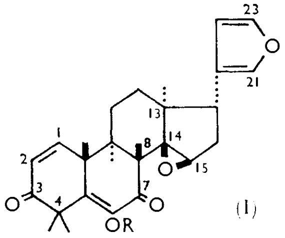
217. *Infrared Studies of Terpenoid Compounds. Part I. Hydrogen Bonding in Cedrelone and Related Compounds.*

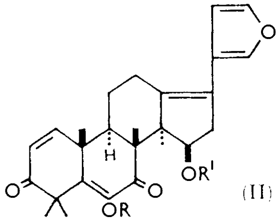
By T. Cairns, G. Eglinton, and S. G. McGeachin.

Cedrelone (I; R = H) is a natural product whose chemistry and precise stereochemistry have been firmly established. Spectra of solutions of cedrelone and related compounds characterize the intramolecular hydrogen bonds closing the planar five-membered diosphenol ring and a twisted seven-membered ring. Additional data illustrate the constancy of both ν(CO) and ν(OH) when certain intramolecular situations are held relatively constant.

The presence or absence of intramolecular hydrogen bonding in natural products can frequently be inferred from an examination of the hydroxyl stretching frequencies obtained with dilute solutions in inert solvents.[1] Such information can have considerable diagnostic value but there are few instances in the literature where the spectral data refer to molecules of precisely known stereochemistry. The complete structure of the degraded C_{26} triterpene cedrelone [2] (I; R = H) has been recently determined (as the iodoacetate) by *X*-ray crystallography [3] and the present work deals with spectra–structure correlations for cedrelone and related compounds (I to VII). Hydroxyl, carbonyl, and carbon–carbon double bond absorptions are listed in the Tables and illustrated in the Figures, but emphasis is placed on the various types of intramolecular hydrogen bond encountered.



(I)



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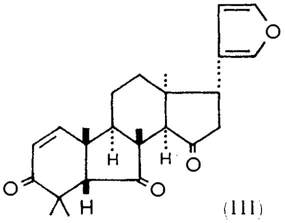
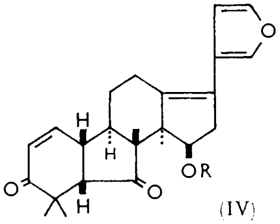


(III)



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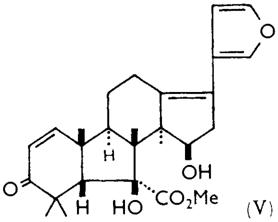

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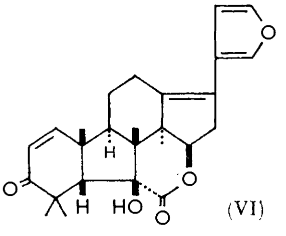

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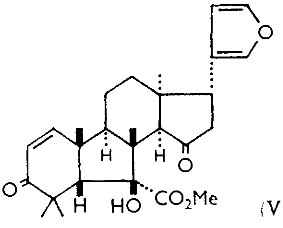

(VII)

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[1] Cole and Muller, *J.*, 1959, 1224; Eglinton, *Unicam Spectrovision*, 1960, **9**, 1.

[2] Hodges, McGeachin, and Raphael, *J.*, 1963, 2515.

[3] Grant, Hamilton, Hamor, Robertson, and Sim., *J.*, 1963, 2506.

