anol as small, yellow needles, m.p. 208° dec. (lit.,[1] m.p. 208–209° dec.).

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Physical and Chemical Properties of Hydroxyflavones. I. Infrared Absorption Spectra of Monohydroxyflavones and Their *O*-Methyl and *O*-Acetyl Derivatives[1,2]

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Infrared carbonyl frequencies in appropriate solution(s), and in solid state, are presented for 1,4-pyrone, chromone, 2-methylchromone, flavone, pyromeconic acid, chromonol, and monohydroxy-, monomethoxy-, and monoacetoxyflavones. The spectral data are interpreted as indicating no significant resonance interactions between hydroxyl, or methoxyl, and flavone carbonyl groups. Solid state (potassium bromide disk) spectral data are presented for the fundamental ring systems and for monohydroxy- and monomethoxyflavones in the 3500–2200- and 1650–650-cm.$^{-1}$ regions. Group frequencies are assigned when possible, with emphasis on O—H and C—H stretching bands, in-plane skeletal vibrations, and out-of-plane deformation bands. Bands possibly associated with the pyrone oxide vibration are discussed. Spectral data, especially O—H, C—H, and carbonyl stretching frequencies, of 5-hydroxyflavone and its deuteration product are compared.

Infrared spectral data have been invaluable in the investigation of virtually all classes of organic compounds.[4–6] In the flavonoid area, of several investigations already reported, the most extensive, perhaps, have been the studies of Hergert and Kurth,[7] and Shaw and Simpson.[8] Frequency shifts caused by methoxyl groups, and 3- and 5-hydroxyl groups are emphasized by the latter group. Hergert and Kurth present a systematic study of acetophenone derivatives, flavanone, and chalcone, and then interpretations of spectra of several rather complex chalcone, flavanone, and flavone derivatives. The latter include quercetin and three of its derivatives, rutin, and 3,3′,4′,5,8-pentahydroxyflavone and its pentaacetate. Both studies[7,8] emphasize carbonyl absorption.

There is agreement on the following points: (1) Suitable substituents at the 5- and 7- positions of flavanones cause large frequency shifts in the flavanone carbonyl stretching frequencies due to resonance or chelation. (2) The 5-hydroxyl group of flavones is involved in hydrogen bonding. There is no agreement on whether introduction of a 7-methoxyl group onto an unchelated flavone molecule decreases the carbonyl stretching frequency or has no effect.

In the present paper, we report spectral characteristics for the fundamental ring systems 4-pyrone (4*H*-pyran-4-one), chromone, flavone, their 3-hydroxyl derivatives, and for the monohydroxyflavones, their methyl ethers, and their acetates. Of the thirty compounds studied, solution carbonyl frequencies have been listed previously for six (Tables I–III). In addition, partial infrared spectral data for 4-pyrone were reported[9] several years ago. The present work is intended to be sufficiently extensive and systematic that it may serve as a basis for future infrared studies of more complex flavonoid molecules. Certain experimental difficulties must be stressed at the outset, however, notably, the sparing solubility of many flavone derivatives in standard spectral solvents. Inasmuch as carbonyl bands can be located reliably in most instances, somewhat greater emphasis has been placed on this function. However, complete solid state spectra are reported for hydroxy- and methoxy flavones, and interpreted to the extent that appears possible. Certain infrared spectral properties of 5-hydroxyflavone and its deuteration product are discussed.

I. *Carbonyl Absorption.* In Tables I–IV are listed carbonyl absorption bands for the compounds of the present work. In Table I are given bands due to the carbonyl group in 4-pyrone, chromone,

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[1] From a portion of the Ph.D. thesis of Walter W. Hanneman, the University of Nebraska, 1958.

[2] This investigation was supported in part by a research grant (E-1703) from the National Institute of Allergic and Infectious Diseases, Public Health Service, and in part by a grant from the University of Nebraska Research Council.

[3] Dow Chemical Fellow, 1956–1957; Public Health Service Research Fellow of the National Institute of Dental Research, 1957–1958.

[4] L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, J. Wiley and Sons, Inc., New York, 1958.

[5] F. A. Miller, *Organic Chemistry*, Vol. 3, H. Gilman, Ed., J. Wiley and Sons, Inc., New York, 1953, pp. 128–158.

[6] A. R. Katritzky, *Quart. Rev. (London)*, **13**, 353 (1959).

[7] H. L. Hergert and E. F. Kurth, *J. Am. Chem. Soc.*, **75**, 1622 (1953).

[8] B. L. Shaw and T. H. Simpson, *J. Chem. Soc.*, 655 (1955).

[9] A. Ross, *Proc. Roy. Soc. (London)*, A **113**, 208 (1926); *Chem. Zentr.*, **1927** I, 2422.

TABLE I

INFRARED CARBONYL ABSORPTION BANDS OF CERTAIN FUNDAMENTAL RING SYSTEMS AND THEIR 3-HYDROXYL DERIVATIVES

	Carbonyl Band, Cm.$^{-1}$			
Compound	Of KBr disk	Of Nujol mull	Of CCl_4 solution	Of dioxane solution
1,4-Pyrone	1659	1658	1677	
Chromone	1655	1653	1665	
2-Methylchromone	1643	1645	1663	
Flavone	1647	1646	1652[a]	1650
Pyromeconic acid	1651	1651	1643	
Chromonol	1638	1636	1635	
Flavonol	1610[b]	1609	1622[c]	1624

[a] Previously reported value,[8] 1649 cm.$^{-1}$ [b] Shoulder present at 1627 cm.$^{-1}$ [c] Previously reported value,[8] 1619 cm.$^{-1}$

TABLE II

INFRARED CARBONYL ABSORPTION BANDS OF MONOHYDROXYFLAVONES

	Carbonyl Band, Cm.$^{-1}$				
Position of OH	Of KBr disk	Of Nujol mull	Of CCl_4 solution	Of dioxane solution	Δ[a]
3	[b]	[b]	[b]	[b]	−26
5	1653	1651	1652[c]	1654	+4
6	1639	1640		1646	−4
7	1628	1626		1648	−2
8	1630	1628		1648	−2
2′	1632	1633		1648	−2
3′	1620	1618		1649	−1
4′	1633	1631		1648	−2

