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INFRARED STUDIES OF CHROMONES—I
CARBONYL AND HYDROXYL REGIONS

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Abstract—Quantitative IR solution data in carbon tetrachloride and chloroform are recorded for the CO and OH regions of 31 chromones. In the 1580–1700 cm^{-1} region, 5-hydroxychromones show three main maxima, the two of highest frequency, at 1663 ± 3 cm^{-1} and 1630 ± 5 cm^{-1} in CCl_4 (1661 ± 2 cm^{-1} and 1627 ± 5 cm^{-1} in $CHCl_3$), being sufficiently intense as to possess high CO character. Typically, 5-alkoxychromones exhibit two intense maxima in this region, 1663 ± 3 cm^{-1} and 1613 ± 7 cm^{-1} in CCl_4 (1657 ± 2 cm^{-1} and 1608 ± 12 cm^{-1} in $CHCl_3$). Diagnostically useful changes in contour and principal peak positions can be seen for substituted and annellated 5-hydroxychromones. In the 2500–3650 cm^{-1} region, the stretching frequencies of OH groups at the most commonly encountered positions (C-5, C-7, and 2-CH_2OH) in natural chromones, are identified.

IT IS becoming evident[1–3] that derivatives of 2-methylchromone (**2**), normally having an OH substituent at C-5, are more abundant in nature than was previously thought.[4] Although NMR[5] and mass spectrometric[6] data have been reported for a number of such compounds, IR spectroscopy as an aid to structural elucidation has been largely overlooked[7–11] and yet may be extremely useful in determining the site of attachment of additional alkyl and oxygen[11] substituents and the size of additional rings.

During our structural studies[1] on some 5-hydroxychromones from *Ptaeroxylon obliquum* quantitative IR solution spectra were systematically recorded but the data obtained were at first sight too complex to be of immediate structural value. Like the simpler 4-pyrones[12–14] several peaks of high intensity were found to be present in the 1580–1700 cm^{-1} region, and direct assignment of any one of these bands to the CO stretching frequency was not possible.

When the spectra of the structurally simpler 2-methylchromone (**2**) and 5-hydroxy-2-methylchromone (**3**) were compared, the most intense bands in the CO region were surprisingly close at 1665 and 1661 cm^{-1} (CCl_4) respectively despite the considerable intramolecular H-bonding in the latter compound.[4,15] This anomalous behaviour of a strongly chelated OH group having only a small lowering effect on the CO stretching frequency has been observed for 5-hydroxyflavanones[10,16–18] though not for the related 5-hydroxyflavanones[16–18] and 2-hydroxyacetophenones[16] in which strong intramolecular H-bonding also occurs.

Hergert and Kurth[16] found that in acetophenones a 2-OH group lowers the CO stretching frequency by ~50 cm^{-1} and 5-hydroxyflavanones show analogous behaviour. Spectral shifts arising from structural changes in the flavones are not so clearly defined. Although an OH group attached to C-5 of the flavone nucleus chelates strongly with the CO group, this chelation has only a very slight batho-

chromic effect on the CO stretching frequency[10,18,19] which is generally taken as the most intense band in the 1600–1700 cm^{-1} region. Thus the wavenumber lowering is not greater than 5 cm^{-1} and in some cases a slight increase is observed.[20]

In the present studies, quantitative IR values for the CO regions of 31 chromones in chloroform and carbon tetrachloride solutions are recorded (Tables 1 and 2). Although the composite nature of the absorptions in the CO region of 5-hydroxychromones is not interpreted herein,[21] the effects of changes in molecular structure on the spectral pattern is shown to be diagnostically useful. The OH stretching frequencies (Table 3) are found to vary considerably with the position of attachment of the OH function.

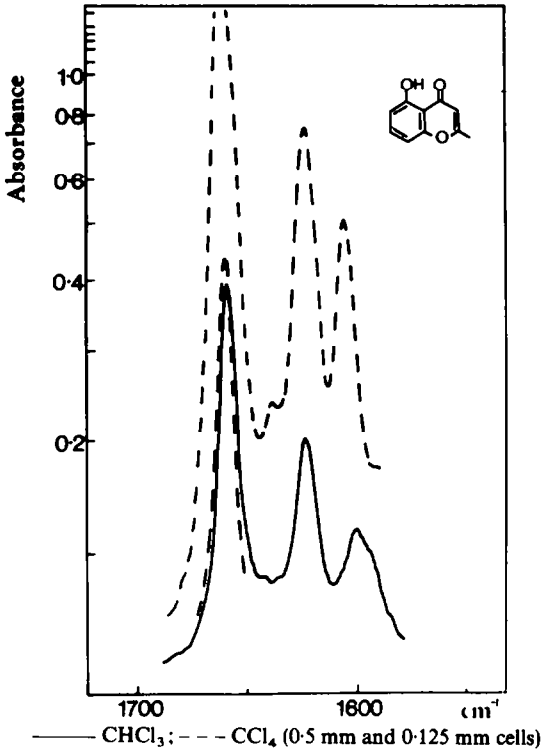


FIG. 1

5-Hydroxychromones

Carbonyl region. A complex spectrum (Fig. 1) is obtained for 5-hydroxy-2-methylchromone (3) with the major band (ε 1500) at 1661 cm^{-1} (CCl_4) considerably sharper than the principal broad intense absorption centred at 1665 cm^{-1} (CCl_4) in the spectrum (Fig. 2) of 2-methylchromone (2). Two further intense peaks are present at 1625 (ε 585) and 1606 (ε 395) cm^{-1} in the former spectrum. The 1665 cm^{-1} band of 2-methylchromone undergoes a bathochromic shift of 15 cm^{-1} when the spectrum (Fig. 2) is recorded in chloroform and presumably represents the CO stretching frequency since a solvent shift of this magnitude might be expected.[22] On the other hand the spectrum of 5-hydroxy-2-methylchromone is basically unchanged when recorded in chloroform (Fig. 1).