EXPERIMENTAL

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 [3000 lines per inch (2150—3650 cm.$^{-1}$) and 1500 lines per inch (650—2150 cm.$^{-1}$)] operated under vacuum. The calibration was checked against the spectrum of water vapour after each group of measurements. The hydroxyl and carbonyl absorptions were scanned at 4·6 and 8·0 cm.$^{-1}$ per min., respectively. Frequency measurements for the " free " and intrabonded hydroxyl and carbonyl bands are believed to be accurate to ± 1 cm.$^{-1}$. The linearity of the percentage transmission scale was checked by Shrewsbury's procedure,[4] and the intensities were measured on bands of not less than 10% transmission. The theoretical spectral slit-width, computed from tables supplied by Unicam Instruments Ltd., was 5·5 cm.$^{-1}$ at 3600 cm.$^{-1}$, 4·5 cm.$^{-1}$ at 3350 cm.$^{-1}$, and 3·4 cm.$^{-1}$ at 1700 cm.$^{-1}$. Unless specified otherwise, peaks were symmetrical; the apparent half-band widths, $\Delta\nu_{\frac{1}{2}}^{a}$, are quoted to the nearest integer; where necessary they were determined by reflection of the undisturbed wings of the unsymmetrical bands. Intensities are given as apparent extinction coefficients, ε^{a}, (l. mole^{-1} cm.$^{-1}$) rounded to the nearest 5 units and measured from a solvent–solvent base-line superimposed on the record of the spectrum of the solution (determined with solvent in the reference beam).

Materials.—AnalaR carbon tetrachloride was used without further purification. AnalaR chloroform was dried several times by passage through a column of blue silica gel before direct use. Spectroscopic grade bromoform was used without further purification. The carbon tetrachloride–ether solutions were prepared by using sodium-dried ether which was rapidly dispensed to avoid absorption of atmospheric moisture; cell paths of 2 mm. (hydroxyl region) and 0·5 mm. (carbonyl region) were employed. The preparations of compounds (I) to (VII) have been described elsewhere.[2]

The arabic numerals used in the text, Tables and Figures refer to the compounds examined and related to them as follows (Table 1 should be consulted for the relevant Roman numerals):

1. Cedrelone methyl ether
2. Cedrelone acetate
3. 1,2-Epoxycedrelone acetate
4. 1,2-Dihydrocedrelone acetate
5. Hexahydrocedrelone acetate
6. Cedrelone
7. 1,2-Epoxycedrelone
8. 1,2-Dihydrocedrelone
9. Hexahydrocedrelone
10. Isocedrelone diacetate
11. 23-Acetylisocedrelone diacetate
12. 21-Acetylisocedrelone diacetate
13. Isocedrelone acetate
14. Isodihydrocedrelone acetate
15. Isocedrelone
16. Isodihydrocedrelone
17. Norketone (III)
18. Norketone (IV); 15-Oxo
19. Norketone (IV; R = H)
20. Norketone acetate (IV; R = Ac)
21. Isocedrelonic acid
22. Isocedrelonic acid lactone
23. Methyl neoisocedrelonate

RESULTS AND DISCUSSION

The results are detailed in Tables 1 and 2 and summarized in Table 3. One important structural feature of cedrelone and its close relatives (I) is that ring C is held in the boat conformation. Other related compounds (II) have the more favoured chair conformation in ring C and are referred to as isocedrelones.

In both cedrelone methyl ether (I; R = Me) and cedrelone acetate (I; R = Ac) the presence of a conjugated enone system in ring A and in ring B is characterized by a single, intense, symmetrical absorption at *ca.* 1700 cm.$^{-1}$ (in CCl_4; Table 1, compounds 1 and 2). The high extinction coefficient of this absorption accords with the presence of two carbonyl groupings. Introduction of an epoxide grouping at positions 1 and 2 as in 1,2-epoxycedrelone acetate (Table 1, compound 3) splits the carbonyl absorption into two well-defined bands: the higher-frequency band at 1722 cm.$^{-1}$ (in CCl_4) is attributed to the carbonyl adjacent to the epoxide group in ring A, and the lower frequency absorption at 1708 cm.$^{-1}$ (in CCl_4) is assigned to the ring B carbonyl. Saturation of the double bond in ring A (compounds 4 and 5) slightly reduces the absorption frequencies of both carbonyl groups as compared with those observed for the 1,2-epoxy compound.[5] Even so, the ring A carbonyl frequency for the 1,2-dihydro-compounds is somewhat higher (1714 cm.$^{-1}$ in

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[4] Shrewsbury, *Unicam Spectrovision*, 1958, **6**, 1.