[a] Algebraic difference between hydroxyflavone carbonyl frequency in dioxane and flavone carbonyl frequency in dioxane (1650 cm.$^{-1}$). [b] Carbonyl bands are listed in Table I. [c] In agreement with the previously reported value.[8]

flavone, and the 3-hydroxyl derivatives of these substances. 2-Methylchromone is included for comparison with flavone. The shifts toward lower carbonyl frequencies in solution spectra of the two series, 4-pyrone, chromone, flavone, and pyromeconic acid ,(3-hydroxy-4-pyrone), chromonol (3-hydroxychromone), flavonol (3-hydroxyflavone), are largely those expected because of increased conjugation of the carbonyl group. However, the shifts are of smaller magnitude than those observed in the series acetone, acetophenone, chalcone, or benzophenone.[7] Comparison of solution carbonyl frequencies of the pyrone and its 3-hydroxyl derivative indicates that introduction of the 3-hydroxyl group into the 4-pyrone, chromone, and flavone molecules causes shifts of −34, −30, and −30 cm.$^{-1}$, respectively. These large shifts probably are indicative of some type of hydrogen bonding in the pyromeconic acid and chromonol molecules, which possibly is similar to that in flavonol, as discussed previously.[8] The carbonyl frequency of 4-pyrone is only slightly higher than that cited as typical of $\alpha,\beta,\alpha',\beta'$-unsaturated ketones.[10]

TABLE III

INFRARED CARBONYL ABSORPTION BANDS OF MONOMETHOXYFLAVONES

	Carbonyl Band, Cm.$^{-1}$				
Position of OCH_3	Of KBr disk	Of Nujol mull	Of CCl_4 solution	Of dioxane solution	Δ[a]
3	1637	1638	1648		−4
5	1645	1649	1653		+1
6	1637	1639	1650		−2
7	1650	1653	1650[b]	1650	−2
8	1637	1638	1649		−3
2′	1642	1642	1649		−3
3′	1649	1650	1653[c]		+1
4′	1642	1647	1648[d]		−4

[a] Algebraic difference between methoxyflavone carbonyl frequency in CCl_4 and flavone carbonyl frequency in CCl_4 (1652 cm.$^{-1}$). [b] Previously reported value,[8] 1640 cm.$^{-1}$ [c] Previously reported value,[8] 1655 cm.$^{-1}$ [d] Previously reported value,[8] 1653 cm.$^{-1}$

TABLE IV

INFRARED CARBONYL ABSORPTION BANDS OF MONOACETOXYFLAVONES

	Absorption Band, Cm.$^{-1}$					
	Of KBr disk		Of Nujol mull		Of CCl_4 solution	
Position of $OCOCH_3$	Ester C=O	Flavone C=O	Ester C=O	Flavone C=O	Ester C=O	Flavone C=O
3	1757	1646	1756	1647	1782	1660
5	1755	1647	1756	1648	1774	1655
6	1750	1645	1752	1644	1773	1655
7	1761	1637	1759	1638	1774	1658
8	1759	1655	1757	1654	1779	1657
2′	1761	1637	1760	1638	1776	1655
3′	1751	1640	1753	1643	1773	1656
4′	1759	1643	1757	1645	1773	1656

In Table II are collected spectral data pertaining to carbonyl absorption in the monohydroxyflavones. Only the hydrogen-bonded systems, flavonol and 5-hydroxyflavone, are sufficiently soluble in carbon tetrachloride to permit study in this solvent. However, all hydroxyflavones are soluble in the basic solvent dioxane. Carbonyl frequencies observed in this solvent are remarkably constant and quite close to the carbonyl frequency of flavone itself in the same solvent (Table I). Although dioxane may not be an ideal solvent, it is concluded that no appreciable resonance interactions between hydroxyl and carbonyl groups are apparent in monohydroxyflavone molecules in dioxane solution.

In Table III are presented carbonyl absorption bands for the monomethoxyflavones. This series is ideal for study because of solubility of its members in carbon tetrachloride, a standard spectral solvent. The methoxyflavones are of theoretical interest, for at least hypothetically, the methoxyl groups at the 2′-, 4′-, 5-, and 7- positions can show resonance interactions with the pyrone carbonyl group. The data of Table III indicate that the solution carbonyl absorption band of each monomethoxyflavone is in fact very close to that of

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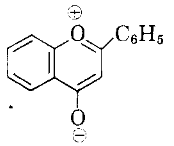
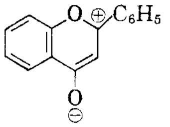
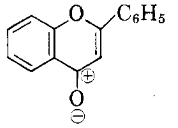
(10) Ref. 4, p. 132; ref. 5, p. 152.

flavone itself (Table I). We conclude that there is no significant resonance interaction between methoxyl and carbonyl groups in any monomethoxyflavone molecule in the ground state. Perhaps this is not surprising in 2′- and 4′-methoxyflavone, since the substituent group probably would have a direct influence only on the pi electrons of the side phenyl group. The side phenyl group thus altered might have an influence on the electron distribution of the flavone carbonyl group, but such a secondary influence could hardly be large. However, a methoxyl group at the 5- or 7- position, attached directly to the ring carrying the pyrone carbonyl group, hypothetically is in a position to exert a stronger influence. A methoxyl group at the *o*- or *p*-position of acetophenone is known to have a marked influence on the carbonyl frequency.[7] However, our data indicate that the electron distribution in the pyrone carbonyl group is influenced very little by methoxyl groups, even at the 5- and 7- positions. Possibly structures Ia, Ib, and Ic make sufficiently important resonance contributions to the structure of the flavone molecule, in absence of hydrogen bonding, that other resonance interactions are of slight importance.


Ia


Ib


Ic

The carbonyl bands of the monoacetoxyflavones are outlined in Table IV. Solution spectra show the ester carbonyl band in the range expected for phenolic esters.[11] The solution flavone carbonyl frequencies of the acetoxyflavones are the highest observed in the present series. Apparently, the acetoxyflavones possess the flavone carbonyl group in its least polarized state.

One area of additional interest is the direction and magnitude of shifts when solution and solid state carbonyl frequencies (Tables I–IV) are compared. In virtually all instances, carbonyl frequencies are lower in the solid state than in solution. Notable exceptions are pyromeconic acid, which shows a small increase, and chromonol, 5-hydroxyflavone, 7-methoxyflavone, and 4′-methoxyflavone, which show nearly identical carbonyl frequencies in solid state and solution. This relative constancy of absorption in the 5-hydroxyflavone spectra affords additional support for the intramolecular nature of the hydrogen bond involving the 5-hydroxyl and pyrone carbonyl groups. The potassium bromide disk spectrum of flavonol has a shoulder at 1627 cm.$^{-1}$, which may be associated with the carbonyl vibration. Chromonol and flavonol then would be similar in that both show small shifts. Bands in the 1624–1610-cm.$^{-1}$ region cannot be assigned unequivocally to the carbonyl group, since phenyl in-plane skeletal vibrations also can occur here (Table VI). Hence the solid state carbonyl band assignments for flavonol in Table I must be regarded as distinctly tentative.