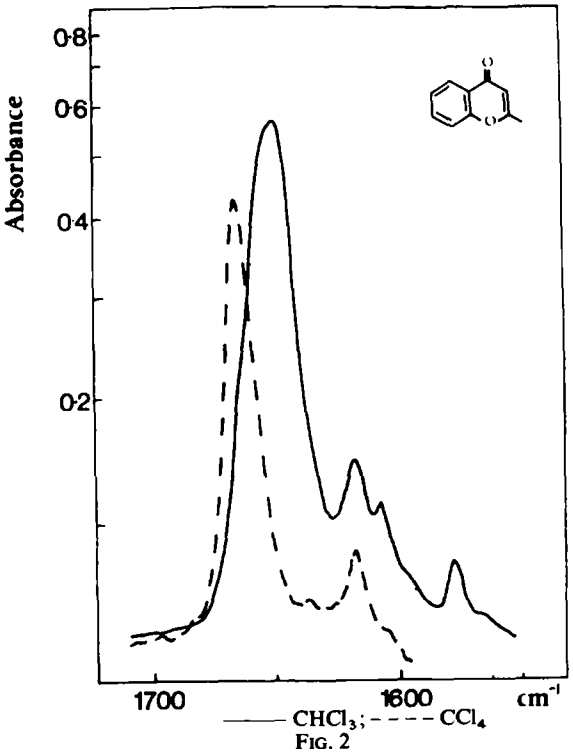

Absorbance
0·8
0·6
0·4
0·2
1700
1600
cm⁻¹
O
O
—— $CHCl_3$; - - - - CCl_4

FIG. 2

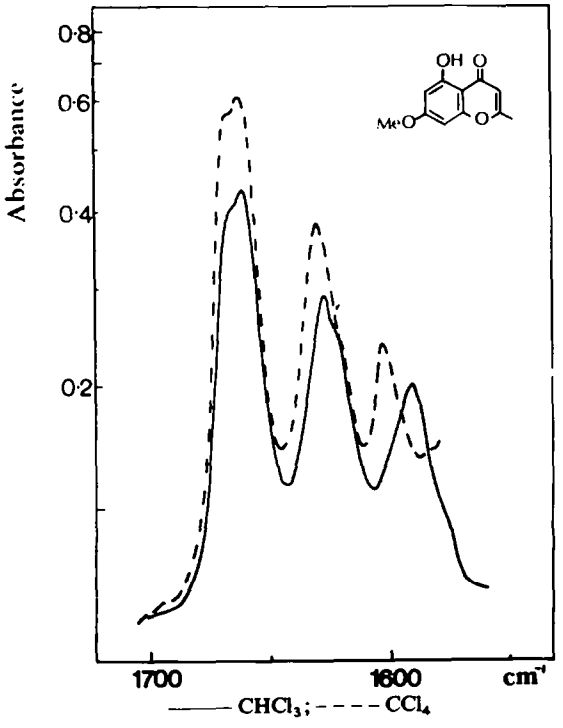
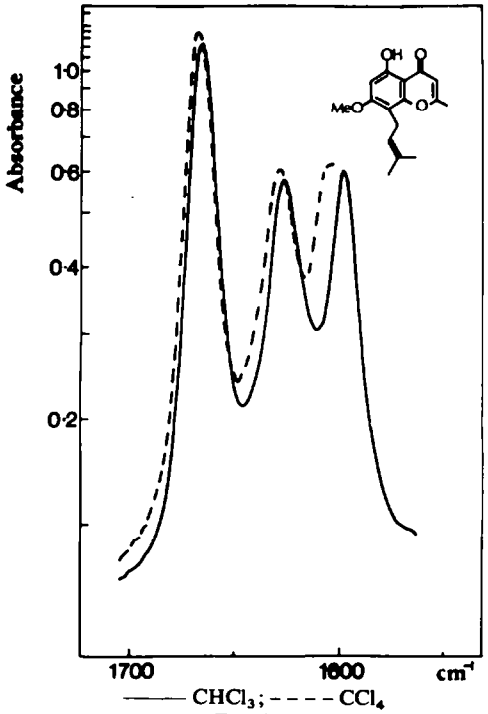

Absorbance
0·8
0·6
0·4
0·2
OH O
MeO
O
1700
1600
cm⁻¹
—— $CHCl_3$; - - - - CCl_4

FIG. 3

For solubility reasons it was not possible to obtain a solution spectrum of 5,7-dihydroxy-2-methylchromone. The spectral behaviour of 5-hydroxy-7-methoxy-2-methylchromone (**4**) (Fig. 3) parallels that of 5-hydroxy-2-methylchromone. This suggests that a 5-OH substituent has a dominating effect on the CO region since the spectrum of **4** is not at all like that of 7-methoxy-2-methylchromone (*vide infra*). The positions of the two major broad peaks at 1666 and 1630 cm^{-1} (CCl_4), (Fig. 3) in this case partially resolved into doublets, are again almost unaffected by change of solvent. It is interesting that for both **3** and **4** the least intense peak [1606 and 1602 cm^{-1} (CCl_4) respectively], shows the largest solvent shift [1601 and 1590 cm^{-1} ($CHCl_3$) respectively], a phenomenon previously noted for the 1613 cm^{-1} band[13,14] of 4-pyrone.[12,23]

Various substituted and modified 5,7-dihydroxychromones are available from natural sources. In general they exhibit spectral characteristics similar to those of the parent system but some useful variations with structure were noted.

Isopentenyl and isopentyl substituents in position 6 have little effect on the spectral profile. Thus the chromones of the peucenin and dihydropeucenin series,[1,24] (**5–8**) all show their most intense maximum at 1660 ± 1 cm^{-1} ($CHCl_3$) and exhibit typically three decreasing intensity maxima. 8-Alkylated chromones of the heteropeucenin[3] and dihydroheteropeucenin series[1,3,25] (**9–11**) differ significantly from the 6-alkylated series in that the absorption of the band at 1590 cm^{-1} ($CHCl_3$) is noticeably more intense than that of the neighbouring 1620 cm^{-1} band (Fig. 4). This effect is also shown by an 8-OMe substituent. Thus 6-ethyl-5,7-dihydroxy-8-methoxy-2-methylchromone (**12**) possesses a substituent in both the 6 and 8 positions, but the profile



—— $CHCl_3$; - - - - CCl_4

FIG. 4

of the spectrum more closely resembles that of a heteropeucenin derivative, the peak at 1604 cm^{-1} (CCl_4) being of greater intensity than the 1631 cm^{-1} absorption.

A number of naturally occurring 5-hydroxychromones and their derivatives contain 5-, 6-, or 7-membered rings fused through oxygen at C-7 to the benzenoid ring of the chromone nucleus. Some regularity in their spectral features has been found.

Linear annellation of the 5-hydroxychromone system with a dihydrofuran ring, as in umtatin[3] (13), gives a spectrum consisting of three well separated broad and approximately symmetrical peaks similar to the parent system. The most intense band at 1674 cm^{-1} (CCl_4) is however considerably higher (13 cm^{-1}) than the major peak in the spectrum of 5-hydroxy-2-methylchromone (3) and 8 cm^{-1} higher than that of 5-hydroxy-7-methoxy-2-methylchromone (4). Similar spectral behaviour has been found for visamminol[26] (14) and dihydrokhellinol[27] (15).