[5] Lehmann, Schaffner, and Jeger, *Helv. Chim. Acta*, 1962, **45**, 1031.

TABLE 1.

Carbonyl absorptions of cedrelone and related compounds.

Cmpd No.	System			Additional structural features	Ring A carbonyl						Ring B carbonyl						Additional carbonyl bands						Species
					CCl_4			$CHCl_3$			CCl_4			$CHCl_3$			CCl_4			$CHCl_3$			
	Formula	R	R^1		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}	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}	
1	I	Me			1696 †	11	1290	1692 †	20	940	1696 †	11	1290	1692 †	20	940							
2		Ac			1701 †	18	870	—	—	—	1701 †	18	870	—	—	—	1770	12	500	—	—	—	enol OAc
3		Ac		1,2-Epoxy	1722[b]	10	620	1721[b]	13	320	1708	10	680	1705[b]	20	340	1770	14	460	1763	22	230	enol OAc
4		Ac		1,2-dihydro	1720[b]	11	630	1714sh	19	520	1705[b]	12	740	1702	18	655	1770	14	550	1764	17	500	enol OAc
5		Ac		1,2,20,21,22,23-hexahydro	1720[b]	10	600	1714sh	16	520	1705[b]	12	750	1701[b]	22	625	1770	14	515	1763	17	440	enol OAc
6		H			1695[b]	20	540	1685sh	—	—	1678[b]	15	570	1678[b]	18	770							
7		H		1,2-epoxy	1723	11	585	1719	20	465	1681	13	535	1681	19	450							
8		H		1,2-dihydro	1718	10	665	1713	17	465	1678	13	550	1677	18	440							
9		H		1,2,20,21,22,23-hexahydro	1717	9	645	1712	17	440	1678	12	565	1676	19	420							
10	II	Ac	Ac		1698 †[a]	13	1060	1694 †[a]	19	705	1698 †[a]	13	1060	1694 †[a]	19	705	1766	15	670	1759[a]	25	490	enol OAc
																	1743	17	560	1729	35	420	OAc ($C_{(15)}$)
11		Ac	Ac	23-acetyl	1699 †[b]	10	1120	1693 †[b]	14	750	1699 †[b]	10	1120	1693 †[b]	14	750	1767	15	680	1760[a]	20	430	enol OAc
																	1743[b]	18	560	1729	33	395	OAc ($C_{(15)}$)
																	1688sh	10	740	1683	—	—	Ac ($C_{(23)}$)
12		Ac	Ac	21-acetyl	1697 †[b]	14	1330	1688 †	26	920	1697 †[b]	14	1330	1688 †	26	920	1767	14	610	1760[a]	20	350	enol OAc
																	1744	19	490	1730	29	290	OAc ($C_{(15)}$)
																	1692sh	—	—	1688 †	26	920	Ac ($C_{(21)}$)
13		Ac	H		1699	15	—	1695[b]	18	475	1672	20	—	1667[b]	22	460	1771	15	—	1764	18	470	enol OAc
14		Ac	H	1,2-dihydro	1721	12	—	1714	20	490	1672	15	—	1665	22	350	1772	15	—	1764	24	560	enol OAc
15		H	H		1699[a]	—	—	1685[a,b]	22	320	1622	—	—	1619[a]	25	340							
16		H	H	1,2-dihydro	1718	11	560	1713	17	420	1623[b]	11	540	1620	17	450							
17	III				1692	16	—	1683	22	480	1758 †	11	—	1751 †	16	750	1758 †	11	—	1751 †	16	750	Ring D CO
18	IV			15-keto	—	—	—	1683	21	525	—	—	—	1755 †	14	800	—	—	—	1755 †	14	800	Ring D CO
19		H			1691	14	670	1683	23	495	1718[b]	17	385	1714[b]	26	290							
20		Ac			1690	15	620	1682	25	470	1742 †	23	725	1738 †	31	655	1742 †	23	725	1738 †	31	655	OAc($C_{(15)}$)
21	V				1688[b]	14	—	1677[b]	22	620							1705[b]	15	—	1703[b]	21	425	Ester CO
22	VI				1686	12	470	1677	20	520							1753	15	450	1743	25	445	Lactone CO
23	VII				1690	18	—	1683	21	—							1742 †	16	—	1735 †	22	—	Ester CO
																	1742 †	16	—	1735 †	22	—	Ring D CO