From Table II, it is evident that rather large solid state to solution shifts in carbonyl frequency occur in the spectra of most hydroxyflavones. 6-Hydroxyflavone, in the crystal lattice of which intermolecular hydrogen bonds seem inherently likely, 5-hydroxyflavone, and possibly flavonol are exceptional. The latter two substances may contain intramolecular hydrogen bonds, so that exceptional spectral properties are not surprising. It is concluded that rather strong intermolecular hydrogen bonds probably are present in the crystal lattices of 7-, 8-, 2′-, 3′-, and 4′-hydroxyflavone, but that the intermolecular hydrogen bond in the crystal lattice of 6-hydroxyflavone is relatively weak. The positions of the solid state O—H stretching bands (Part IIa) are in general agreement with this hypothesis. Methoxyl derivatives (Table III), formed from hydroxyflavones which appear to be strongly intermolecularly hydrogen-bonded in the solid state, show relatively smaller shifts. Most of the acetates again show rather large shifts (Table IV), but in these substances the polar carbonyl portion of the acetyl group could conceivably participate in intermolecular dipolar interactions. It is apparent that while intermolecular hydrogen bonding very probably is significant when structurally possible, other types of intermolecular interactions also may be important in flavone derivatives.

II. *Solid state spectra.* Infrared spectra have been determined in the 4000–650-cm.$^{-1}$ region for the compounds of the present study, in potassium bromide disks to eliminate interference from the five bands of Nujol.[12] The strong Nujol bands near 2900 cm.$^{-1}$ interfere in locating C—H, and in some cases, O—H stretching vibrations. The problems arising from the use of potassium bromide disks, notably irreproducible spectra,[13] are recognized. However, comparison of the flavone carbonyl frequency of thirty compounds in both potassium bromide disks and Nujol mulls showed differences of greater than 3 cm.$^{-1}$ in only two cases (Tables I–IV). In no case was the difference greater than 5 cm.$^{-1}$ Complete potassium bromide and Nujol spectra of flavone were identical with respect to location of bands, although the peaks in the Nujol spectrum were somewhat sharper. All solid state spectra including those determined in potassium bromide disks, are subject to the problem that certain bands may originate from some type of crystal interaction, rather than to a vibration of the molecule itself. Absorption bands

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(11) Ref. 4, p. 179.

(12) Ref. 5, pp. 133–134, 150.

(13) A. W. Baker, *J. Phys. Chem.*, **61**, 450 (1957); ref. 4, pp. 379–380.

for 4-pyrone and pyromeconic acid in the 1650-650-cm.$^{-1}$ region are presented in Table V. Spectral characteristics for the remaining compounds in the 1650-650-cm.$^{-1}$ region (with exception of carbonyl bands) are outlined in Tables VI-IX. With the exception of the acetates (Table IV), there was no significant absorption in the 2200-1660-cm.$^{-1}$ region.

TABLE V

SOLID STATE[a] INFRARED SPECTRAL DATA FOR 4-PYRONE AND PYROMECONIC ACID

4-Pyrone		Pyromeconic Acid	
Band,[b] cm.$^{-1}$	Vibrational assignment	Band,[b] cm.$^{-1}$	Vibrational assignment
1640s	C=C stretching, asymmetric	1620s	C=C stretching, asymmetric
1609s	C=C stretching, symmetric	1567m	C=C stretching, symmetric
1468m	In-plane skeletal	1462m	In-plane skeletal
1421s	In-plane skeletal	1407m	
1319s	C—O—C stretching, asymmetric	1327m	
1218w		1243s	C—O—C stretching, asymmetric
1200m		1210m	
1030w		1112m	
1010w		999m	
925s	C—H out-of-plane deformation	951w	
		888m	C—H out-of-plane deformation
855s	C—H out-of-plane deformation		
		875w	
		863w	
		845m	C—H out-of-plane deformation
		763w	
		755w	
		703w	

[a] As KBr disk. [b] Band intensities are given by s = strong, m = medium, w = weak.

a. *O—H[14] and C—H[15] stretching bands.* The fundamental ring systems, 4-pyrone and chromone, contain C—H stretching bands at 3080 cm.$^{-1}$ The pyromeconic acid spectrum does not contain a band readily assignable to either —C—H or O—H stretching, but instead a rather broad, smooth band from 3090 to 3250 cm.$^{-1}$ In contrast, the infrared curve for chromonol shows a fairly sharp, medium strong band at 3295 cm.$^{-1}$, assigned to O—H stretching, and a C—H band at 3100 cm.$^{-1}$ It is possible that the hydrogen bond is weaker in the chromonol molecule than that in the pyromeconic acid molecule in the solid state.

Infrared curves in the O—H and C—H stretching region are given in Figs. 1 and 2 for the substances indicated. The band near 3100 cm.$^{-1}$ in the flavone spectrum is attributed to —C—H stretching. The spectrum of 5-hydroxyflavone in this region is similar to that of flavone, and contains no definite band readily assignable to O—H stretching.

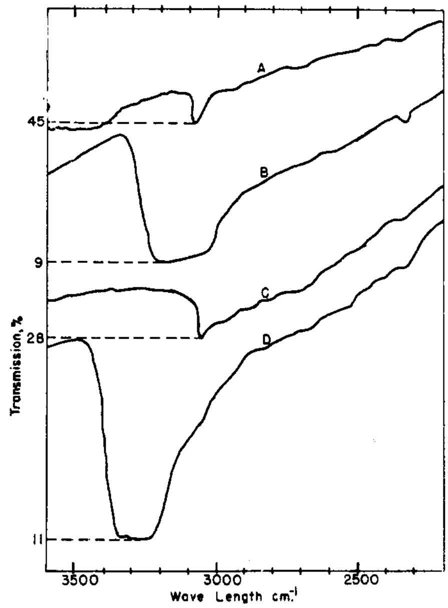

Fig. 1. Infrared absorption curves for A. Flavone, B. 3-Hydroxyflavone, C. 5-Hydroxyflavone, D. 6-Hydroxyflavone

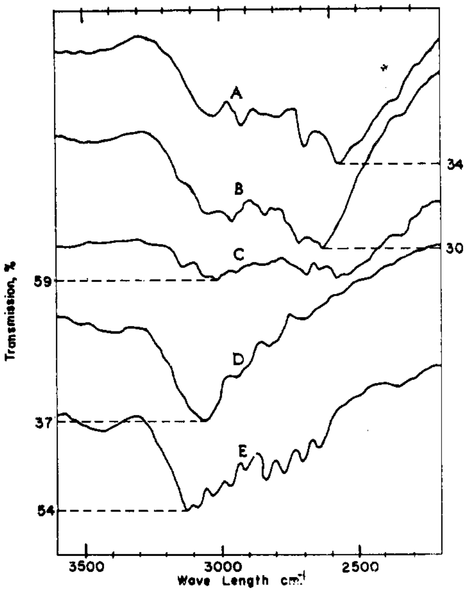

Fig. 2. Infrared absorption curves for A. 7-Hydroxyflavone, B. 8-Hydroxyflavone, C. 2′-Hydroxyflavone, D. 3′-Hydroxyflavone, E. 4′-Hydroxyflavone

The possibility that the 5-O—H stretching band is masked by the C—H stretching band is considered in Part III. The spectra of 3- and 6-hydroxyflavone show the O—H stretching band at sufficiently high frequencies that it can be recognized. However, in the remaining cases (Fig. 2), the O—H stretching frequencies are displaced towards such low values that they cannot be unequivocally assigned. The infrared curves are complex, and the O—H bands may be overlapped by C—H bands. Nonetheless, it is apparent that the O—H stretching bands in 7-, 8-, 2′-, 3′-, and 4′-hydroxyflavone have been displaced toward much lower frequencies

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(14) Ref. 4, pp. 95-111.