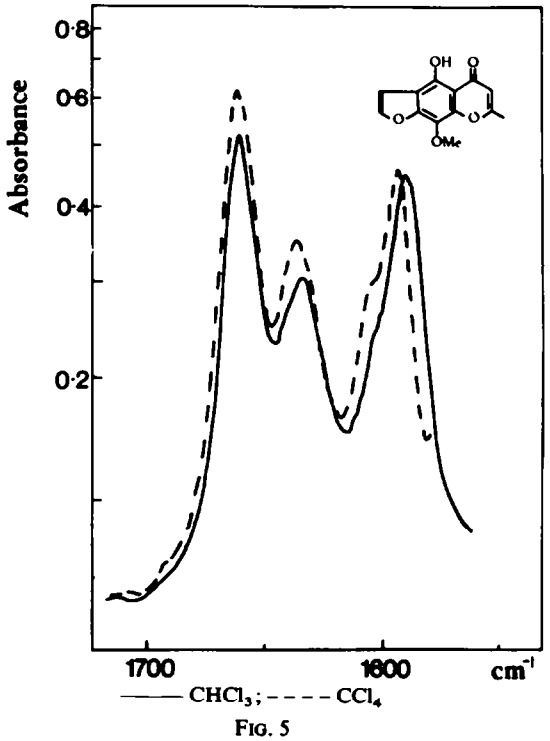


FIG. 5

The spectrum (Fig. 5) of the 5-hydroxyfuranochromone, khellinol[26, 28] (16) however is similar to that of 5-hydroxy-7-methoxy-2-methylchromone (4) and has the principal absorption at the normal position of 1663 cm^{-1} (CCl_4). The considerable increase in relative intensity of the broad 1596 cm^{-1} band is consistent with the presence of an 8-substituent but may also reflect the effect of extended conjugation from the furan ring. Only a small solvent shift is observed for all peaks. 5-Hydroxyfurano-chromones should therefore be easily recognisable since the corresponding 5-hydroxydihydrofuranochromones are readily afforded by hydrogenation over 5% rhodium–charcoal with concomitant change of contour and increase in frequency of the principal absorption.

A 6-membered ring appears to have no significant annellation effect. Thus isopeucenin[24] (**17**) absorbs at 1659 cm^{-1} ($CHCl_3$) and shows a spectrum similar to that of the non-cyclized analogue peucenin 7-methyl ether (**6**). The pyranochromone, ptaerochromenol[3] (**18**) has its major absorption at 1664 cm^{-1} ($CHCl_3$). The contour of this spectrum, with a strong band at 1585 cm^{-1}, is somewhat similar to that of khellinol; like khellinol, ptaerochromenol possess an 8-substituent and a further double bond in conjugation with the chromone nucleus.

By comparison with 5-hydroxy-7-methoxy-2-methylchromone (**4**) which absorbs at 1663 cm^{-1} ($CHCl_3$), a small lowering effect, perhaps useful for future structural studies, is produced by annellation of an oxepin ring. Thus karenin[1] (**19**) has its major absorption at 1658 cm^{-1} ($CHCl_3$) and values of 1656 and 1654 cm^{-1} are found for desoxykarenin[1] (ptaeroxylin)[3] (**20**) and dihydroptaeroxylin[1] (**21**) respectively.

Although it is known that allyl alcohols normally show weak OH-π H-bonding,[29] substitution of a 2-hydroxymethyl for a 2-methyl group has very little effect on the 1580–1700 cm^{-1} region of 5-hydroxychromone spectra. Thus karenin (**19**) and ptaeroxylin (**20**) show very similar absorption and umtatin (**13**) and visamminol (**14**) have almost superimposable spectra.

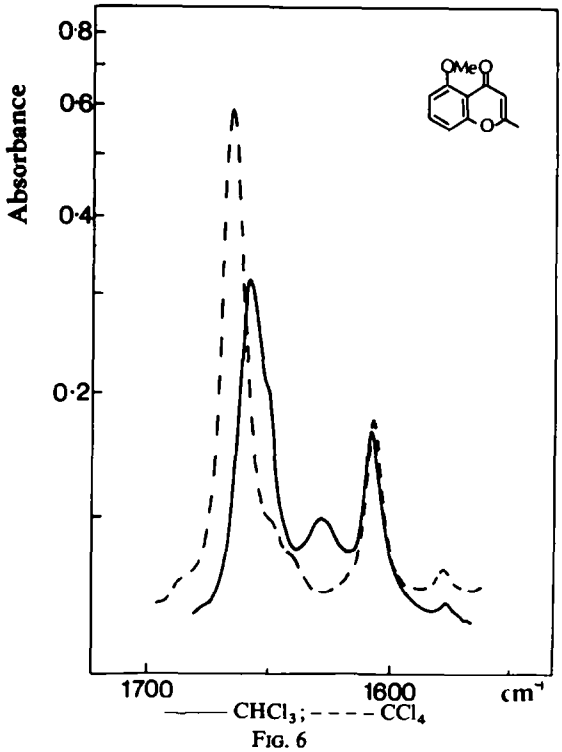
In the 1580–1700 cm^{-1} region, all 5-hydroxychromones possess three significant maxima, the two of higher frequency being sufficiently intense as to imply CO stretching character in both. Moreover these two bands at $\sim$1660 and $\sim$1630 cm^{-1} show a constant wavenumber separation of 34 ($\pm$5) cm^{-1} in both carbon tetrachloride and chloroform, the values of both peaks being consistently 2–3 cm^{-1} lower in the latter solvent. This very slight change in band position with change of solvent polarity is not inconsistent however with both main bands having considerable CO character since a strongly intramolecularly H-bonded CO group would not be expected to solvate readily.

5-Alkoxychromones

Carbonyl region. Although chromones having an OH group in position 5 are only slowly converted to the corresponding methyl ethers,[4] the spectra of such derivatives, and especially the shift of the major band with solvent, may well be useful for characterizing 5-hydroxychromones.

