Studies in the Steroid Group. Part LXVII. Infra-red Absorption of Disubstituted* cis*Ethylenic Centres.*

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The spectroscopic examination of steroids containing disubstituted *cis*-double bonds in the various possible positions in rings A, B, and C is reported. The particular importance of the C–H out-of-plane bending region (800—650 cm.$^{-1}$) in the infra-red spectrum for establishing the presence of such groupings is emphasized; the 3000 cm.$^{-1}$ region gives additional information. The data for the 800—650 cm.$^{-1}$ region and for the olefinic stretching region (near 1650 cm.$^{-1}$) can be correlated with the degree of steric strain in the unsaturated bonds. The steroid results are compared with those obtained with some simpler analogues.

The presence of isolated tri- and tetra-substituted ethylenic groups in steroid nuclei, and in favourable cases their actual positions, can be established by use of infra-red and ultra-violet spectroscopy (Jones, Humphries, Packard, and Dobriner, *J. Amer. Chem. Soc.*, 1950, **72**, 86; Bladon, Fabian, Henbest, Koch, and Wood, *J.*, 1951, 532; Bladon, Henbest, and Wood, *J.*, 1952, 2737). The success of these studies prompted a more detailed investigation of steroids containing nuclear disubstituted olefinic bonds, necessarily *cis* in configuration (for brevity, these will be referred to as " *cis*-bonds ").

It is well known that disubstituted *cis*- and *trans*-olefins absorb in three well-separated regions of the infra-red spectrum, and that related pairs of acyclic hydrocarbons can thus be readily differentiated, especially in the olefinic C–H out-of-plane bending region (1000—650 cm.$^{-1}$) (cf. Sheppard and Simpson, *Quart. Reviews*, 1952, **6**, 1; McMurry and Thornton, *Analyt. Chem.*, 1952, **24**, 318). Although disubstituted *cis*- and *trans*-olefins usually show bands near 700 and 970 cm.$^{-1}$ respectively, detailed assignment of bands for compounds other than simple olefinic hydrocarbons may be rendered difficult by the complexity of the spectra in this region (cf. *inter al.*, Sinclair, McKay, Myers, and Jones, *J. Amer. Chem. Soc.*, 1952, **74**, 2578; Crombie, *J.*, 1952, 2997).

In the cyclic series the spectra of the unsubstituted *cyclo*alkenes containing four- to ten-membered rings have been recorded (*cyclo*butene, Roberts and Sauer, *J. Amer. Chem. Soc.*, 1952, **74**, 3192; *cyclo*pentene, A.P.I., " Catalog of Infra-red Spectral Data," Serial No. 696; *cyclo*hexene, Shreve, Heether, Knight, and Swern, *Analyt. Chem.*, 1951, **23**, 282; A.P.I., *op. cit.*, nos. 201, 697; *cyclo*heptene, Kohlrausch, " Hand- und Jahrbuch der Chemischen Physik," Vol. IX, **6**, 349; *cyclo*octene, Cope and Estes, *J. Amer. Chem. Soc.*, 1950, **72**, 1128; *cis*- and *trans-cyclo*nonene, Blomquist, Liu, and Bohrer, *ibid.*, 1952, **74**, 3643; *cis*- and *trans-cyclo*decene, Blomquist, Burge, and Sucsy, *ibid.*, p. 3636; Prelog, Schenker, and Gunthard, *Helv. Chim. Acta*, 1952, **35**, 1598). Comparison of these results is difficult because the experimental conditions employed vary, and in many cases only a few of the band positions are given. It appears, however, that in the four- and five-membered rings the stretching frequencies are affected in the expected way by steric strain, *i.e.*, raised olefinic C–H and lowered double-bond stretching frequencies.

Jones *et al.* (*loc. cit.*, 1950) have investigated the 3000 and 1650 cm.$^{-1}$ regions of some Δ^{2}- and Δ^{11}-steroids, most of which contained carbon–oxygen bonds as well as the *cis*-

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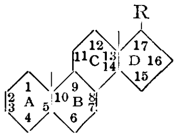
* Part LXVI, *J.*, 1954, 736.

bonds. Apart from this no systematic work appears to have been carried out on fused-ring systems containing *cis*-bonds.