(15) Ref. 4, pp. 34-35, 64-67.

TABLE VI

SOLID STATE[a] INFRARED SPECTRAL DATA[b]: AROMATIC IN-PLANE SKELETAL VIBRATIONS OF CHROMONE AND FLAVONE DERIVATIVES

Substance	Bands(s) 1[c, d]	Band(s) 2[c, d]	Band(s) 3[c, d]	Band(s) 4[c, d]
Chromone	1600s or 1615s	1563s	1466s	1407s?
2-Methylchromone	1610s	1575s	1467s or 1453m	1440m or 1426m
Chromonol	1607s-br	1568s-br	1495m or 1474s	1430s
Flavone	1627sh 1610s	1573m	1502m 1474s	1457m
Flavone derivatives				
3-OH	1610s?	1564s 1548sh	1486s 1475s	1450s 1418s?
5-OH	1617s	1590s 1550sh	1473s	1457s 1417s?
6-OH[e]	1622s 1602s	1590s 1573s	1478s	1403m?
7-OH	1613s	1583s-br 1552s	1513s 1479sh	1460m
8-OH[f]	1603sh	1590sh 1565s-br	1515sh 1494s	1457s 1419s?
2′-OH[g]	1615s 1608sh	1593m 1567s	1481m	1455s 1407m?
3′-OH	1600s	1568s	1485s	?
4′-OH[h]	1604s	1582s 1569s	1518m-br 1487s	1460m-br
3-OCH_3	1606s	1565m	1494m 1469s	1442s
5-OCH_3	1600s	1573w	1495m 1477s	1456m 1442s
6-OCH_3	1617s 1606s	1583s 1571s	1490s 1473s	1437s
7-OCH_3	1624s 1603s	1580sh	1494w-br 1470w	1450sh 1442s
8-OCH_3	1601s	1583s 1573s	1496s	1447s
2′-OCH_3	1610s 1600s	1583s 1570s	1500s 1475s	1442s
3′-OCH_3[i]	1607s	1572s 1565sh	1474s	1450s 1438s
4′-OCH_3[j]	1620m 1607s	1573m 1562sh	1480sh 1470s	1445sh 1432m

[a] As KBr disk. [b] Absorption band frequencies are expressed in cm.$^{-1}$ [c] For significance of notation 1, 2, 3, and 4, see ref. 6. [d] Intensity of bands is given by s = strong, m = medium, w = weak; sh = shoulder on strong or medium band; br = broad. [e] Additional bands: 1543sh. [f] Additional bands: 1550sh, 1532sh. [g] Additional band: 1577sh. [h] Additional band: 1473sh. [i] Additional bands: 1543sh, 1493sh, 1482sh. [j] Additional band: 1513m.

relative to that in 6-hydroxyflavone, and that the intermolecular hydrogen bonds present in the crystal lattice probably are quite strong. Corroboration is found in the carbonyl bands of these hydroxyflavones (Table II).

b. *Spectra of fundamental ring systems.* Spectra of 4-pyrone and pyromeconic acid in the 1650- to 650-cm.$^{-1}$ region are listed in Table V. Certain tentative assignments are included. A comparison of the spectra of 4-pyrone and 4,4-dimethylcyclohexadiene-2,5-one-1[16] shows that the cyclohexadienone derivative contains no medium or strong band in the region 1400 to 1260 cm.$^{-1}$, although weak bands are present at 1311 and 1366 cm.$^{-1}$ Accordingly, our assignment of the 1319-cm.$^{-1}$ band, which is nearly as strong as the carbonyl band, to asymmetric oxide stretching appears reasonable. In the 1112- to 1407-cm.$^{-1}$ region of the spectrum of pyromeconic acid, exact assignment hardly appears possible. However, the strong band at 1243 cm.$^{-1}$ has been rather arbitrarily assigned as indicated, on the basis of the strength of the band.

c. *Aromatic in-plane skeletal vibrations.*[6,17] In Table VI are listed bands possibly associated with aromatic in-plane skeletal vibrations. Other workers have noted as many as four bands associated with in-plane skeletal vibrations in the spectra of monocyclic aromatic systems. In both chromone and flavone derivatives, there is present the complication of the pyrone system, which absorbs in this region (Table V). Also, in flavones there are two benzene nuclei. No attempt has been made to assign frequencies to a specific ring system. One of the bands near 1600 cm.$^{-1}$ in chromone may be associated with a stretching mode of the 1,4-pyrone ring. In flavone derivatives, two bands obviously could be due also to the two benzenoid rings. The presence of a high frequency band in the vicinity of 1620 cm.$^{-1}$ for 6-hydroxy- and 6-methoxyflavone, 7-methoxy-, and 4′-methoxyflavone can be correlated with the occurrence in spectra of *para*- and unsymm.-tri-substituted benzene rings of bands with frequencies as high as 1650 cm.$^{-1}$ In the present series, a strong or medium band near 1575 cm.$^{-1}$ is readily recognized. Presumably this band is sometimes strong due to conjugation either of the carbonyl group with the benzenoid part of the chromone core, or of the side phenyl with the pyrone double bond at the 2,3- position. With the 1480- and 1447-cm.$^{-1}$ bands, unequivocal assignment is not possible in the spectrum of 2-methylchromone, since methyl groups also absorb in this region. Lower frequency bands in the 1450–1400-cm.$^{-1}$ region of hydroxyflavone spectra are difficult to assign, since O—H in-plane deformation bands can occur near 1400 cm.$^{-1}$

d. *Absorption in 1400- to 1000-cm.$^{-1}$ region.* Although it is known in a general way which vibrations of chromone and flavone derivatives occur in this region, specific band-structure correlations appear impossible without additional extensive experimentation. The region is of interest, since bands due to the oxide function of the pyrone ring may occur here. Other bands possible in the appropriate derivatives are O—H[14] and C—H[6]

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(16) J. Derkosch and W. Kaltenegger, *Monatsh.*, 90, 877 (1959).

