Sci. Instr.*, 1953, **30**, 52).

(b) *Preparation of Flavanones and Flavones.*—M. p.s were determined on a Kofler block and are corrected.

Methoxyflavones. These were prepared by oxidation of the appropriate chalkones with excess of selenium dioxide in boiling amyl alcohol. The products were isolated by steam-distillation of the solutions and repeated recrystallisation (from light petroleum, or benzene–light petroleum) of the residual solids.

5-*Hydroxy*-7 : 3′-*dimethoxy- and -3′-methoxy-flavones.* Methyl sulphate (2·8 ml.) was added to a solution of 5 : 3′-dihydroxy-7-methoxyflavone (Part II, *loc. cit.*, 110 mg.) in ethanol (20 ml.) and aqueous N-sodium carbonate (30 ml.). After 30 min., excess of water was added, and the solid repeatedly recrystallised from propanol. 5-*Hydroxy*-7 : 3′-*dimethoxyflavone* formed needles (75 mg.), m. p. 132—133°, exhibiting a violet ethanolic ferric colour (Found: C, 68·7; H, 4·9. $C_{17}H_{14}O_5$ requires C, 68·5; H, 4·7%). Its *acetate* formed colourless prisms, m. p. 155—157°, from ethanol (Found: C, 67·2; H, 4·6. $C_{19}H_{16}O_6$ requires C, 67·1; H, 4·8%).

Methylated by the same procedure, 5 : 3′-dihydroxyflavone (Part II, *loc. cit.*) yielded its 3′-*methyl ether* in colourless needles, m. p. 145—148°, from ethanol, giving a violet ethanolic ferric colour (Found: C, 71·7; H, 4·7. $C_{16}H_{12}O_4$ requires C, 71·6; H, 4·5%). Its *acetate* formed colourless needles, m. p. 120—122°, from ethanol (Found: C, 69·8; H, 4·8. $C_{18}H_{14}O_5$ requires C, 69·7; H, 4·6%).

3-*Hydroxy*-7 : 3′-*dimethoxyflavone.* 2′-Hydroxy-3 : 4′-dimethoxychalkone (1 g.) in hot ethanol (10 ml.) and aqueous sodium hydroxide (8 g., in 10 ml. of water) was oxidised with 30% hydrogen peroxide (10 ml.). Isolated by the standard method, 3-hydroxy-7 : 3′-dimethoxyflavone (von Kostanecki and Widmer, *Ber.*, 1904, **37**, 4159) was obtained in cream-coloured needles, m. p. 171—172°, from ethanol (Found : C, 68·8; H, 4·8. Calc. for $C_{17}H_{14}O_5$: C, 68·5; H, 4·8%).

We are indebted to Professor T. R. Seshadri for generous gifts of 5-hydroxyflavanone and 3 : 5-dihydroxyflavone, and to Mr. J. L. Hales for determining the infra-red light-absorption spectra. One of us (B. L. S.) thanks the Department of Scientific and Industrial Research for a Senior Research Award.

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