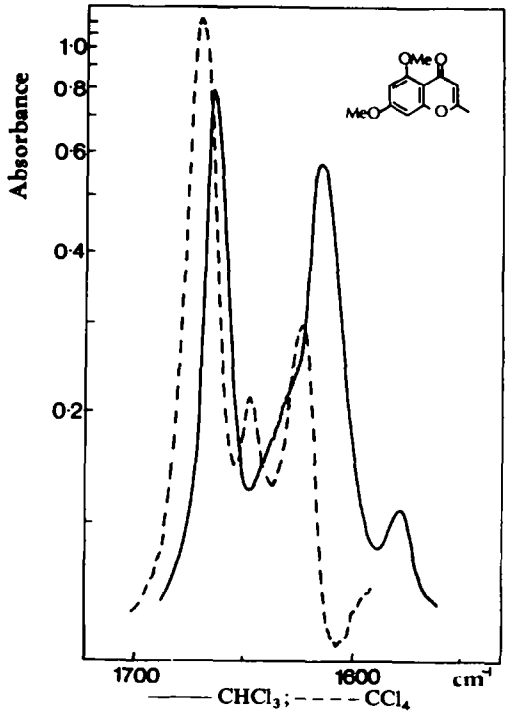
The spectrum (Fig. 6) of 5-methoxy-2-methylchromone (**22**) is considerably simpler than that (Fig. 1) of its OH analogue (**3**) with only two intense bands at 1665 (ε 1620) and 1607 (ε 580) cm^{-1} in carbon tetrachloride. The former absorption, presumably the CO stretching frequency since it shows a solvent shift of 7 cm^{-1} to 1658 cm^{-1} in chloroform, is noticeably close in frequency to that of the principal band of 5-hydroxy-2-methylchromone in the same solvent.

The spectrum of 7-methoxy-2-methylchromone (**23**) with two principal absorptions at 1661 and 1614 cm^{-1} (CCl_4) shows certain of the characteristics of its 5-OMe isomer (**22**). This might be anticipated since OMe substituents at C-5 and C-7 have similar vinylogous electronic relationships with the CO group. However, the marked solvent dependence of the 1661 cm^{-1} peak which shifts to 1648 cm^{-1} in chloroform resembles the behaviour of 2-methylchromone (**2**) and, by contrast to 5-methoxy-2-methylchromone, is consistent with the 1661 cm^{-1} absorption being allocated to a less hindered CO group which is more readily solvated. The analogy with the 5-substituted isomer (**22**) is not complete for in 7-methoxy-2-methylchromone the



—— $CHCl_3$; - - - - CCl_4

FIG. 6



—— $CHCl_3$; - - - - CCl_4

FIG. 7

absorption at 1614 (ε 880) cm^{-1} (CCl_4) is more intense than the corresponding absorption of **22** at 1607 (ε 580) cm^{-1} and shifts further in chloroform.

The spectrum (Fig. 7) of 5,7-dimethoxy-2-methylchromone (**24**) is, not unexpectedly, similar to the spectra of both 5- and 7-methoxy-2-methylchromone with two sharp intense maxima at 1666 and 1620 cm^{-1} (CCl_4), but quite markedly different to that (Fig. 3) of its 5-OH analogue (**4**). Both bands shift to lower frequency when the spectrum is recorded in chloroform; the former appears at 1659 cm^{-1} with a decrease in intensity while the latter at 1610 cm^{-1} is much more intense.

Data for a number of 5-alkoxychromones are recorded in Table 2. The spectra of such compounds are quite distinctive; they possess two intense maxima at 1657 ± 2 and ~1600 cm^{-1} ($CHCl_3$) showing a larger and less constant wavenumber separation (42–64 cm^{-1}) than the 5-hydroxychromones. It would seem likely that the absorption at 1664 ± 2 cm^{-1} (CCl_4) which shows a bathochromic shift, normally of 7 cm^{-1}, in chloroform must represent the CO stretching frequency. The other important absorption at ~1600 cm^{-1} is probably an aromatic mode since it is more intense when a 7-OMe substituent is present. Thus for the series 5-methoxy-2-methylchromone (**22**), 7-methoxy-2-methylchromone (**23**), 5,7-dimethoxy-2-methylchromone (**24**), and peucenin dimethyl ether (**25**) the pertinent values are 1608 (ε 660), 1609 (ε 805), 1610 (ε 930), and 1602 (ε 1160) cm^{-1} ($CHCl_3$) respectively. Phenol methyl ethers normally give more intense aromatic stretching modes that the parent phenols and it is consistent that in 5-hydroxy-2-methylchromone the band at 1601 cm^{-1} ($CHCl_3$) is weak (ε 390).

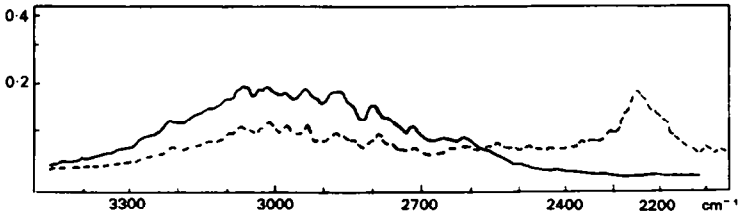
The diagnostically useful variations in principal peak positions with substitution observed for the 5-hydroxychromones are not manifested in the spectra of the corresponding 5-methoxychromones, where recorded. Thus the values in chloroform (1654–1657 cm^{-1}) of the CO stretching frequencies for substituted and annellated 5-methoxychromones are close to that (1658 cm^{-1}) of the parent 5-methoxy-2-methylchromone.

Hydroxychromones

Hydroxyl region. Considerable attention[8,10,16–19] has been given to the location of OH stretching frequencies in flavones but the closely related naturally occurring chromones, in which only a few positions are found to bear OH groups, have not yet been treated in any detail.

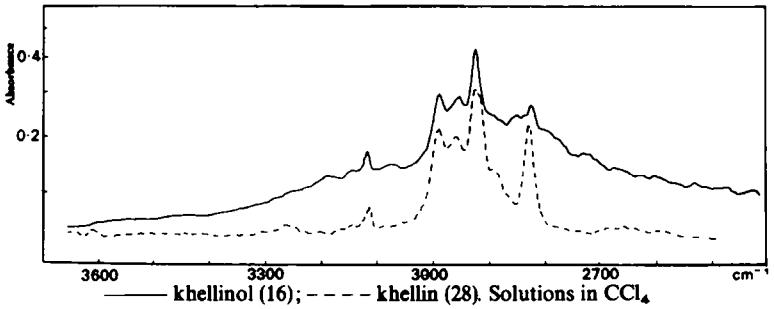
From chromatographic and other behaviour there is evidence for strong chelation in 5-hydroxyflavones.[4] Normally, chelation should result in considerable displacement of both the OH and CO stretching bands to lower frequencies.[30] Surprisingly, none of the 5-hydroxyflavones studied showed any marked lowering of the CO band and very similar behaviour has been noted for 5-hydroxychromones (*vide supra*). However, in 5-hydroxyflavones the OH band is displaced to lower frequency and extensively broadened;[8,10,16–19] indeed the lack of a readily detectable OH stretching frequency is characteristic of the system. It has been found that the spectra of flavone[17] and 5-deuteroxyflavone[31] are considerably simpler in the 2600–3050 cm^{-1} region and an O–D stretching band near 2250 cm^{-1} is clearly evident in the spectrum of the latter compound. The weak bands in the 2600–3050 cm^{-1} region of the spectrum of 5-hydroxyflavone are therefore associated with the OH stretching vibrations.[10,19,31]