(17) Ref. 4, pp. 69–74.

in-plane deformation modes, C—O stretching bands of enolic,[14] phenolic,[14] and methoxyl groups,[18] and various C—C stretching modes; data are in Table VII.

Since oxide bands usually are very strong,[18] the three strongest bands are indicated for the first twelve entries in Table VII, and the four strongest for the methoxyflavones. In chromonol and flavonol, the three strongest bands lie in the region commonly assigned to oxide stretching vibrations.[18] In chromonol, the band at 1206 or 1292 cm.$^{-1}$ possibly is associated with the pyrone oxide vibration. Flavonol has corresponding bands at 1215 and 1286 cm.$^{-1}$ In chromone, the strongest bands are at 1346 and 1317 cm.$^{-1}$, frequencies which appear rather high for the oxide band. However, the oxide band in 4-pyrone itself is at 1319 cm.$^{-1}$ (Table V). In flavone, the only bands of appreciable strength in this region are at 1382 and 1231 cm.$^{-1}$ Possibly the band at 1231 cm.$^{-1}$ results from the pyrone oxide function.

To assign the pyrone oxide vibration in other hydroxyflavones, phenolic C—O stretching and O—H in-plane deformation bands also must be located. In view of the intermolecular hydrogen bonds present (Part IIa), the O—H deformation band could be expected near 1400 cm.$^{-1}$ Accordingly, the three strongest bands could involve C—O stretching modes resulting from pyrone oxide and phenolic hydroxyl functions, as well as in-plane deformation vibrations of the phenolic O—H. Assignments more specific than this do not appear warranted.

Most spectra in Table VII show a series of weak to medium bands in the range 1000 to *ca.* 1290 cm.$^{-1}$ Some of these undoubtedly are associated with aromatic C—H in-plane deformation modes.

TABLE VII

SOLID STATE[a] INFRARED SPECTRAL DATA FOR CHROMONE AND FLAVONE DERIVATIVES IN 1400–1000-CM.$^{-1}$ REGION

Substance	Infrared Absorption Bands, (Cm.$^{-1}$)[b, c]
Chromone	1346s,[g] 1317s,[h] 1257s, 1236s, 1193s, 1127s,[i] 1077m, 1037m, 1012m
2-Methylchromone	1388s,[g] 1360s,[h] 1332m, 1293m, 1250m, 1224m,[d] 1215m, 1175m, 1153m, 1122s,[i] 1039m, 1025m, 1010m
Chromonol	1360s, 1344m, 1292s,[i] 1206s,[g] 1163s,[h] 1153s,[h] 1118s, 1003w
Flavone	1382s,[g] 1313m, 1285w,[d] 1264m, 1231m,[i] 1196w, 1133m,[h] 1105w, 1080w,[d] 1047m, 1033m, 1013w
Flavone derivatives	
3-OH	1351s,[f] 1305s, 1286s,[d, i] 1248s,[f] 1215s,[g] 1195sh, 1187sh, 1155m, 1130s,[h] 1077s, 1035m
5-OH	1368sh, 1361m, 1328sh, 1317m,[e] 1298m,[i] 1258s,[g] 1228s,[h] 1161m, 1121m, 1105m, 1077m, 1057m, 1034m
6-OH	1380sh, 1356s,[h] 1304m, 1295sh, 1256s,[i] 1231s,[g] 1164m, 1128m, 1103w, 1078m, 1047m, 1030m, 1002m
7-OH	1387s,[g] 1360m, 1318m,[e] 1313m,[e] 1287m, 1263s,[h] 1191m, 1173m,[i] 1140m, 1095m, 1043m, 1030m, 1004w
8-OH	1382s,[g] 1306sh, 1300s,[h] 1265sh, 1257m,[d] 1220m, 1180s,[i] 1151m, 1077m, 1051s, 1028m, 1002w
2′-OH	1383s,[g] 1327m,[i] 1298m, 1270w, 1252s,[h] 1227w, 1162m, 1137m, 1116w, 1053w, 1037w, 1014w
3′-OH	1391s,[g] 1353m,[d] 1337m, 1317m, 1308sh, 1284m,[d] 1249m,[h] 1229m, 1200m, 1161w, 1136m,[i] 1089w,[d] 1052w, 1022w,[d] 1000w
4′-OH	1393s,[h] 1337w, 1300m, 1265s,[g] 1224w, 1183m,[i] 1138w, 1117w, 1047w, 1015w[d]
3-OCH_3	1382s,[h] 1332m, 1293m, 1282sh, 1241s,[j] 1212s,[i] 1182m, 1167m, 1145s,[g] 1110m, 1076m, 1034sh, 1028m, 1000m
5-OCH_3	1380s,[i] 1348sh, 1324m, 1305m, 1288s,[j] 1268s,[h] 1222m, 1185w, 1171w, 1096s,[g] 1080m, 1071sh, 1034m, 1020m
6-OCH_3	1360s,[g] 1316m, 1295m, 1280m, 1253s,[i] 1205s,[j] 1176m, 1165m, 1126m, 1076s, 1048m, 1028s, 1021s[h]
7-OCH_3	1376s,[g] 1333w, 1283sh,[j] 1269s,[i] 1185w, 1158s,[h] 1093m, 1026m, 1015m
8-OCH_3	1382s,[g] 1356s, 1315m, 1281s,[h] 1248s, 1227s, 1197s, 1180s,[j] 1150s, 1062s,[i] 1043m, 1003m
2′-OCH_3	1377s,[g] 1339m, 1316m, 1300s,[i] 1275s, 1257s,[h] 1230s, 1195s, 1180sh, 1164m, 1150sh, 1130s,[j] 1063m, 1035m, 1023s, 1010m
3′-OCH_3	1371s,[g] 1348s, 1335sh, 1296s,[i] 1276s, 1252s,[h] 1230s, 1215s, 1193m, 1164m, 1156m, 1133m, 1093m, 1084m, 1035s,[j] 1019m
4′-OCH_3	1382s,[g] 1335m, 1316m, 1268s,[h] 1257m,[j] 1224sh, 1197s,[i] 1136m, 1126m, 1058w, 1043w, 1027m, 1023sh

[a] As KBr disk. [b] Intensity of bands is given by s = strong, m = medium, w = weak; sh = shoulder on strong or medium band. [c] Slight shoulders and very weak bands are omitted. [d] Broad band. [e] Borderline medium to weak band. [f] Borderline medium to strong band. [g] Strongest band in this region. [h] Second strongest band. [i] Third strongest band. [j] Fourth strongest band.

e. *Absorption in 1000- to 650-cm.$^{-1}$ region.*[6,19] Out-of-plane deformation frequencies for aromatic and pyrone C—H bonds are expected in this region. Absorption bands in the 1000–650 cm.$^{-1}$ range are collected in Tables VIII and IX. With the exception of the pyrone-*H*, assignments in Table VIII are based largely on extensive studies by other workers. The present study indicates that, with two exceptions, in flavones with an unsubstituted side phenyl group, the deformation band for five adjacent hydrogen atoms lies in the range 773 ± 5 cm.$^{-1}$ The second band for this system is in the range 691 ± 13 cm.$^{-1}$ The band involving four adjacent hydrogen atoms in appropriate derivatives is found in the narrow range 756 ± 6 cm.$^{-1}$ In

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(18) Ref. 4, pp. 114–120.