The most obvious application of data from fundamental steroid olefins is for diagnostic purposes in this and related fields. However, since the double bonds are located in rings of different degrees of rigidity, the results should have a wider significance in establishing relations between spectra and molecular environment. A *cis*-bond can be accommodated in five different positions in the six-membered rings A, B, and C. Compounds containing 1 : 2-, 2 : 3-, and 3 : 4-double bonds have been examined as hydrocarbons (cholestenes), whereas the representatives with 6 : 7- and 11 : 12-double bonds have hydroxyl or ester groupings at $C_{(3)}$ and/or $C_{(24)}$; however, these other groups are considered to be sufficiently far removed from the unsaturated centres to cause no appreciable alteration in the spectroscopic properties of the double bond (cf. discussion by Bladon *et al. locc. cit.*, 1951, 1952).



Spectroscopic Work.—The spectra were recorded on a Perkin-Elmer model 21 double-beam spectrometer fitted with a sodium chloride prism. Matched cells were used in order to compensate for solvent absorption. The solutions and path-lengths used were: 3100—2900 cm.$^{-1}$, approx. 0·05M-solutions in carbon tetrachloride, 1-mm. cells; 1800—1600 cm.$^{-1}$, similar solutions in 2-mm. cells; 900—650 cm.$^{-1}$, approx. 0·1M-solutions in carbon disulphide, 0·5-mm. cells. The accuracy of the frequency measurements for sharp bands is estimated as ±10, ±4, and ±2 cm.$^{-1}$ at 3000, 1700, and 800 cm.$^{-1}$ respectively. In the 800—650 cm.$^{-1}$ region the intensities and average frequencies were calculated for the bands listed in the Table by using the expressions:

$$\text{Intensity } (\varepsilon) = \frac{1}{cl}\log_{10}\left(\frac{100 - y}{100 - x}\right)_\nu. \quad \text{Average frequency} = \Sigma\nu(x - y)_\nu/\Sigma(x - y)_\nu$$

where c = concentration of solution in moles/l., l = path-length in cm., x = % absorption at the frequency ν cm.$^{-1}$ of maximal absorption with solution in the sample beam and solvent in the reference beam, y = % absorption at the same frequency with solvent in both beams. The combined intensities are the sums of the intensities of the separate bands. The main inaccuracy expected in calculations based on % absorption is that no allowance is made for the effect of finite slit width. [The most exact methods circumvent this difficulty by measuring absorption areas rather than peak heights (Ramsay, *J. Amer. Chem. Soc.*, 1952, **74**, 72; Jones, Ramsay, Keir, and Dobriner, *ibid.*, p. 80). These methods require well-separated bands and are difficult to apply to the more crowded 800—650 cm.$^{-1}$ region.] However, under the conditions used in this work (spectral slit width, 2·4—3·3 cm.$^{-1}$, maximal absorption generally 40—70%), errors involved in using % absorption are greatly reduced. The reproducibility of the method was checked by examining cholest-3-ene under differing conditions of background absorption and concentration. Separate determinations gave ε = 235 and 240 for y = 2 and 7% and c = 0·043 and 0·092M, respectively.

The results are tabulated.

Infra-red frequencies (cm.$^{-1}$) of steroids containing disubstituted cis-*double bonds.*

(Sh denotes shoulder on a neighbouring strong band. In the 800—650 cm.$^{-1}$ region figures in parentheses denote intensities.)

	3100—2950	1700—1600	800—650				Combined intensity	Average frequency	Refs.
Δ^1-*Compounds.*									
a Cholest-1-ene *	2995	1644	—	748(65)	718(125) 700(115)	—	305	719	1
b Cholest-1-en-3β-ol	3021	1644	—	751(195)	—	—	195	751	1
c 3β-Acetoxycholest-1-ene	Not measured		—	754(155) 742(60)	—	—	215	750	1
Δ^2-*Compound.*									
d Cholest-2-ene *	3034	1653	774(35)	—	—	664(145)	180	692	—
Δ^3-*Compound.*									
e Cholest-3-ene *	3015	1647	773(110)	—	—	671(125)	235	718	—

TABLE. (*Continued.*)