There is ample evidence[1,4] that in chromones having an OH group at C-5, the most commonly encountered position, strong intramolecular H-bonding occurs to the pyrone CO group. Thus isopeucenin[1,24] (**17**), a 5-hydroxychromone, is markedly different in its properties from the isomeric allopeucenin[1,24] which possesses a 7-OH group. The former compound is considerably more soluble in ether and exhibits a much greater chromatoplate mobility. Again, 5-hydroxy-2-methylchromone is far less polar in its chromatographic behaviour than 5-methoxy-2-methylchromone in which chelation has been removed. Moreover, successive additions of methanol to a carbon tetrachloride solution of dihydropeucenin 7-methyl ether (**8**) has no effect on the absorption in the 1580–1700 cm^{-1} region. This suggests that the pyrone CO group is so strongly bonded intramolecularly that complex formation with methanol does not occur. The chemical shift value (τ −2·32 in CCl_4) reported[15] for the OH proton in the NMR spectrum of 5-hydroxy-2-methylchromone and the values (τ −2·90 and −3·06 in $CDCl_3$) found for dihydropeucenin (**7**) and isopeucenin (**17**) respectively are much lower than the chemical shift range (τ 5·3 to 5·6 in CCl_4) normally observed[32] for phenols. This is additional evidence for strong chelation in the 5-hydroxychromone system.



——— 5-Hydroxy-2-methylchromone (3); - - - - (3), deuterium enriched 5-hydroxyl. Solutions in CCl_4.

FIG. 8



——— khellinol (16); - - - - khellin (28). Solutions in CCl_4

FIG. 9

5-Hydroxychromones possess no absorption maxima in the 3300–3600 cm^{-1} region. However, a weak absorption envelope extends from 2400 to 3300 cm^{-1} ($\Delta\nu_{\frac{1}{2}}$ ~450 cm^{-1}) underlying the sharp C—H stretching frequencies (Figs 8 and 9) and it is assumed that the entire envelope is associated with various stretching modes of the chelated 5-OH group. The absence of absorption of this type in the spectrum (Fig. 9) of the 5-methoxychromone, khellin[26,33] (**28**) supports this assignment. After treatment of a chloroform solution of 5-hydroxy-2-methylchromone with deuterium oxide, the spectrum shows a dimunition in intensity of the broad absorption centred at 2970 cm^{-1} and possesses a new, considerably sharper ($\Delta\nu_{\frac{1}{2}}$ ~85 cm^{-1})

maximum at 2220 cm^{-1} (Fig. 8). If the latter band is assumed to be the stretching frequency of the 5-deuteroxyl group, the position of the 5-OH stretching maximum can be estimated[31,34] by multiplication of the deuteroxyl frequency by 1·35. The calculated maximum at 2995 cm^{-1} is in reasonable agreement with the estimated midpoint of the broad OH envelope. It has been noted[31] for 5-hydroxyflavones that deuteration results in the appearance of a OD stretching band much sharper than the corresponding OH absorption.

An OH group located at C-7 is found in a number of naturally occurring 5-hydroxychromones. For solubility reasons it was not possible to obtain solution data for the OH regions of 7-hydroxy- and 5,7-dihydroxy-2-methylchromone. When the 7-OH group is flanked by a bulky substituent in the ortho position, a steric buttressing effect is observed. Thus for the 7-hydroxychromones, dihydropeucenin[1,24] (**7**) and dihydroheteropeucenin[1] (**10**), which possess a large isopentyl group in the 6- and 8-positions respectively, the free OH band appears as a doublet centred at ~3615 cm^{-1}, the separation of the components being ~26 cm^{-1}. A similar phenomenon has been reported[35] for *o*-t-butylphenols, and is ascribed[36] to two conformations of the OH group.

When a dimethylallyl residue is adjacent to the 7-OH group as in peucenin[1] (**5**), intramolecular OH-π interaction occurs, resulting in two OH stretching frequencies at 3588 and 3387 cm^{-1} which show no alteration in relative intensity on dilution. Both peaks are absent in the spectrum of peucenin 7-methyl ether. Although a separation of 127 cm^{-1} between the free (3614 cm^{-1}) and the bonded (3487 cm^{-1}) OH frequencies of *o*-(3,3-dimethylallyl) phenol has been recorded,[29,37] the $\Delta\nu$(OH) value for peucenin is much greater (201 cm^{-1}). This implies[1,39] an H-bond energy of ~3 k cal/mole for the intramolecular association of the 7-OH and the dimethylallyl substituent. It is reasonable to assume that this outstandingly strong OH-π interaction arises from the polar character of the 7-OH group, which is the result of the vinylogous electron-withdrawing effect of the pyrone CO group, aided by the basicity of the allyl double bond having the positive inductive effect of the two Me substituents.[38]

When a 7-OH group is flanked by an OMe group as in **12** and **26**, intense intramolecularly bonded OH stretching frequencies are found at 3513 and 3517 cm^{-1} respectively. These values are considerably lower than the value of 3558 cm^{-1} found[40] for *o*-hydroxyanisole and may again reflect the acidic nature of the 7-OH group.

The 2-hydroxymethyl group of karenin[1] (**19**), ptaerochromenol[3] (**18**), and umtatin[3] (**13**) exhibits a free stretching frequency at ~3615 cm^{-1} (ε ~90). At concentrations greater than 0·015 molar this OH participates in intermolecular H-bonding, producing a broad bonded OH frequency at ~3400 cm^{-1} which disappears on dilution. It is notable that the free OH band at 3615 cm^{-1} is rather broad which may suggest that being an allylic alcohol the 2-hydroxymethyl group is undergoing intramolecular OH-π H-bonding with the 2,3-double bond,[29] but that the bonded conformations are not sufficiently rigid to produce a splitting of the OH spectrum. It has already been noted that this weak bonding has no observable effect on the CO region. The corresponding OD absorption at 2663 cm^{-1} is considerably sharper ($\Delta\nu_{\frac{1}{2}}$ ~30 cm^{-1}).

