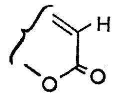
733. *Infrared Studies with Terpenoid Compounds. Part II.*[1] *Carbonyl Absorptions of γ-Lactones*

By R. P. M. Bond, T. Cairns, J. D. Connolly, G. Eglinton, and K. H. Overton

Carbonyl absorption bands of irregular outline are reported for saturated γ-lactones in various solvents. Additional data extend the literature findings for αβ-unsaturated γ-lactones and lend support to the Fermi resonance explanation for the split carbonyl bands shown by some of these compounds.

LACTONES containing the basic system (A) almost invariably exhibit carbonyl absorptions of complex shape,[2] and Fermi resonance[3] involving the carbonyl stretching frequency and the first overtone of the γ(CH) of the α-hydrogen has been postulated by Jones and his colleagues.[2] The relative intensities of the observed pairs of bands are dramatically solvent-dependent and the frequencies show much smaller and more irregular shifts[4] ($\Delta\nu = \nu_{\text{hexane}} - \nu_{\text{solvent}}$) than do those of normal carbonyl groups.[5]



(A)

The availability[6] of a number of sesquiterpenoid lactones has enabled us to make a study of the carbonyl absorptions under conditions of high resolution, and it has become evident that the complexity is not confined to the system (A), but is also displayed, though to a lesser degree, by saturated five-ring lactones. Again, the relative intensities of the various peaks and shoulders are solvent-dependent and solution in the more polar or more powerful hydrogen-bonding solvents is accompanied by a shift of the absorption centre to lower frequency.

EXPERIMENTAL

Materials.—β-Angelicalactone (I) and γ-butyrolactone (II) were obtained commercially and purified by distillation. Campholenolactone (X) and dihydrocampholenolactone (IX) were prepared as described elsewhere.[7] Their purity has been checked by gas–liquid chromatography. The sesquiterpenoid lactones[6] (III ⟶ VIII) used were all of analytical purity. Compounds (XI) and (XII) were kindly supplied by Professor W. S. Johnson.[8] Carbon tetrachloride and n-hexane (AnalaR) were used without further purification, but chloroform (AnalaR) was freed from ethanol by two successive passages through blue silica gel before use. Tetrachloroethylene was purified by passage through chromatographic silica gel. Freshly sublimed *p*-cresol was used and precautions taken to avoid absorption of moisture.

Measurements.—Spectra were recorded linearly in cm.$^{-1}$ as percentage transmission with a Unicam S.P. 100 double-beam infrared spectrophotometer equipped with an S.P. 130 sodium chloride prism-grating double monochromator [1500 lines per inch (625—2150 cm.$^{-1}$) and 3000 lines per inch (2150—3650 cm.$^{-1}$)] operated under vacuum as described previously.[1] Carbonyl bands were scanned at 18 cm.$^{-1}$ per min. for carbon tetrachloride and chloroform solutions, and at 12 cm.$^{-1}$ for n-hexane solutions. Heated cells of the J2 type from Research and Industrial Instruments Co. Ltd. were used with electrically heated jackets. The nuclear magnetic resonance spectra were obtained with a Perkin-Elmer model R 10 Spectrometer (60 Mc./sec.).

Full spectra (3650—650 cm.$^{-1}$) of the lactones were recorded for solids as potassium chloride discs and for liquids as liquid films. They will appear in the D.M.S. Index (Butterworths) as card nos. 12953 to 12959.

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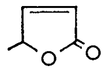
RESULTS AND DISCUSSION