	3100—2950	1700—1600	800—650				Combined intensity	Average frequency	Refs.
Δ⁶-*Compounds.*									
f Cholest-6-en-3β-ol	3000	1633	772(70)	739(70)	729(60) 710(60)	—	260	738	2
g 3β-Acetoxycholest-6-ene	3017 Sh	1639	771(90)	739(75)	729(65) 704(60)	—	290	737	2
h 3β-Acetoxycholest-6-en-5α-ol	3014	1638	—	752(175)	—	—	175	752	3
i 3β-Acetoxyergosta-6 : 22-diene-5α : 8α-diol	3010 Sh	1653	—	752(95)	—	—	95	752	4
Δ¹¹-*Compounds.*									
Methyl 3α-hydroxychol-11-enate	3033	1620	832(85) 794(40)	769(45) 751(50)	725(125)	—	345	771	5
k Methyl 3α-acetoxychol-11-enate	3045	1623	833(75) 796(30)	769(35) 753(45)	726(135)	—	320	770	5
3α : 24-Dihydroxychol-11-ene (mull in Nujol)	3045	1620	830 790	768 748	724	—	—	—	5
m 3α : 24-Diacetoxychol-11-ene	3043	1623	832(70) 796(50)	769(30) 753(55)	724(140)	—	345	768	5
n Methyl 3α : 9α-epoxychol-11-enate	3050	1626	839(55) 800(30) 772(45)	749(115) 739(90)	—	—	335	772	5
o 3β-Acetoxy-5α : 22α-spirost-11-ene	Not measured		831(35) 796(35) 781(30)	766(70) 760(100) 749(40)	703(100)	—	410	760	6
Diene.									
p Cholesta-2 : 6-diene	3020	1646	—	759(275)	694(65)	664(200)	540	709	2
Epidioxides.									
q 2α : 5α-Epidioxycholest-3-ene	3066	†	—	769(65)	711(95) 699(65)	—	225	724	7
r 5α : 8α-Epidioxyergosta-6 : 22-dien-3β-ol	3044 Sh	†	779(55)	—	723(70)	—	125	747	8
s 3β-Acetoxy-5α : 8α-epidioxyergosta-6 : 22-diene	3040 Sh	†	780(45)	—	721(60)	—	105	746	8
3β-Acetoxy-5α : 8α-epidioxyergosta-6 : 9(11) : 22-triene	3019 Sh	†	798(60) 773(25)	741(40)	713(85)	—	210	748	9
Steroids without cis-*bonds.*									
u Cholestane	—	—	799(5)	736(10)	—	—	15	—	—
v Cholestan-3β-ol	—	—	797(10)	732(25)	—	665(25)	60	—	—
w 3β-Acetoxycholestane	—	—	—	732(20)	—	—	‡	—	—
x 3β-Acetoxy-5α : 8α-epidioxyergosta-22-ene	—	—	796(35)	766(15) 738(25)	—	667(20)	95	—	10
Simpler compounds.									
*cyclo*Pentene (A.P.I. data)	3065	1613	—	—	—	—	—	—	—
*cyclo*Hexene	2995	1650	—	—	718(70)	—	70	718	—
3 : 3-Dimethyl*cyclo*hexene	2988	1645	—	—	729(125) 717(65)	—	190	724	11
*cyclo*Hexen-3-ol (liquid film)	3018	1661	—	—	724	668	—	—	—
cis-*p*-Menth-2-ene-1 : 4-diol	2995	1647	—	772(75)	710(40)	—	115	748	12
Ascaridole	3035	†	—	—	730(50)	695(140)	190	706	—
Acyclic *cis*-olefins	~3020	1660—1630	—	—	730	675	~60	—	13

* Purified *via* dibromides. † Several weak bands in this region.

‡ A broad band at 803 cm.$^{-1}$ (ε = 45), extending to well below 800 cm.$^{-1}$.

1, Henbest and Wilson, forthcoming publication. 2, Barton and Rosenfelder, *J.*, 1949, 2459; Wintersteiner and Moore, *J. Amer. Chem. Soc.*, 1950, **72**, 1923. 3, Henbest and Jones, *J.*, 1948, 1792. 4, Achtermann, *Z. physiol. Chem.*, 1933, **217**, 281. 5, Materials kindly supplied by Dr. K. Folkers and Dr. Max Tishler (cf. Bladon, Henbest, and Wood, *J.*, 1952, 2737). 6, Kindly supplied by Dr. J. Elks (Glaxo Laboratories Ltd.). 7, Kindly supplied by Dr. Werner Bergmann. 8, Windaus and Brunken, *Annalen*, 1928, **460**, 225. 9, Bladon *et al.*, *J.*, 1952, 4883. 10, Clayton, Henbest, and Jones, *J.*, 1953, 2015. 11, Prepared by pyrolysis of the stearate of 2 : 2-dimethyl*cyclo*hexanol by Mr. B. L. Shaw of this Department. 12, Richter and Presting, *Ber.*, 1931, **64**, 878. 13, McMurry and Thornton, *Analyt. Chem.*, 1952, **24**, 318.