TABLE 1. IR ABSORPTIONS OF CHROMONES IN THE 1580–1700 CM^{-1} REGION

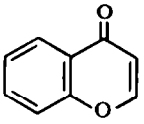
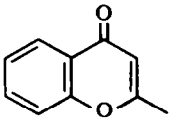
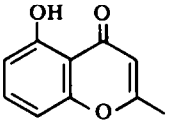
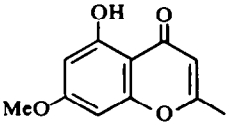
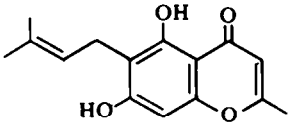
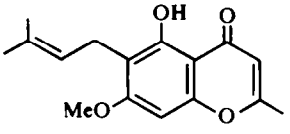
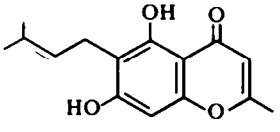
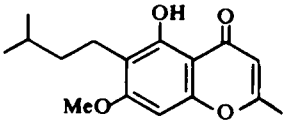
		$CHCl_3$			CCl_4		
		ν	$\Delta\nu_{\frac{1}{2}}$	ε^a	ν	$\Delta\nu_{\frac{1}{2}}$	ε^a
1		1654	16	1050	1668	12	1060
		1621	13	235			
		1606	13	170	1620	10	210
2		1650	14	1060	1665	12	1050
		1618	13	230			
		1607	13	170	1618	12	200
3		1659	9	1360	1661	8	1500
					1639		165
		1624	10	680	1625	9	585
		1601	14	390	1606	10	395
4		1663[d]	14	1180	1666[d]	15	1240
		1626[d]	18	770	1630	17	790
		1590	16	490	1602	13	495
5		1659	15	870	1661		
		1633	25	560	1635		
		1589	19	480			
6		1661	12	1120			
		1627	28	490			
		1593	25	410			
7		1659	15	810			
		1630	29	440			
		1590	24	360			
8		1661	13	1090	1663	10	1140
		1627	27	410	1630	19	415
		1591	24	350			

TABLE 1—*continued*

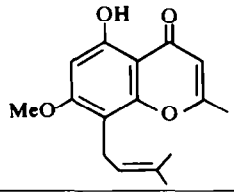
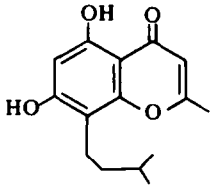
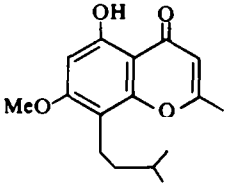
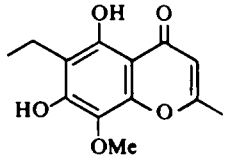
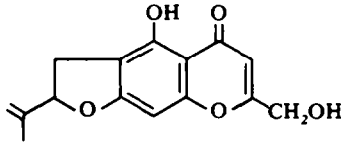
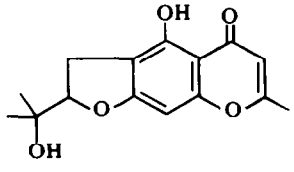
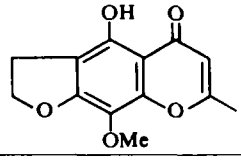
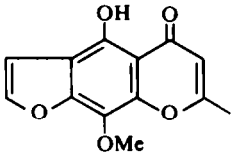
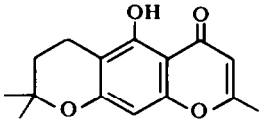
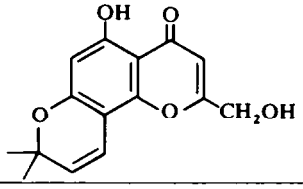
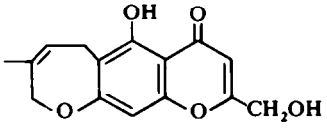
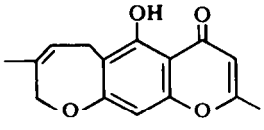
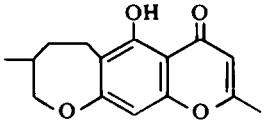
		$CHCl_3$			CCl_4		
		ν	$\Delta\nu_{\frac{1}{2}}^{a}$	ε^{a}	ν	$\Delta\nu_{\frac{1}{2}}^{a}$	ε^{a}
9		1661 1622 1593	10 14 15	1180 510 550	1663 1624	10 16	1175 470
10		1663 1624 1591	12 25 23	1010 340 360			
11		1661 1622 1594	12 20 15	825 355 390			
12		1661 1629 1597	9 22 19	970 425 465	1663 1631 1604	10 23 17	840 375 420
13		1672 1639 1595	14 21 13	975 555 525	1674 1643	11 20	1180 600
14		1671 1636 1593	14 17 13	925 770 420			
15		1668 1637 1590	15 24 24	690 300 390	1668 1637 1594	12 24 15	855 350 520

TABLE 1—*continued*

		$CHCl_3$			CCl_4		
		ν	$\Delta\nu_{\frac{1}{2}}^{d}$	ε^{a}	ν	$\Delta\nu_{\frac{1}{2}}^{d}$	ε^{a}
16		1661 1636 1604^{i} 1592	16 27 23	695 325 580	1663 1639 1606^{i} 1596	15 25 15	700 335 550
17		1659 1628 1584	12 26 22	1015 540 400			
18		1664 1644 1615 1585	11 21 13 15	1390 290 310 720	1666	10	~1400
19		1658 1629 1602	14 28 26	1010 545 370			
20		1656 1627 1595	14 29 23	1010 560 390	1658 1629	11 27	1260 560
21		1654 1623 1592	12 25 23	1105 550 385			

Molarities in the range 0·001–0·01 M. ν and $\Delta\nu_{\frac{1}{2}}^{d}$ are in cm^{-1}.
d, doublet; *i*, inflection.