The present work examines the solvent dependence of the absorptions occurring in the ν(C=O) region between 1700 and 1800 cm.$^{-1}$. The results, in general, support and extend the literature findings.[2] In the lactones examined (I ⟶ XII), these absorptions are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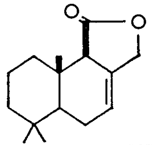
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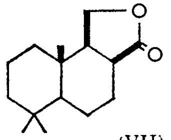
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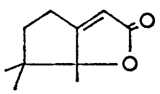
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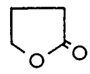
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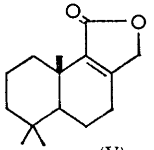
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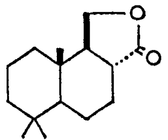
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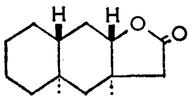
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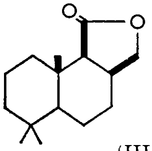
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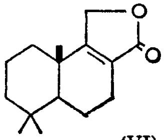
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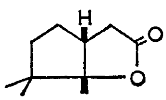
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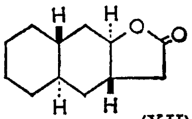
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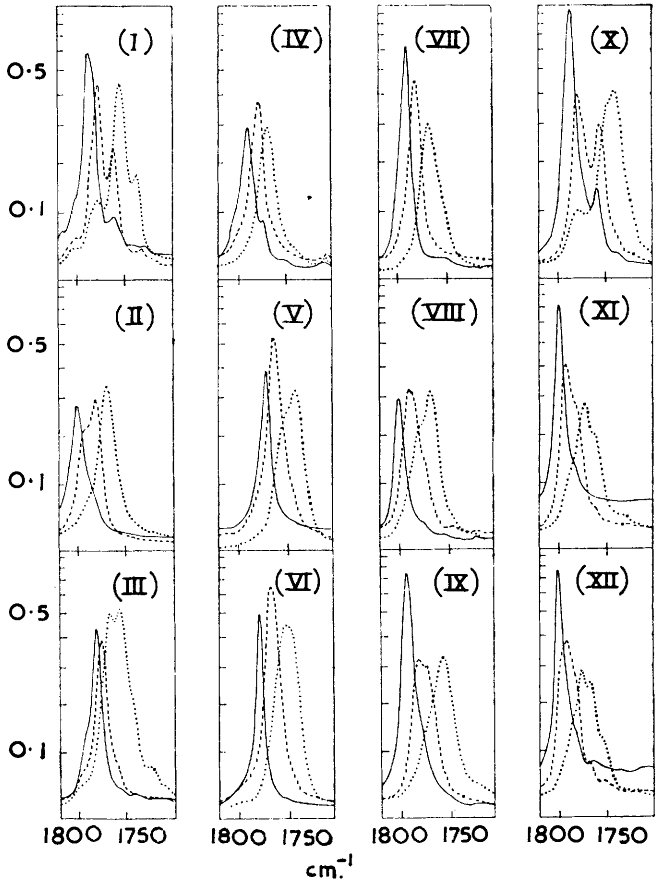

FIGURE 1. Absorptions in the carbonyl stretching region of the twelve lactones (I ⟶ XII) in n-hexane, carbon tetrachloride, and chloroform. Curves indicate n-hexane (——), carbon tetrachloride (– – – –), and chloroform (····). Solutions (*ca.* 0·01M) examined in 0·5 mm. cells.

Absorptions in the carbonyl stretching region of the lactones (I $\longrightarrow$ XII) in various solvents

		n-Hexane			CCl$_4$			CHCl$_3$		
No.	Compound	ν	$\Delta\nu_{\frac{1}{2}}{}^{a}$	ε^{a}	ν	$\Delta\nu_{\frac{1}{2}}{}^{a}$	ε^{a}	ν	$\Delta\nu_{\frac{1}{2}}{}^{a}$	ε^{a}
(I)	β-Angelicalactone	1800	sh	200	1802	sh	100	1804	—	w
		1791	13	1120	1783	15	840	1784	22	230
		1762	—	140	1765	11	445	1759	15	845
								1741	12	325
(II)	γ-Butyrolactone	1801	16	500	1796	sh	415	1793	sh	—
		1787	sh	—	1784	11	570	1774	19	630
(III)	Dihydrodrimenin	1798	sh	—	1797	sh	—	1770	26	480
		1787	11	880	1779	13	800	1760		500
					1758	sh	—			
(IV)	Drimenin	1789	14	595	1781	15	705	1771	19	630
		1772	sh	170						
(V)	Isodrimenin	1773	10	730	1766	14	1095	1751	sh	500
								1741	28	670
(VI)	Confertifolin	1777	7	1000	1769	14	1235	1750	27	930
(VII)	*cis*-Dihydroconfertifolin	1791	9	1000	1779	13	925	1772	22	685
(VIII)	*trans*-Dihydroconfertifolin	1801	12	900	1792	18	680	1782	sh	420
					1778	sh	—	1770	27	620
(IX)	Dihydrocampholenolactone	1791	11	870	1783	26	600	1757	27	650
					1775					
(X)	Campholenolactone	1786	9	1300	1783	18	760	1782	23	180
		1758	—	190	1759	14	575	1752	sh	—
								1744	24	700
(XI)		1805	9	1310	1797	21	820	1777	27	530
					1787	sh	610	1766	sh	370
(XII)		1806	8	1370	1796	23	800	1780	28	560
					1786	sh	520	1772		520

Solutions *ca.* 10 mM run in 0·5 mm. cells. —, Not measured. sh, shoulder. w, weak.

complex and also markedly solvent-sensitive (Figure 1). Bifurcate bands in the carbonyl region of compounds containing a single carbonyl function can have their origin in conformational equilibria,[9] solvent–solute interactions,[10] hot transitions,[11] Fermi resonance,[12] or vibrational coupling.[12] Other explanations such as intermolecular hydrogen bonding through enolic forms and by methylene groups [13] are at variance with normal experience. We have tried to establish the origin of the irregularly shaped bands and these attempts, involving the effects of solvent, temperature, and of an additional solute, are discussed below. Some more general points are dealt with first.