(19) Ref. 4, pp. 75–81.

TABLE VIII

Aromatic and Pyrone C—H Out-of-Plane Deformation Frequencies[a] for Chromone and Flavone Derivatives

	5 Adjacent H			3 Adjacent H		2		
Substance	Band 1	Band 2[b]	4 Adjacent H	Band 1	Band 2	Adjacent H	Single H	Pyrone H
Chromone	—	—	757s[c]	—	—	—	—	838s[e] and/or 864s[d]
Chromonol	—	—	762s[c]	—	—	—	—	855s[d]
2-Methyl-chromone	—	—	760s[c]	—	—	—	—	845s[e]
Flavone	771s[c]	687m	758s[d]	—	—	—	—	853m
Flavone derivatives								
3-OH	777s	703s	758s[c]	—	—	—	—	—
3-OCH_3	796m?	687s	761s[c]	—	—	—	—	—
5-OH	752s[c]	687m	—	801s[d]	?	—	—	847s
5-OCH_3	774s[e]	688s[c]	—	798s[d]	?	—	—	850m or 856m
6-OH	773s[d]	683m	—	—	—	808m[e]	872w	841s[c]
6-OCH_3	777s[c]	693s[e]	—	—	—	817s[d]	868m	846s or 855m
7-OH	776–769m[g]	684m[f]	—	—	—	821m	912m?	843m[f] or 853m
7-OCH_3	768m[c]	678m	—	—	—	818m[e]	906w?	850m[d]
8-OH	778m[c]	698m	—	806m	722m[h]	—	—	843m or 856m[e]
8-OCH_3	773s[c]	678s or 716m	—	805s	716m[h]	—	—	844m
2′-OH	—	—	756m[c] and 743m[e]	—	—	—	—	865sh
2′-OCH_3	—	—	758s[c] and 743s[d]	—	—	—	—	857s[e]
3′-OH	—	—	757m	780s[c]	706m[b]	—	871m[e]	849m
3′-OCH_3	—	—	757s[d]	782s or 772s[e]	694m[b]	—	875s[c]	?
4′-OH	—	—	753m[e] or 774m[d]	—	—	834m[c]	—	?
4′-OCH_3	—	—	750m[e] or 770s[d]	—	—	828s[c]	—	845sh

[a] Absorption maxima in cm.$^{-1}$ for KBr disks. Intensities are given by s = strong,, m = medium, w = weak, sh = shoulder. [b] Assigned to skeletal out-of-plane deformation mode. See ref. 6. [c] Strongest band in 650–1000-cm.$^{-1}$ region. [d] Second strongest band in 650–1000-cm.$^{-1}$ region. [e] Third strongest band in 650–1000-cm.$^{-1}$ region. [f] Two bands equally strong, strongest in 650–1000-cm.$^{-1}$ region. [g] Doublet. [h] Possibly associated with skeletal out-of-plane deformation mode.

the spectra of 7-hydroxy- and 7-methoxyflavone, the single hydrogen out-of-plane deformation band is quite tenuous, since the pyrone-*H* deformation band may interfere (sequel). It is entirely possible that one of the bands in the 850-cm.$^{-1}$ region, tentatively assigned to the pyrone-*H*, actually is associated with the deformation of the single hydrogen on the benzenoid part of the chromone core of 7-hydroxy- and 7-methoxyflavone.

In virtually all chromone and flavone derivatives, a medium or strong band is present near 850 cm.$^{-1}$, which may be ascribed to the pyrone C—H out-of-plane deformation vibration. Such an assignment is supported by the presence of bands in this region in the moncyclic pyrones (Table V), and by the absence of a strong or medium band near 850 cm.$^{-1}$ in the spectrum of 3-methoxyflavone. In 3′-methoxy- and 4′-hydroxyflavone no band whatsoever occurs near 850 cm.$^{-1}$ However, bands at 875 and 834 cm.$^{-1}$, respectively, are unusually strong. Possibly coupling of some type occurs between aromatic and pyrone C—H deformation modes.

In addition to the out-of-plane C—H deformation bands outlined in Table VIII, there are several other peaks in the 1000- to 650-cm.$^{-1}$ region (Table IX). These bands could be associated with various C—C and C—O stretching modes, as well as with additional C—H out-of-plane vibrations of an unknown type.

III. *Deuteration of 5-hydroxyflavone.* Previous spectral studies[8] of 5-hydroxyflavone have indicated that the infrared curve of this substance is anomalous in certain respects, notably, absence of both a readily detectable O—H stretching band and a carbonyl band shift to lower frequencies under the influence of the hydrogen bond. The present study confirms these observations (Fig. 1; Tables I and II).

In an effort to obtain better resolution in the O—H stretching region, both potassium bromide disk and carbon tetrachloride solution spectra of 5-hydroxyflavone were examined with the aid of lithium fluoride optics. The solid state spectrum still contained only one distinct band, at 3063 cm.$^{-1}$ which very probably is associated with the C—H vibration. In saturated carbon tetrachloride solution, 5-hydroxyflavone showed a distinct band at 3067 cm.$^{-1}$, a broad band at *ca.* 3035 cm.$^{-1}$, weak broad bands at 2850, 2787, and 2710 cm.$^{-1}$, very weak bands at 2972 and 2895 cm.$^{-1}$, and a shoulder at 3085 cm.$^{-1}$ From this solution spectrum, it is concluded that the O—H stretching band, if present at all, is quite weak, unless it is masked by the C—H stretching band at 3067 cm.$^{-1}$

In an effort to obtain 5-deuteroxyflavone for spectral study, the insoluble sodium salt of 5-hydroxyflavone was deuterated by the action of phosphorus pentoxide in deuterium oxide. The deuteration product possessed a melting point 25° higher than that of 5-hydroxyflavone and was markedly less soluble in carbon tetrachloride. The