The C=C *Stretching Region.*—Isolated double bonds give rise to only low-intensity stretching bands, and when a 1 : 2-disubstituted *trans*-olefin is concerned the vibration may be infra-red inactive (Sheppard and Simpson, *loc. cit.*). Under the conditions employed here more than one band is usually present between 1600 and 1700 cm.$^{-1}$. The strongest band in this region has been taken to be the olefinic stretching frequency; the weaker ones are probably overtones or combination tones of strong bands lower in the spectrum. The values so obtained for compounds *d, j,* and *k* agree within experimental error with those recorded by Jones *et al.* (*loc. cit.*, 1950).

As discussed earlier (Bladon *et al., loc. cit.*, 1951), increased steric strain in cyclic olefins would be expected to reduce the double-bond stretching frequency (cf. values for *cyclo*hexene and *cyclo*pentene). In the simplest steroid *cis*-olefins (*a, d, e, f,* and *j*), the frequency order is $\Delta^2 > \Delta^3 > \Delta^1 > \Delta^6 > \Delta^{11}$. This order (with the possible exception of Δ^3 versus Δ^1) is that which could be predicted by consideration of the probable strains. Thus, the Δ^{11}-bond is situated in ring C, the most rigid and strained of the three six-membered rings (*trans*-fused to two other rings, one five-membered; cf. also data on $\Delta^{9(11)}$-steroids, Bladon *et al.*, 1951). The Δ^6-bond is present in the somewhat less rigid ring B, and the remainder are in the relatively flexible ring A. There is much chemical evidence indicating that Δ^2-olefins are more stable than Δ^3-compounds when rings A and B are *trans*-fused (as in the examples studied in this work) [cf. predominance of Δ^2-olefins produced on dehydration of 3-hydroxy-compounds and their derivatives; oxidation (to 2 : 3-*seco*diacids), bromination (at $C_{(2)}$), and enol acetylation (to Δ^2-3-acetates) of 3-ketones of the 5α-series]. Although hyperconjugation (as in conjugated dienes, cf. Barton and Brooks, *J.*, 1951, 257) may play some part in these relative stabilities (4 hydrogen atoms in Δ^2-, and 3 in Δ^3-steroids), strain is likely to be much more important. Thus the direction of oxidation and enol acetylation of 3-ketones is reversed when rings A and B are *cis*-fused (3 : 4-*seco*diacids and Δ^3-3-acetates being produced), while, of course, the number of hydrogen atoms in hyperconjugation with the Δ^2- and Δ^3-bonds is the same as in the A–B-*trans*-compounds. Comparable reactions at $C_{(2)}$ would indicate the relative stabilities of Δ^1- and Δ^2-steroids, but the only pertinent observation is that by Ruzicka, Plattner, and Furrer (*Helv. Chim. Acta*, 1944, **27**, 524) who describe the oxidation of cholestan-2-one to the 2 : 3-*seco*diacid obtained previously from cholestan-3-one. This may be taken as an indication of the superior stability (less strain) of Δ^2- compared with Δ^1-compounds. The infra-red results are thus in line with the chemical evidence.

Steroid epidioxides and ascaridole give a number of rather ill-defined low-intensity bands in this region, and reliable identification of the olefinic stretching bands becomes impossible.

The Olefinic C–H *Out-of-plane Bending Region.*—These deformation frequencies occur in the 1000—650 cm.$^{-1}$ region. The bands associated with *cis*-bonds in acyclic olefins generally appear near 700 cm.$^{-1}$, but their positions are known to be rather variable (Sheppard and Simpson, *loc. cit.*).

In general, steroids containing *cis*-bonds have been found to show several prominent bands in the 800—650 cm.$^{-1}$ region, while the corresponding saturated compounds give only weak bands. The position of the peaks associated with the *cis*-bonds distinguishes them from the bands at 850—790 cm.$^{-1}$ given by the trisubstituted olefins (Bladon *et al., loc. cit.*, 1950) which are often of lower intensity [*e.g.*, cholest-5-ene has bands at 833 ($\varepsilon = 70$) and 800 cm.$^{-1}$ ($\varepsilon = 65$)].