The lactones show the simplest carbonyl bands in n-hexane solution, and if the approximate peak positions are compared over the limited range of compounds examined, one can conclude that it is not possible to distinguish saturated γ-lactones from their $\alpha\beta$-unsaturated counterparts by simple inspection of the peak maxima. However, it is true that in the present Series the saturated lactones lie in the range 1806—1787 cm.$^{-1}$ while the $\alpha\beta$-unsaturated compounds absorb between 1791 and 1773 cm.$^{-1}$. This partial overlap is, of course, the result of the competing effects of conjugation and strain.[14] Where direct comparison is possible between an $\alpha\beta$-unsaturated five-ring lactone and the corresponding dihydro-compound then the latter does absorb to slightly higher frequency, but stereochemical differences can also produce significant frequency shifts, as for example, between lactones (VII and VIII). It is more difficult to compare the different lactones in carbon tetrachloride and chloroform solution because of the more irregular shapes, or even the splitting, of the bands in the latter solvent. However, if an approximate estimate of the position of the band centre is made then, it is found that the shifts, hexane to chloroform, range from 18 to 36 cm.$^{-1}$, with the smaller shifts being encountered with the lactones

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(III, IV, and VII), where there might be some grounds for assuming a steric inhibition to solvation.

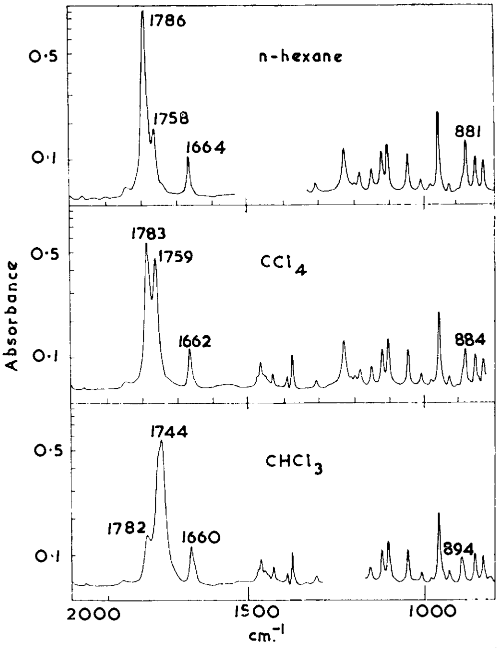

FIGURE 2. The spectrum of campholenolactone (X) recorded over the range 800—2000 cm.$^{-1}$ for *ca.* 0·05 M-solutions (0·1 mm. cells) in n-hexane, carbon tetrachloride, and chloroform.