TABLE IX

UNASSIGNED INFRARED ABSORPTION BANDS[a] OF CHROMONE AND FLAVONE DERIVATIVES IN 1000–650-CM.$^{-1}$ REGION

Substance	Infrared Bands, (Cm.$^{-1}$)[b, c]
Chromone	970m, 959m, 802m, 773s, 677m
2-Methylchromone	960s, 883m, 786s, 678m, 656m
Chromonol	981m, 883m, 797w,[d] 702m, 694m
Flavone	962w, 927w, 910m, 884w, 870w, 783m, 672m
Flavone derivatives	
3-OH	990m, 927m, 898s, 864m, 837w,[d] 795w, 663s
5-OH	998m, 931w, 900w, 707w, 675m
6-OH	933w,[d] 914m, 815sh, 728m, 655m
7-OH	959w, 732w, 723w, 672m
8-OH	982m, 963w, 883m, 738m
2′-OH	911w, 877m, 815w,[d] 780w, 767sh
3′-OH	958m, 882m, 804sh, 739w, 680w, 670w
4′-OH	960w,[d] 910w, 668w[d]
3-OCH_3	950m, 920w, 893s, 862w, 834w, 707m, 675m, 665m
5-OCH_3	998m, 975w, 942m, 763s, 677m
6-OCH_3	998m, 977m, 960m, 912m, 872w, 801m, 710m, 653m
7-OCH_3	667m
8-OCH_3	972w, 940m, 913m,[d] 871m, 837sh, 749s, 653m
2′-OCH_3	945w, 906m, 868m, 792w, 778w, 675m, 661m
3′-OCH_3	998m, 938m, 808m, 739m, 660m
4′-OCH_3	983w, 952w, 910m, 868w, 813sh, 788w, 668w

[a] Of KBr disks. [b] Intensity of bands is given by s = strong, m = medium, w = weak; sh = prominent shoulder on strong or medium band. [c] Slight shoulders and very weak bands are omitted. [d] Broad band.

potassium bromide disk spectrum (sodium chloride optics) of the deuteration product possessed a very broad band in the region 2740 to 2900 cm.$^{-1}$, which was the strongest in the 3500- to 2000-cm.$^{-1}$ region, broad bands at 2370 and 2310 cm.$^{-1}$, and a very weak band at 2210 cm.$^{-1}$ The potassium bromide disk spectrum (lithium fluoride optics) possessed the above bands at 2725 to 2860, 2372, 2295, and 2215 cm.$^{-1}$ In addition, a band was present at 2340 cm.$^{-1}$ In the solution spectrum, which was not completely satisfactory because of slight solubility of the deuteration product in carbon tetrachloride, the broad band near 2800 cm.$^{-1}$ was still discernible, but maximum absorption was only 10%. The lower frequency bands were barely detectable. In the spectra determined under the three conditions, the broad band near 2800 cm.$^{-1}$ obscured any band near 3060 cm.$^{-1}$ In certain cases, however, a shoulder near 3060 cm.$^{-1}$ was present.

The complex spectrum of the deuteration product does not permit unequivocal location of a single band corresponding to O—D stretching. Nonetheless, it is interesting that bands do appear near 2300 cm.$^{-1}$, and that these bands are not present in the 5-hydroxyflavone spectra. If the 2295 cm.$^{-1}$ peak, the strongest near 2300 cm.$^{-1}$, is arbitrarily assigned to O—D stretching and the ratio of the 3063 cm.$^{-1}$ peak of 5-hydroxyflavone to this band determined, then a value of 1.33 is obtained, fairly close to the theoretical $\sqrt{2}$.[20] Thus it is conceivable that the O—H stretching band of 5-hydroxyflavone is masked by the C—H vibration at 3063 cm.$^{-1}$ It is also possible that one of the other bands in the 3000-*ca.* 2850-cm.$^{-1}$ region corresponds to O—H stretching, for ratios of O—H to O—D stretching bands under 1.30 have been observed in hypothetically similar 1-hydroxyanthraquinone derivatives.[21]

In carbon tetrachloride solution, the deuteration product has the carbonyl band at 1640 cm.$^{-1}$, a value which is 12 cm.$^{-1}$ lower than that of flavone and 5-hydroxyflavone (Tables I and II) in this solvent. Thus the carbonyl absorption of the deuteroxyl derivative does not appear anomalous, although the shift toward lower frequency is rather small. The low frequency of any 5—O—H stretching band, relative to corresponding frequencies for "normal", nonhydrogen-bonded hydroxyl groups, indicates that the hydrogen bond in 5-hydroxyflavone probably is strong.[14,22] If any O—H stretching band present is assumed to be weak (a valid assumption unless the O—H and C—H stretching frequencies coincide exactly), then possibly the O—H bond is nonlinear.[22] The deuteron bond in the deuteroxyl derivative may be similar, although it probably is less strong than the hydrogen bond. The anomalous location of the carbonyl band in the 5-hydroxyflavone spectrum, and the very broad band near 2800 cm.$^{-1}$ in the spectrum of the deuteration product, are potentially important phenomena in the hydrogen bond area which remain unexplained.[23]

A comparison of appropriate spectral data in the 1400–650-cm.$^{-1}$ region shows that at least seven bands in the 5-hydroxyflavone spectrum are missing in the deuteration product curve. The spectrum of the deuteration product shows six distinct bands, one weak band, and one shoulder in the 1000–650-cm.$^{-1}$ region, none of which are evident in the 5-hydroxyflavone curve. In addition, the spectrum of 5-hydroxyflavone contains a strong band at 1417 cm.$^{-1}$, while the deuteration product curve has only a shoulder at 1415 cm.$^{-1}$ If the ratios of the 1417, 1317, 1121, and 1057-cm.$^{-1}$ bands of 5-

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(20) R. B. Barnes, R. C. Gore, U. Liddel, and V. Z. Williams, *Infrared Spectroscopy*, Reinhold Publishing Corp., New York, 1944, p. 14.

(21) D. Hadzi and N. Sheppard, *Trans. Faraday Soc.*, **50**, 911 (1954).

(22) H. Tsubomura, *J. Chem. Physics*, **24**, 927 (1956); C. M. Huggins and G. C. Pimentel, *J. Phys. Chem.*, **60**, 1615 (1956); ref. 21.

(23) Although the broadening of the 2800 cm.$^{-1}$ band might be discussed in very general terms, an explanation of the specific case at hand is not offered; for a more complete discussion of this controversial area, *cf.* N. Sheppard, *Hydrogen Bonding*, Papers of Symposium at Ljubljana 1957, Pergamon Press, London, 1959, p. 85.

hydroxyflavone to the 1018, 951, 814, and 772-cm.$^{-1}$ bands of the deuteration product are determined, values of 1.39, 1.38, 1.38, and 1.37, respectively, are obtained, quite close to the theoretical $\sqrt{2}$. Possibly these shifts can be accounted for on the basis of the expected *O*-deuteration process, combined with deuteron bond and solid state anomalies. However, it also is possible that *O*-deuteration was accompanied to a certain extent by C-deuteration.