Examination of the compounds in which there is no oxygenated substituent near the *cis*-bond shows that each position of the double bond is associated with a definite absorption pattern. Since the bands within these patterns often have similar intensities it is impossible to assign any particular peak to the out-of-plane vibration. The reason for the multiplicity of bands in most of the compounds studied is not obvious. It may be noted that *cyclo*hexene, the only completely symmetrical olefin, resembles the acyclic compounds in giving only a single band, and it is possible that the " unsymmetrical environment " of the *cis*-bonds in the other compounds is connected with the more complex absorption pattern (the steroid olefins can all be considered as unsymmetrical with respect to the degree of substitution of adjacent atoms and strain differences in the single bonds joined to the unsaturated centre). (It is possible, of course, that further characteristic bands may be present below 650 cm.$^{-1}$, but in the absence of experimental data this cannot be discussed further.)

In order to help towards an interpretation of the somewhat complex absorption observed in this region, an " average frequency " has been computed for each compound (relative intensities have been taken into account in these calculations; use of ε values instead of % absorption makes little difference to the figures obtained). While the physical significance of this average frequency cannot be assessed until the origin of the multiple absorption is known, use of this quantity leads to a rationalisation of the results. Thus, the average frequencies of the simplest steroid olefins (*a, d, e, f,* and *j*) are in the order previously observed in the double-bond stretching region; these deformation frequencies however, are ***raised*** by increase in strain. (The Δ^{11}-compounds are exceptional in giving significant bands just above 800 cm.$^{-1}$. These are included in the Table as they occur regularly in compounds *j, k, l, m,* and *n*, and thus appear to be members of the Δ^{11}-band group. Even if they are omitted, the average frequencies of the Δ^{11}-steroids are still higher than those of the other types.*)

Individual intensities of the steroid peaks (ε *ca.* 50—150) are of the same order as those of the simpler derivatives of *cyclo*hexene examined. Compared with acyclic *cis*-bonds (ε *ca.* 60) all the *cyclo*hexene compounds (including steroids) tend to give somewhat stronger bands. The values of the band intensities (or combined intensities) of the Δ^{6}- and Δ^{11}-compounds may be influenced by the presence of the oxygenated substituents. Although such groups are not expected to give bands in this region, or to influence the positions of the olefinic peaks (if sufficiently far removed from the *cis*-bond, see below), their presence may enhance the intensity of individual olefinic peaks, or alternatively may increase the general level of absorption (cf. *u, v, w,* and *x*). However, comparison of the Δ^{1}-, Δ^{2}-, and Δ^{3}-hydrocarbons (*a, d,* and *e*) shows that the combined intensity of cholest-1-ene (ε 305) is much greater than those of its two isomers (ε 180 and 235). Possibly the intensities are influenced by the degree of substitution on the two *adjacent* carbon atoms, which is known to be important for ultra-violet absorption intensities of identically substituted olefins (Bladon *et al., loc. cit.*, 1952). The *cis*-bond in cholest-1-ene is linked to the quaternary $C_{(10)}$ and to a methylene group, $C_{(3)}$, and the relatively high intensity of the Δ^{1}-peaks may be due to the dissymmetry of this substitution (dissymetry and combined intensity decrease in the order $\Delta^{1} > \Delta^{3} > \Delta^{2}$). In this connection it may be noted that 3 : 3-dimethyl*cyclo*hexene has a higher intensity than *cyclo*hexene, and that β-amyradiene-II (effectively a 4 : 4-dimethyl-Δ^{2}-steroid) absorbs more strongly (combined ε 285; unpublished work) than cholest-2-ene (ε 180) in the 800—650 cm.$^{-1}$ region.

An increase in the number of functional groups (oxygenated groups in the present study) renders interpretation of the experimental results more difficult. Thus, although variation in the nature of oxygenated groups at positions distant from the *cis*-bond causes little alteration in the spectra (cf. *f* and *g*; *j, k,* and *m*), introduction of such groups nearer to the ethylenic bond may profoundly alter the band positions and intensities. For example, the three steroid allylic alcohols (*b, h,* and *i*) are exceptional in that each shows only a single band (near 750 cm.$^{-1}$ in each case; however, *cyclo*hexen-3-ol shows a doublet). The combined intensities of these steroid alcohols are less than those of the olefins lacking the hydroxyl group (the intensity decrease is most marked in the doubly allylic diol *i*).