Figure 1 reveals that the general pattern is such that some lactones show several shoulders, or even distinct bands, in the carbonyl region and that these vary in intensity with change of solvent as the main carbonyl absorption moves through the region. However, the overall intensity, as measured by the approximate band area, over the carbonyl region is much the same in the three solvents, no matter how split up the band. Only the pair of αβ-unsaturated lactones (I and X) bearing an α-hydrogen show marked splitting in all three solvents. The other unsaturated lactones (IV, V, and VI) show much smoother band contours rather like those of the saturated lactones (II, III, VII, IX, XI, and XII). Campholenolactone (X) exhibits the phenomenon most markedly; thus there is a shift of the main absorption band from 1786 cm.$^{-1}$ in n-hexane to around 1750 cm.$^{-1}$ in chloroform. This direction of shift is characteristic of that found for the stretching absorption of an $X^{\delta+}=O^{\delta-}$ dipole, and is attributed to an intermolecular association[12] of the type[12] $X^{\delta+}=O^{\delta-} \cdots HCCl_3$. It is conceivable that more than one band could result from the presence of several solute–solvent species, but this seems unlikely in view of the complexity shown in carbon tetrachloride, for which specifically orientated complexes seem unreasonable. At this juncture, one might assign the absorption at 1786 cm.$^{-1}$ (in n-hexane) to the stretching absorption of the C=O bond. However, the band at lower frequency (1758 cm.$^{-1}$ in n-hexane and 1759 cm.$^{-1}$ in carbon tetrachloride) increases in intensity at the expense of the higher frequency band, and it is evident that the true position for ν(C=O) cannot be determined by simple inspection. This transference of intensity in the 1700—1800 cm.$^{-1}$ region is further illustrated in Figure 2. The remainder of the spectrum is practically unaltered by change of solvent, indicating that a solvent-sensitive conformational equilibrium is not present, since different conformers normally have several different absorption bands. There is, however, a band at 881 cm.$^{-1}$ (in n-hexane), $\Delta\nu_{\frac{1}{2}}{}^{a} = 8$ cm.$^{-1}$, $\varepsilon^{a} = 190$, which progressively increases in frequency as the polarity of the solvent is increased. This absorption band is in the region expected for the out-of-plane deformation vibration of the α-hydrogen attached to the double bond and we assume that this is the correct assignment. Indeed, Jones and collaborators have already suggested[2] that Fermi resonance with the first overtone, 2γ(CH), of this vibration might be responsible for the bifurcate absorptions reported for the carbonyl regions of other lactones of type (A). Our data accord well with their findings; thus, in the case of campholenolactone (X), the main band in the carbonyl region *decreases* in frequency as the polarity of the solvent is increased, while the band assigned to the γ(CH) of the α-hydrogen *increases* in frequency; in the absence of Fermi resonance, the first overtone of 2γ(CH) would be expected to lie near 1762, 1786, and 1788 cm.$^{-1}$ in n-hexane, carbon tetrachloride, and chloroform, respectively. If we assume that, for a solution of campholenolactone (X) in n-hexane, the intense band at 1786 cm.$^{-1}$ and the small peak at 1758 cm.$^{-1}$ represent largely unperturbed ν(C=O) and 2γ(CH) absorptions, respectively, then normal solvent-shifts of the former would bring it to about 1776 cm.$^{-1}$ in CCl_4 and 1756 cm.$^{-1}$ in $CHCl_3$. Fermi resonance would then be maximal in CCl_4 where the two interacting frequencies are closest, *ca.* 1776 and 1778 cm.$^{-1}$. Decreased interaction would be expected in chloroform where the two frequencies would again be well separated, though now in the reverse order. Hence, in the case of campholenolactone (X), Fermi resonance between ν(C=O) and 2γ(CH) could account reasonably well for the observed solvent-dependence of the absorptions in the carbonyl region. Solvation undoubtedly does affect the α-hydrogen in some specific way as indicated not only by the upward shift of the band assigned to γ(CH) in the infrared but also by the downfield shift of the signal due to this proton in the n.m.r. When going from n-hexane to carbon tetrachloride to chloroform only the triplet due to this proton was seen to move appreciably, thus: τ(n-hexane) = 4·42, $\tau(CCl_4)$ = 4·37, $\tau(CHCl_3)$ = 4·26.

Fermi resonance with 2γ(CH) can only be part of the answer, for β-angelicalactone shows more complex absorption still and the lactones which do not possess α-olefinic hydrogens also exhibit irregular or partially split bands. However, there is no uniform behaviour in the saturated lactones and some (*e.g.*, VI and VII) have fairly sharp single peaks in all three solvents. A simple saturated γ-lactone can have a high ν(C=O) frequency and a very high apparent intensity (peak height) where the band is sharp, *e.g.*, (XI), ν(C=O) = 1805 cm.$^{-1}$ and ε^a = 1310, in n-hexane. In any case, a single conformer should give a sharp carbonyl band in the absence of Fermi resonance, but there is the complicating factor that enhanced resonance could occur if the geometry of this single conformer happened to be favourable. Other overtones and combinations must be involved if Fermi resonance is indeed the correct explanation, but there seems little hope of locating the relevant fundamentals. The strong absorptions in the 1300—900 cm.$^{-1}$ region, which are ascribed to ν(C–O) modes, are possibilities, but we are unable to correlate their frequencies with those in the carbonyl region. Each lactone displays several strong bands (ε^a, 150—500) but the regions of strongest absorption are often quite different. Thus, for lactones (V) and (VI) the strongest bands are clustered around 1000 cm.$^{-1}$, for (IX) and (X) they are near 1240, 1100, and 950 cm.$^{-1}$, and for (II) there is only one intense band near 1250 cm.$^{-1}$, with weaker absorptions near 1030 cm.$^{-1}$. Changes in ring strain, steric interactions, and bond hybridisation presumably engender the wide variations encountered within this region. Incidentally, these strong, sharp absorptions, when they appear as low as 900 cm.$^{-1}$ in the spectrum of a γ-lactone, are readily confused with γ(CH) absorptions for doubly-bonded carbon.