EXPERIMENTAL

All melting points are uncorrected.

4-Pyrone. This substance was kindly donated by Dr. Reuben Jones, Eli Lilly and Co.; m.p. 31–32°, lit.[24] m.p. 32.5°.

Pyromeconic acid. The known procedure[25] of thermal decarboxylation of comenic acid gave pyromeconic acid, m.p. and lit.[25] m.p. 117°.

Chromone. This compound, m.p. 56–58°, lit.[26] m.p. 59°, was prepared by the method of Ruhemann and Stapleton.[26]

Chromonol. This substance, m.p. and lit.[27] m.p. 181°, was synthesized by the method of Arndt and Kallner.[27]

2-Methylchromone. This compound, m.p. 69–70°, lit.[28] m.p. 70–71°, was kindly donated by Professor C. S. Hamilton of this laboratory.

Flavone, hydroxyflavones, and derivatives. Flavone derivatives were prepared by known procedures or slight modifications thereof. General preparative methods, melting points, and literature melting points are listed in Table X.

Deuteration of 5-hydroxyflavone. 5-Hydroxyflavone (0.39 g.) was dissolved in a small quantity of anhydrous methanol. Several drops of concd., nearly saturated aqueous sodium hydroxide were added. The bright yellow sodium salt of 5-hydroxyflavone which formed immediately was collected by filtration and dried. To 50 mg. of the sodium salt were added 2 ml. of 99.5% deuterium oxide, and then anhydrous phosphorus pentoxide until the salt dissolved. The resulting solution was diluted with 5 ml. of 99.5% deuterium oxide. The pale yellow precipitate which formed was collected by filtration, washed with a small quantity of 99.5% deuterium oxide, and dried; m.p. 181° (as compared to m.p. 156° for 5-hydroxyflavone). In the 2000–650-cm.$^{-1}$ region, the infrared spectrum of the deuteration product in potassium bromide disk showed the following absorption bands: 1645s, 1603s, 1583s, 1525m-br, 1468sh, 1459s, 1446s, 1415sh, 1325w, 1281m, 1256m-br, 1227s, 1195m, 1164m, 1105m-br, 1082m-br, 1018s-br, 951m, 925m, 885m, 865m, 846m, 814m, 802m, 796sh, 772m, 750sh, 725w, 700m, 681m, 660m.

Infrared spectral measurements. All spectra were measured with a Perkin-Elmer Model 21 recording spectrophotometer, with sodium chloride optics unless otherwise indicated. Solid state potassium bromide disk spectra were determined with several thicknesses of the disk as necessary to make the weaker bands sufficiently intense to be located and still maintain strong bands at intensities suitable for accurate location.

TABLE X

FLAVONE DERIVATIVES: MELTING POINTS AND METHODS FOR SYNTHESIS

Substance	Method for Preparation[a]	M.P.	Lit. M.P.
Flavone	A	95–96	96–97[b]
Flavone derivatives			
3-OH	E	170–172	169–170[c]
5-OH	B	158–159	156–157[d]
6-OH	A	235.5–236.5	231–232[e]
7-OH	A	244	240[f]
8-OH	B	250–252	249–250[g]
2′-OH	B	246–247	249–250[h]
3′-OH	B	209–211	207–208[h]
4′-OH	B	269–271	269–270[h]
3-OCH_3	C	112–114	114[i]
5-OCH_3	A	131	133[j]
6-OCH_3	C	163–164	162[k]
7-OCH_3	C	108–110	110–111[f]
8-OCH_3	A	200–201	199–200[g]
2′-OCH_3	A	102–103	103[h]
3′-OCH_3	A	130–131	131–132[h]
4′-OCH_3	A	156–157	158.5[l]
3-OAc	D	108–110	110–111[c]
5-OAc	D	145–146	145[d]
6-OAc	D	157–158	157–158[e]
7-OAc	D	130–131	129–130[f]
8-OAc	D	136–138	137–138[g]
2′-OAc	D	88.5–89.5	88.5–89[h]
3′-OAc	D	98–99	97[h]
4′-OAc	D	135–137	137[h]

[a] A. Baker-Venkataraman rearrangement [*J. Chem. Soc.*, 1381 (1933); 1767, 1953 (1934)] of appropriate *o*-aroyloxyacetophenone, followed by ring-closure of resulting *o*-hydroxydiaroylmethane with acetic acid–sulfuric acid. B. Demethylation of the methoxyflavone with hydrogen iodide. C. Methylation of the hydroxyflavone with dimethyl sulfate and potassium carbonate in acetone. D. Acetylation with acetic anhydride at reflux, 2–4 drops of pyridine as catalyst. E. Obtained from Eastman Kodak Co. [b] T. S. Wheeler, *Org. Syntheses*, **32**, 73 (1952). [c] S. Kostanecki and W. Szabranski, *Ber.*, **37**, 2820 (1904). [d] S. Sugasawa, *J. Chem. Soc.*, 1483 (1934). [e] S. Kostanecki, R. Levi, and J. Tambor, *Ber.*, **32**, 331 (1899). [f] I. Heilbron, *Dictionary of Organic Compounds*, Vol. 2, Oxford University Press, New York, 1953, p. 767. [g] S. Ruhemann, *Ber.*, **46**, 2196 (1913). [h] M. T. Bogert and J. K. Mareuš, *J. Am. Chem. Soc.*, **41**, 95 (1919). [i] T. Emilewicz and S. Kostanecki, *Ber.*, **32**, 312 (1899). [j] H. Simonis and S. Danischewski, *Ber.*, **59**, 2916 (1926). [k] D. W. Hill and R. R. Melhuish, *J. Chem. Soc.*, 1165 (1935). [l] L. S. Hattori, *Acta Phytochim.*, **2**, 99 (1925); *Chem. Abstr.*, **20**, 2162 (1926).

Solution spectra in carbon tetrachloride were determined on either saturated or dilute solution, as permitted by solubility. When a sufficiently concentrated solution could be prepared, a 0.1-mm. sodium chloride cell was used. With very dilute solutions, a 1.0-mm. cell was used. A matched cell containing pure solvent was employed in balancing the beam to correct for solvent absorption. All solution spectra in dioxane were determined in matched 0.1-mm. sodium chloride cells. All carbonyl frequencies in dioxane or carbon tetrachloride solution, or in Nujol mulls (Tables I–IV), were corrected as necessary by reference to the 1700- and 1637-cm.$^{-1}$ bands in the water vapor–carbon dioxide spectrum.

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