Molarities generally in the range 1 to 20 mM, but some solutions were saturated and of unknown concentration. ν and $\Delta\nu_{\frac{1}{2}}^{a}$ are in cm.$^{-1}$. Cell paths: for CCl_4 5 mm., $CHCl_3$ 0·51 mm. — Not measured.[4]

† Two or more bands superimposed at this frequency; only one set of data (ν_{max}, $\Delta\nu_{\frac{1}{2}}^{a}$, ϵ^{a}) is quoted and correlations based on these values are more tentative, since the contributions of the individual stretching absorptions cannot be observed. [a] Asymmetric band. [b] $\Delta\nu$ ^{a}calculated by using the undisturbed wing of asymmetric bands. sh Shoulder, $\Delta_{\frac{1}{2}}^{a}$ calculated as in [b].

TABLE 2.

Hydroxyl and carbon–carbon double bond absorptions of cedrelone and related compounds.

Cmpd No.	System			Additional structural features	Ring B hydroxyl						Ring D hydroxyl						Carbon–carbon double bonds					
					CCl_4			$CHCl_3$			CCl_4			$CHCl_3$			CCl_4			$CHCl_3$		
	Formula	R	R¹		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}	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}
1	I	Me															(1654)	sh	vw			
																	(1621)	sh	vw	1622	—	vw
3		Ac		1,2-epoxy													(1617)	—	—	1615	(17)	(50)
4		Ac		1,2-dihydro													(1615)	—	—	1612	(16)	(130)
5		Ac		1,2,20,21,22,23-hexahydro													1623	(25)	w	1610	(15)	(95)
6		H			3417	41	115	3425	64	90							1629	(13)	(145)	1627	(19)	(180)
7		H		1,2-epoxy	3418	38	120	3428	58	95							1629	(13)	(140)	1630	(18)	(150)
8		H		1,2-dihydro	3418	39	125	3430	64	90							1627	(10)	(160)	1626	(15)	(170)
9		H		1,2,20,21,22,23-hexahydro	3420	38	120	3430	60	85							1626	(10)	(150)	1624	(13)	(180)
10	II	Ac	Ac														1638	(20)	(115)	1637	(28)	(115)
11		Ac	Ac	23-acetyl													1639	(18)	(125)	1638	(22)	(120)
12		Ac	Ac	21-acetyl													1639	—	(100)	1638	—	(60)
13		Ac	H								3460	(120)	—	3415	195	95	1630	—	w	1630	(20)	(225)
14		Ac	H	1,2-dihydro							3450	(120)	—	3410	br	—				1628	(24)	(210)
15		H	H		3413 *b*	56	—	3418 †*a*	115	145	3475 *b*	98	—	3418 †*a*	115	145	1658	—	—	1659	—	(145)
16		H	H	1,2-dihydro	3415 *b*	50	190	3418 †	105	200	3466 *b*	80	130	3418 †	105	200	1658	11	200	1658	15	135
19	IV	H									3470	76	110	3440	126	80				1631	—	—
21	V				3530	29	—	3525 *b*	58	80	3602	28	—	3604 *a*	52	95						
22	VI				3595	16	110	3593	20	100							1629	—	—			
23	VII				3546 *a*	85	—	3520	100	—												

Values in parenthesis are approximate. For symbols see Table 1. Cell paths, $\nu(OH)$: for CCl_4 2 cm.; $CHCl_3$ 2 mm; $\nu(C{=}C)$: for CCl_4 5 mm., $CHCl_3$ 0·51 mm. Dilutions were made but no change was encountered. Compound 1, and others, have a weak to medium strength band near 1600 cm.$^{-1}$ (in $CHCl_3$) which is assigned to one of the stretching modes of the furyl group (cf. ref. 13).