We have sought further information by submitting two of the lactones to measurement at high temperatures and in the presence of a second solute. The absorptions in the ν(C=O) regions of solutions (*ca.* 0·4M) of β-angelicalactone (I) and campholenolactone (X) in tetrachloroethylene were examined at 30 and 75°. No clearly defined change was observed apart from the expected slight reduction in peak height at the higher temperature and no definite conclusion may be drawn though these results could be taken as negative evidence in favour of the Fermi resonance explanation. Addition of *p*-cresol to a solution of a lactone in n-hexane brings about specific solvation of the lactone group by the *p*-cresol molecules. The association (Figure 3) is of the type $Me{\cdot}C_6H_5{\cdot}OH \cdots O{=}C{<}$, as evinced by the low values for ν(OH) and the "carbonyl band"—in the case of campholenolactone (X), *ca.* 3420 and 1744 cm.$^{-1}$, respectively. The shifting of the equilibrium towards the complex with increasing *p*-cresol concentration is apparent from the data in Figure 3 and there is clearly a general resemblance between the carbonyl region observed for a *p*-cresol–lactone complex and that for the lactone alone in the chloroform solution. This is in keeping with the results for solution spectra of, *inter alia*, cyclohexanones[10,15] and sulphoxides.[12] Although it seems that the equilibrium has not been displaced as far as complete complex formation, the bands show fine structure indicative of Fermi resonance. In the hydroxyl region, competing self-association[16] of the *p*-cresol gives rise to cresol dimer, and trimer or polymer absorptions near 3500 and 3200 cm.$^{-1}$, respectively; at the 0·064M-*p*-cresol concentration there may be some complex formation of the type ArOH · · · · ArOH · · · · O=C$<$.

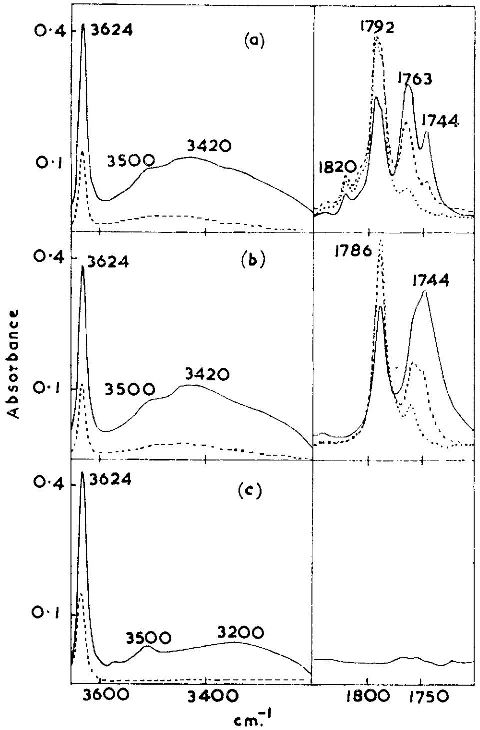

FIGURE 3. Absorptions in the hydroxyl and carbonyl stretching regions for solutions (*ca.* 0·015M) of (a) β-angelicalactone (I) and (b) campholenolactone (X) in n-hexane alone (· · · ·), and in mixtures of n-hexane and *p*-cresol (– – – –, 0·016M, and ——, 0·064M). Absorptions are also recorded for n-hexane solutions of (c) *p*-cresol (– – – –, 0·016M; and ——, 0·064M). All measurements in 0·5 mm. cells.

In carbon tetrachloride, γ(CH) for campholenolactone (X) is assigned to the band at 884 cm.$^{-1}$ (Figure 2). Introduction of *p*-cresol into the solution brings about the appearance of a shoulder at 890 cm.$^{-1}$ which is accordingly attributed to the γ(CH) for the cresol–lactone complex. Here, and in the case of chloroform solvation, the effect is probably brought about by the shift of the π electrons of the double bond which would accompany donation of electron density by the carbonyl group to the phenolic proton.

In summary, carbonyl absorption bands of complex shape seem to be a fairly common feature of γ-lactones, whether they possess αβ-unsaturation or not. Fine structure is especially prominent in those αβ-unsaturated lactones which bear an α-hydrogen, and here Fermi resonance with 2γ(CH) probably supplies part of the explanation. The problem merits further study, particularly by isotopic substitution and by the solvation complex approach.

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