TABLE 2. IR ABSORPTIONS OF 5-ALKOXYCHROMONES IN THE 1580–1700 cm^{-1} RBGION

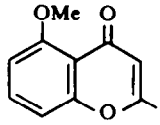
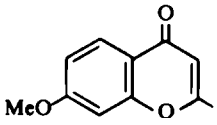
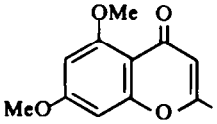
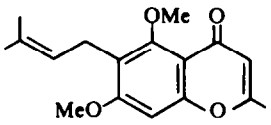
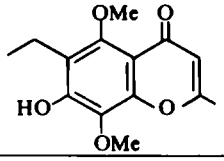
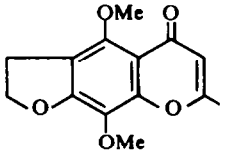
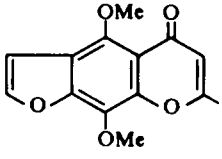
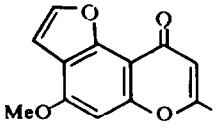
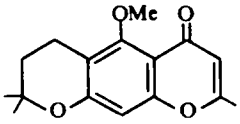
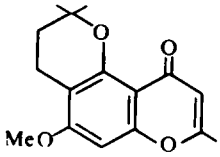
		$CHCl_3$			CCl_4		
		ν	$\Delta\nu_{\frac{1}{2}}^{a}$	ε^{a}	ν	$\Delta\nu_{\frac{1}{2}}^{a}$	ε^{a}
22		1658	12	1330	1665	9	1620
		1628	21	360	1650[f]		
					1642[f]		
		1608	10	660	1607	9	580
23		1648	13	1370	1661	14	1310
		1636i		330	1640		225
		1609	15	805			
		1575		130	1614	10	880
24		1659	9	1290	1666	9	1640
		1610	13	930	1644	17	270
		1574	12	150	1620	11	395
25		1656	11	1230	1663	9	1670
		1627			1641	16	170
		1602	12	1160			
26		1657	10	1210	1664	9	1290
		1631	12	410	1643	13	310
		1596	15	850			
27		1657	12	1120	1662	9	1160
					1637	16	320
		1615	23	918			
					1620	17	570
28		1655	14	1090	1661	11	1260
		1636i			1645	23	150
		1620	18	630			
		1598	17	170	1624	15	335
29		1648	14	690			
		1631	26	170			
		1607	14	410			

TABLE 2—*continued*

		$CHCl_3$			CCl_4		
		ν	$\Delta\nu_{\frac{1}{2}}^{a}$	ε^{a}	ν	$\Delta\nu_{\frac{1}{2}}^{a}$	ε^{a}
30		1654	10	1365	1660	12	1420
		1631	26	410	1643	30	265
		1600	10	1275	1608	10	1195
31		1658	11	1560	1664	10	1540
		1626	—	320	1640	—	220
		1604	11	1750	1606	9	1455

EXPERIMENTAL

IR soln measurements were carried out by Mrs. F. Lawrie and Miss A. M. Robertson, on a Unicam SP 100 Mark II spectrophotometer (prism/grating monochromator) operated with evacuated optics. The spectra were recorded linearly in wavenumbers as optical density and calibration was checked against the spectrum of water vapour after each set of measurements. Frequency determinations for resolved bands are believed to be accurate to ± 1 cm^{-1}. The apparent half band widths, $\Delta\nu_{\frac{1}{2}}^{a}$, are quoted to the nearest integer and where necessary were determined by reflection of the undisturbed wings of unsymmetrical bands. Intensities are specified as apparent extinction coefficients, ε^{a} (1 mole^{-1} cm^{-1}), rounded to the nearest five units, measured from a solvent-solvent base line and corrected, where necessary, for enhancement of intensity by contiguous bands. It was not possible on occasions to obtain data in CCl_4 below 1610 cm^{-1}, since, dependent on the cell used, the solvent absorbed most of the incident radiation. Similarly $CHCl_3$ solns transmitted less than 25% of the incident radiation in the region 3000–3150 cm^{-1}. In the 1580–1700 cm^{-1} region, spectra were recorded using cell paths of 0·125, 0·2 or 0·5 mm and in the 2500–3650 cm^{-1} region cell paths of 0·5 mm and 2·0 mm were employed. The structure of all the chromones were confirmed by NMR spectra, recorded by Mr. J. Gall and Mrs. S. J. Hamilton, on a Perkin Elmer R 10 and a Varian HA 100 spectrometer on solns in $CDCl_3$ with TMS as internal standard. Microanalyses were carried out by Mr. J. M. L. Cameron.

Synthesis and characterization of the chromones

The simple 2-methylchromones were prepared[41] by condensation of the appropriate *o*-hydroxyacetophenone derivative with Ac_2O and mild base hydrolysis of the resulting 3-acetylchromone. Chromatographic techniques in general replaced the method of isolation recommended in the literature.

Chromone, (**1**) m.p. 55° (lit.[10] 56–58°) was kindly supplied by Dr. R. I. Reed, Glasgow.

2-Methylchromone, (**2**) m.p. 70–71° (lit.[42] 71°) was prepared by the method of Block and von Kostanecki.[10,42]

5-Hydroxy-2-methylchromone, (**3**) m.p. 90–91° (lit.[43] 92°) was synthesized from 2,6-dihydroxyacetophenone by the method of Limaye and Kelkar.

5-Methoxy-2-methylchromone, (**22**) m.p. 100–102° (lit.[44] 105°) was prepared by methylation (MeI, anhyd K_2CO_3, refluxing acetone) of 5-hydroxy-2-methylchromone and purified by TLC in MeOH-$CHCl_3$ (1:19) and sublimation at 95°/0·01 mm.

7-Methoxy-2-methylchromone, (**23**) m.p. 112–113° (lit.[45] 113–114°) was prepared by diazomethylation of 7-hydroxy-2-methylchromone[46] and purified by vacuum sublimation.

5-Hydroxy-7-methoxy-2-methylchromone, (**4**) m.p. 119–120° (lit.[47] 120°) was synthesized from 5,7-dihydroxy-2-methylchromone,[48] m.p. 282–285° (purified by sublimation at 160°/0·004 mm) by diazomethylation and purified by TLC in $CHCl_3$ and crystallization from ether.

TABLE 3. IR ABSORPTIONS OF HYDROXYCHROMONES—HYDROXYL REGION

Chromone	$CHCl_3$ ν	$CHCl_3$ $\Delta\nu_{\frac{1}{2}}^{c}$	$CHCl_3$ ε^{a}	CCl_4 ν	CCl_4 $\Delta\nu_{\frac{1}{2}}^{c}$	CCl_4 ε^{a}
3	~2975	~450	~60	~2970	~400	~60
4	~2980	~450	~60	~2970	~400	~60
5	3588	45	70	3598		
	3387	129	75	3405		
	~2970	~450	~60			
6	~2970	~450	~60	~2965	~400	~60
7	3626	32	95			
	3598	47	90			
	~2970	~450	~60			
8	~2975	~450	~60	~2965	~400	~60
9	~2970	~450	~60	~2960	~450	~60
10	3625	33	105			
	3600	50	85			
	~2970	~450	~60			
11	~2975	~450	~60			
12	3513	35	160	3517	23	130
	~2980	~450	~60	~2970	~400	~60
26	3517	33	165	3523	23	140
13	3617[b]	45	60	3628	38	90
	3392[b]	180	30			
	3617[c]	43	95			
	~2970	~450	~60	~2975	~400	~60
14	3603	45	35			
	~2975	~450	~60			
16	~2970	~450	~60	~2970	~400	~60
17	~2970	~450	~60			
18	3615[d]	50	30	3625	34	90
	3407[d]	200	65			
	3615[b]	42	85			
	~2970	~450	~60			
19	3615	48	100			
	~2950	~450	~60			
20	~2940	~450	~60	~2930	~480	~50
21	~2950	~450	~60			

[b] 0·015M; [c] 0·00475M; [d] 0·02M.