TABLE 3.

Assignments for stretching absorptions due to carbonyl and hydroxyl functions.

Grouping	Average values ν (cm.$^{-1}$)	$\Delta\nu$ * (cm.$^{-1}$)
3-Ketone in ring A	1720	6
3-Ketone in ring A, 1,2-epoxide	1722	2
3-Ketone in ring A, $\Delta^{1,2}$ and six-membered ring B	1698	9
3-Ketone in ring A, $\Delta^{1,2}$ and five-membered ring B	1689	9
7-Ketone of diosphenol	1679	1
7-Ketone of diosphenol and bonding by 15-hydroxyl	1622	3
7-Ketone of diosphenol methyl ether	1696	4
7-Ketone of diosphenol acetate, cedrelones	1704	3
7-Ketone of diosphenol acetate, isocedrelones	1698	5
7-Ketone of diosphenol acetate and bonding by 15-hydroxyl	1672	6
6-Acetate of diosphenol acetates, ring B	1769	7
15-Acetate, ring D	1743	14
6-Hydroxy of diosphenol in ring B	3416	−8
15-Hydroxyl in ring D, bonding to 7-ketone	3460	45

All data drawn from Tables 1 and 2. * $\Delta\nu = \nu_{CCl_4} - \nu_{CHCl_3}$. Typical variation amongst ν(CO) values ± 3 cm.$^{-1}$.

$CHCl_3$), than has been previously described for a 4,4-dimethyl-3-oxo-5α-system.[6] Lehn, Levisalles, and Ourisson [7] conclude that ring A in such systems exists as a deformed chair—a decision reached after taking into account the interactions between 1,3-diaxial methyl groups. The *X*-ray analysis [3] of cedrelone iodoacetate, however, revealed that ring A possessed a boat-like conformation rather than the alternative half-chair; the former presumably minimizes the non-bonded interactions between the 4-methyl groups and the bulky 6-substituent. The same argument should apply to cedrelone and its simple derivatives whether the particular molecule is in a crystal lattice or is surrounded by relatively inert solvent molecules. There is no marked change in the carbonyl absorptions (Table 1) on passing from carbon tetrachloride to chloroform solution, only the expected lowering in frequency (by 5—10 cm.$^{-1}$) and the increased breadth of the bands.[8] Preferential solvation of the α-epoxy-group may explain the unusually small shifts recorded for the two compounds having this grouping.

In the spectrum of cedrelone itself (compound 6) there are two peaks in the carbonyl region (1695 and 1678 cm.$^{-1}$ in CCl_4; Table 1) and one band in the hydroxyl region (3417 cm.$^{-1}$ in CCl_4; Table 2). The data for dihydrocedrelone (compound 8; Fig. 1) reveal that the higher band, that at 1695 cm.$^{-1}$, in the spectrum of cedrelone is to be attributed to the ring A carbonyl. Incidentally, this absorption moves about 9 cm.$^{-1}$ to lower frequency when ring B is five-membered, presumably as a result of bond-angle changes at the A/B ring junction.