5,7-Dimethoxy-2-methylchromone, (**24**) m.p. 123–124° (lit.[49] 124°) was prepared from 5,7-dihydroxy-2-methylchromone by methylation (MeI, anhyd K_2CO_3, refluxing acetone) and purified by TLC in $CHCl_3$ and crystallization from ether.

Peucenin, (**5**) m.p. 212–214; ptaeroxylin (**20**) (desoxykarenin), m.p. 133–135°; and karenin, (**19**) m.p. 203–204°, were isolated[1] from the heartwood of *Ptaeroxylon obliquum*.

Peucenin 7-methyl ether, (**6**) m.p. 106–107°; dihydropeucenin, (**7**) m.p. 205–207°; dihydropeucenin 7-methyl ether, (**8**) m.p. 105–107°; isopeucenin, (**17**)[24] m.p. 132–134°; dihydroheteropeucenin, (**10**) m.p. 191–193°; and dihydroheteropeucenin 7-methyl ether, (**11**) m.p. 91–93°, were derived[1] from (**5**), and (**21**) m.p. 81–83°, derived[1] from (**20**).

Peucenin 5,7-dimethyl ether (**25**). Peucenin (365 mg) in AnalaR acetone (25 ml) was refluxed for 67 hr in the presence of anhyd K_2CO_3 (1·5 g) and MeI (7·5 ml). After filtration and removal of solvent, the crude product was separated by TLC in $CHCl_3$–light petroleum (b.p. 40–60°) (4:1) and *peucenin 5,7-dimethyl ether* crystallized from ether–light petroleum (b.p. 60–80°) as needles, m.p. 79–80°. (Found: C, 70·85; H, 6.9. $C_{17}H_{20}O_4$ requires: C, 70·8; H, 7·0%), NMR signals at τ[8·34, bs, 3H; 8·22, bs, 3H; 4·89, bt, 1H, J = 8 Hz; 6·61, bd, 2H, J = 8 Hz; 6-(3,3-dimethylallyl)];[1] 7·73, s, 3H, 2-C$\underline{H}_3$; 4·06, s, 1H, 3-$\underline{H}$; 3·45, s, 1H, 8-$\underline{H}$; and 6·15, 6·11 (2 × 3H, s) methoxyls.

*Isopeucenin methyl ether** (**30**). Isopeucenin (**17**) was refluxed in acetone for 22 hr with MeI and anhyd K_2CO_3 and *isopeucenin methyl ether* purified by crystallization from ether as needles, m.p. 91–93°. (Found: C, 70·1; H, 6·75. $C_{16}H_{18}O_4$ requires: C, 70·05; H, 6·6%).

Heteropeucenin 7-methyl ether,[2] (**9**) m.p. 110°; ptaerochromenol,[3] (**18**) m.p. 175°; and umtatin,[3] (**13**) m.p. 178°, also constituents of *P. obliquum*, were kindly supplied by Dr. F. M. Dean, Liverpool.

Khellin (**28**), m.p. 155–156° (lit.[26, 33] 153°) and visamminol (**14**), m.p. 159–160° (lit.[26] 160°) were isolated from the seeds of *Ammi visnaga* L.

Khellinol (**16**), m.p. 201–203° (lit.[26, 28] 201°) was derived from (**28**) by demethylation[26] with 50% HBr and crystallized from EtOAc.

Dihydrokhellin (**15**), m.p. 146–147° (lit.[27] 150°) was prepared from khellin (320 mg) by hydrogenation in EtOAc over 5% rhodium charcoal. After freeing from catalyst and solvent, the mixture of four products was separated by TLC in MeOH–$CHCl_3$ (1:49) and dihydrokhellin (140 mg), isolated from the band of lowest mobility, was crystallized from MeOH.

*Dihydrokhellinol** (**15**), m.p. 176–178° (lit.[27] 176–177°) was prepared from **16** (48 mg) by hydrogenation over 5% rhodium charcoal (165 mg) in EtOAc. After freeing from catalyst and solvent, the mixture of three products was separated by TLC as above and dihydrokhellinol (12 mg) isolated from the band of lowest mobility and purified by sublimation at 124°/0·01 mm.

Isovisnagin (**29**), m.p. 240° (lit.[50] 245–247°) was kindly supplied by Dr. R. I. Reed, Glasgow.

6-Ethyl-7-hydroxy-5,8-dimethoxy-2-methylchromone (**26**), m.p. 169–171° (lit.[51] 173°) was prepared from khellin by hydrogenolysis in EtOAc over Adam's catalyst and purified by TLC [MeOH–$CHCl_3$ (1:19)] and crystallization from MeOH.

6-Ethyl-5,7-dihydroxy-8-methoxy-2-methylchromone (**12**). Khellinol (215 mg) in EtOAc was stirred with Adam's catalyst and H_2 for 0·5 hr. After freeing from catalyst and solvent, the hydrogenolysis product was isolated by TLC ($CHCl_3$) and crystallized from MeOH to give *6-ethyl-5,7-dihydroxy-8-methoxy-2-methylchromone* as pale yellow needles (160 mg), m.p. 177–179° (Found: C, 62·5; H, 5·6. $C_{13}H_{14}O_5$ requires: C, 62·4; H, 5·6%), NMR signals at τ 8·86, t, 3H, J = 8 Hz, —CH_2 C$\underline{H}_3$; 7·29, q, 2H, J = 8 Hz, —C$\underline{H}_2$CH$_3$; 7·63, s, 3H, 2-C$\underline{H}_3$; 6·08, s, 3H,-OC$\underline{H}_3$; 4·01, s, 1H, 3$\underline{H}$; and 3·49, s, 1H, 70-$\underline{H}$.

Deuterated hydroxychromones. Partial enrichment of OH groups with deuterium was obtained by shaking a CCl_4 or $CHCl_3$ soln of the hydroxychromone with a few drops of D_2O (99·8 atom%) followed by evaporation to dryness under suction. Traces of water were removed by purging with benzene vapour.

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