The carbonyl and hydroxyl absorptions of the diosphenol system in cedrelone and derivatives are typically both low in frequency and insensitive to solvation.[8] A planar projection of a Dreiding model of dihydrocedrelone (compound 8) is illustrated in Fig. 2. The intramolecular diosphenol hydrogen bond is in the form of a planar ring with an O · · · O distance of *ca.* 2·8 Å and the angle subtended at the carbonyl oxygen atom by the proton of the hydroxyl group is 80°. This is a particularly well-defined conformation and the intra-bonded ν(OH) absorption is unusually narrow.[9]

We now turn to the isocedrelones (II), which have the more favoured chair conformation in ring C. In the case of isocedrelone diacetate (compound 10) the enone systems in rings A and B are characterized by a very strong absorption at 1698 cm.$^{-1}$ (in CCl_4; Table 1). Replacement of one of the acetate groupings by a hydroxyl group (compound 14) causes the formation of a seven-membered hydrogen bond involving the ring B carbonyl (shift

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[6] Allinger and DaRooge, *Tetrahedron Letters*, 1961, **19**, 676; *J. Amer. Chem. Soc.*, 1962, **84**, 4561.
[7] Lehn, Levisalles, and Ourisson, *Bull. Soc. Chim.*, 1963, 1096.
[8] Brooks, Eglinton, and Magrill, *J.*, 1961, 308.
[9] Cairns and Eglinton, *Nature*, 1962, **196**, 535.

to 1672 cm.$^{-1}$ in CCl_4) and the ring D hydroxyl (Tables 1 and 2, and Fig. 1). When both acetate groupings are replaced by hydroxyls, as in dihydroisocedrelone (compound 16), the ring B carbonyl absorption appears to shift to much lower frequency (1623 cm.$^{-1}$ in CCl_4) and two hydroxyl absorptions are observed at 3415 and 3466 cm.$^{-1}$ (Fig. 1), and hence both hydroxyl groups require to be intramolecularly hydrogen bonded to the carbonyl function in ring B. This is illustrated in the planar projection of the Dreiding model shown in Fig. 2. The planar five-membered ring hydrogen bond of the diosphenol group exists as it does in dihydrocedrelone (compound 8, Fig. 2), but the seven-membered ring formed by the intramolecular hydrogen bond involving the ring D hydroxyl must be twisted. Measurements with the model give an O · · · O distance for this latter hydrogen bond of *ca.* 2·8 Å, the dihedral angle formed by the bonds linking $C_{(17)}$, $C_{(15)}$, and $O_{(4)}$ as 45°, and the angle made by the O–H bond with the line joining the two oxygen centres as 15°. Once again the stereochemistry must be favourable to hydrogen-bond formation, although the breadth of the absorption band is much greater than that of the diosphenol system,

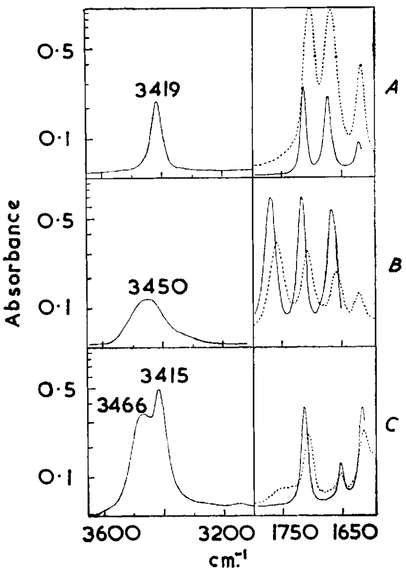

FIG. 1. Absorptions in the hydroxyl and carbonyl stretching regions. *A*, Dihydrocedrelone (8); *B*, dihydroisocedrelone acetate (14); and *C*, dihydroisocedrelone (16) in carbon tetrachloride (full line) and bromoform (broken line). Solutions in carbon tetrachloride in 2 cm. (hydroxyl region) and 5 mm. (carbonyl region) cells; bromoform, 0·47 mm. cells. Concentrations: for carbon tetrachloride solutions compounds 8 and 16 were 1·5 and 1·3 mM respectively while the rest were saturated solutions.

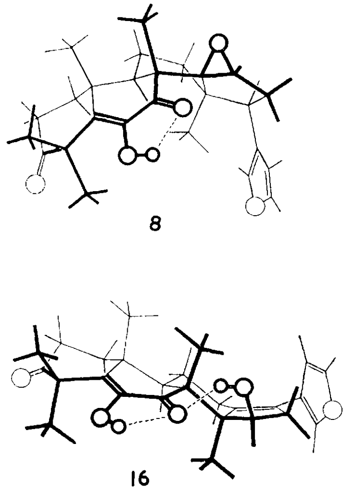

FIG. 2. Projections of Dreiding models of compounds 8 and 16. Thickened lines indicate nearest side of the molecule and dotted lines the hydrogen bonds.

suggesting a greater degree of conformational freedom. However, the ring B carbonyl is actually at a slightly lower value when bonded singly by the ring D hydroxyl rather than by the diosphenol hydroxyl itself (*e.g.*, compounds 13 and 6, respectively; a more closely matched pair of compounds was not available). An interesting and related example of a hydrogen bond closing a seven-membered ring has been provided by Wall *et al.*;[10] the compound is a steroid derivative, 3β-acetoxy-4′-hydroxy-2′-methyl-16,17-butano-5α-androsta-1′,3′,16-trien-12-one, and the oxygen atoms of the phenolic hydroxyl and the cyclohexanone-type carbonyl are held by the rigid framework. The hydrogen bond is quite strong [ν(OH) = 3235 cm.$^{-1}$ and ν(CO) = 1685 cm.$^{-1}$ in CS_2] in spite of the enforced aplanarity of the carbon–oxygen bonds.

Also illustrated in Fig. 1 are the results obtained with bromoform solutions (broken lines). These measurements support our view that the strong band at 1623 cm.$^{-1}$ (in CCl_4) exhibited by dihydroisocedrelone (compound 16) corresponds to the carbonyl (ring B) which is hydrogen bonded by both hydroxyls. If the bands at 1658 and 1623 cm.$^{-1}$ had been mutually involved in Fermi resonance or vibrational coupling, then change of solvent would have altered their relative intensities.[11] We assign the band of medium strength at 1658 cm.$^{-1}$ (in CCl_4) to a double-bond stretching vibration (see below).

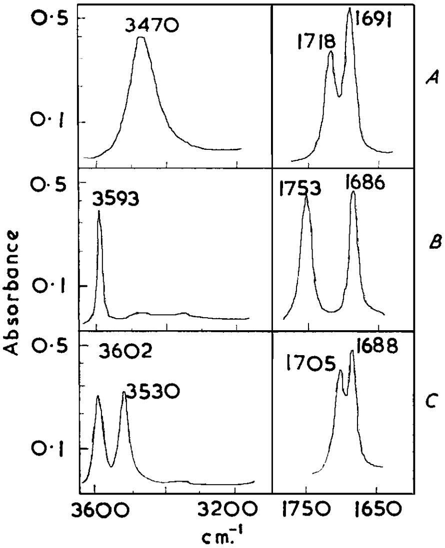

FIG. 3. Absorptions in the hydroxyl and carbonyl stretching regions. *A*, The norketone (19); *B*, isocedrelone acid lactone (22); and *C*, methyl isocedrelonate (21). Solutions in carbon tetrachloride in 2 cm. (hydroxyl region) and 5 mm. (carbonyl region). Concentrations for compounds (19), (22), and (21) were 1·67, 1·72 mM, and saturated respectively.

Absorption data have been obtained for solutions of hexahydrocedrelone (compound 9) and of isocedrelone acetate (compound 13) in carbon tetrachloride–diethyl ether solvent mixtures (up to 50% ether by volume). No marked changes were observed in the intensity, breadth, or position of the hydroxyl and carbonyl absorptions. Diethyl ether normally behaves as a Lewis base,[12] but it is evident that the intramolecularly bonded hydroxyls in these particular molecules are not readily accessible; in compound 9 the methyl groups on position 4 lie very close to the diosphenol hydroxyl and may well prevent approach of the solvent molecules while in both compounds 9 and 13 the intramolecular hydrogen bonds confer some degree of solvent insensitivity. Even so, some indications of intermolecular hydrogen bond formation could be discerned at the higher ether concentrations; thus, there was a new, very broad and low absorption in the hydroxyl region and there was some reduction in the intensity of the intrabonded carbonyl of ring B relative to that of the ring A carbonyl.

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[10] Wall, Serota, Kenney, and Abernethy, *J. Amer. Chem. Soc.*, 1963, **85**, 1844.

[11] Cairns, Eglinton, and Gibson, *Spectrochim. Acta*, 1964, **20**, 31.

[12] Brown, Eglinton, and Martin-Smith, *Spectrochim. Acta*, 1963, **19**, 463.

Contraction of ring B to a five-membered system, as in compound 17 (III), raises the carbonyl stretching frequency to 1758 cm.$^{-1}$ (in CCl_4), but introduction of a hydroxyl into ring D, as in compound 19 (IV; R = H; Table 1 and Fig. 3), gives rise to another seven-membered intramolecular hydrogen bond and ν(CO) falls to 1718 cm.$^{-1}$ with ν(OH) at 3470 cm.$^{-1}$ (all in CCl_4).

Several different intramolecular hydrogen bonds are possible in compound 21 (V; Tables 1 and 2 and Fig. 3). Our tentative conclusion is that the ring B hydroxyl is bonded to the carbonyl of the ester grouping while the ring D hydroxyl is " free." Similarly we conclude that compound 22 (VI; Tables 1 and 2 and Fig. 3) shows the presence of a five-membered intramolecular hydrogen bond between the hydroxyl group and carbonyl of the lactone ring.

In summary, the values quoted in Tables 1 and 2 and summarized in Table 3 illustrate the constancy of both ν(CO) and ν(OH) when certain intramolecular situations are held relatively constant. Similarly, certain minor changes in molecular structure produce consistent changes in ν(CO) and ν(OH), in so far as overlapping permits accurate assignment of bands. Two types of intramolecular hydrogen bond provide the chief interest: the planar five-membered diosphenol system, and the twisted seven-membered system. In both cases, the small solvation shifts may be due to the inability of the solvent molecules such as chloroform and diethyl ether to approach the acceptor sites. The small, but definite, upward shift (CCl_4 to $CHCl_3$) of the diosphenol hydroxyl frequency is especially intriguing as the shift is normally downward for a phenolic hydroxyl, for example.[12]

The assignments for the stretching absorptions of the carbon–carbon double bonds, ν(C=C), are less complete than those of the carbonyl and hydroxyl groups (Table 2). The $\Delta^{1,2}$ absorption has not been located and it is presumed to be of low intensity; the ring A enone system is known [13] to be non-planar. By contrast, the absorption due to the $\Delta^{5,6}$-diosphenol double bond is quite prominent (medium strength, where a carbonyl is termed strong) and is at about 1627 ($\varepsilon \sim 150$), 1612 ($\varepsilon \sim 100$), and 1622 cm.$^{-1}$ for the cedrelone diosphenol itself, the acetate, and the methyl ether, respectively. The same absorption is harder to locate in the isocedrelone series where there is an additional double bond in the 13,17 position. The medium-strength absorptions near 1637 cm.$^{-1}$ in the ring B and D diacetate is presumably due, in part at least, to the 5,6-double bond, but in the free hydroxy-compounds the 7-ketone carbonyl absorption moves into this region and definitive assignments are not feasible. Conceivably, the band near 1658 cm.$^{-1}$ could represent the $\Delta^{13,17}$ bond, with the $\Delta^{5,6}$ absorption hidden within the strong carbonyl band at 1623 cm.$^{-1}$.

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[13] Katritzky and Ambler, " Physical Methods in Heterocyclic Chemistry, Vol. II," Academic Press, New York, 1963, p. 203.