The allylic ether (*n*) has a group of five bands similar to those of the simpler Δ^{11}-compounds and, although the average frequency and combined intensity are near the characteristic Δ^{11}-values, the positions and intensities of the individual bands are considerably altered. These effects also apply to the Δ^{11}-sapogenin (*o*) which shows a group of six bands [sapogenin side-chains do not give appreciable bands in the 800—

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* It would clearly be of interest to examine the spectra in the 5β-series, where the frequency order of Δ^{2}- and Δ^{3}-olefins might be the reverse of that in the 5α-series. Through the courtesy of Professor L. F. Fieser we have been able to record the spectrum of one 5β-compound, methyl chol-3-enate (Fieser and Ettorre, *J. Amer. Chem. Soc.*, 1953, **75**, 1700). This gives bands at 783 (weak) and 678 (medium-strong) cm.$^{-1}$ in the 800—650 cm.$^{-1}$ region (there was insufficient compound to give reliable ε values). The average frequency (~693 cm.$^{-1}$) is less than that of cholest-3-ene, in accord with the greater stability of Δ^{3}-compounds in the A–B-*cis*-series.

650 cm.$^{-1}$ region (Jones, Katzenellenbogen, and Dobriner, *J. Amer. Chem. Soc.*, 1953, **75**, 158)]. Introduction of an epidioxide group at the positions adjacent to the *cis*-bond makes detection of the latter more difficult (cf. rather small intensity differences between *s* and *x*). Such groups tend to increase the average frequency of the neighbouring *cis*-bond (Δ^3, 718 $\longrightarrow$ 724 cm.$^{-1}$; Δ^6, 738 $\longrightarrow$ 747 cm.$^{-1}$), possibly indicating increased strain.

One unconjugated diene, cholesta-2 : 6-diene (*p*), has been examined, the *cis*-bonds being situated in different but neighbouring rings. Its spectrum differs considerably from those of Δ^2- and Δ^6-compounds, and the combined intensity (ε 540) is appreciably greater than the value obtained ($\varepsilon \sim 440$) by adding the intensities of the individual *cis*-bonds.

The Olefinic C–H *Stretching Region.*—In many olefins detection of the olefinic-hydrogen stretching bands is made difficult by their proximity to the relatively more intense saturated C–H stretching bands, and a prism of high dispersive power is generally used (*e.g.*, a lithium fluoride prism was used in our previous work on trisubstituted steroid olefins). However, the lower resolution of sodium chloride is now found to be adequate for the detection of *cis*-bonds. Thus steroids and simpler compounds containing a *cis*-bond exhibit a well-defined peak, or, in the more complex steroids, a marked shoulder, in the 3050—3000 cm.$^{-1}$ region. Numerous observations in these laboratories have shown that the steroid *trans*-Δ^{22}-bond gives either a slight shoulder or no inflection in this range (sodium chloride prism). This difference is probably connected with the greater intensity of the *cis*-band, for the two types of system do not appear to absorb at systematically different frequencies. Other examples of *cis*-bonds' giving better defined peaks in this region are found in the spectra of vitamins A_1 and A_2 and related compounds (Farrar, Hamlet, Henbest, and Jones, *J.*, 1952, 1094), and in long-chain unsaturated acids (Sinclair *et al.*, *loc. cit.*, 1952).

More highly strained olefins are usually expected to absorb at higher frequencies in the olefinic C–H stretching region (cf. *cyclo*pentene and *cyclo*hexene). Indeed, the most strained of the steroids, the Δ^{11}-compounds, absorb at greater frequencies than the remainder (with the exception of some of the epidioxides). However, in the other compounds, variation in double-bond environment causes only small frequency changes, which do not conform to any discernible pattern.

From the present work it is clear that the 800—650 cm.$^{-1}$ region is the most useful for detection of *cis*-bonds in six-membered rings. Its value is enhanced by the fact that mono- and poly-cyclic derivatives of *cyclo*hexene without *cis*-bonds do not often absorb strongly in this range, although many bands are present between 1000 and 850 cm.$^{-1}$ (see, *inter al.*, Beckett, Pitzer, and Spitzer, *J. Amer. Chem. Soc.*, 1947, **69**, 2488). The intensities of the bands in the latter region are generally comparable with those observed with the *cis*-bonds at lower frequencies. In the evidence for the presence of a *cis*-bond in soya-sapogenol-C (*cyclo*hexene ring present) (Meyer, Jeger, and Ruzicka, *Helv. Chim. Acta*, 1950, **33**, 672) and clovene (*cyclo*pentene ring present) (Eschenmoser and Günthard, *ibid.*, 1951, **34**, 2338) bands at 970 and 969 cm.$^{-1}$ are listed. From the published spectra these bands appear to be of only moderate intensity, and in both cases far stronger bands are present near 760 cm.$^{-1}$; these are probably more significant for confirmation of the presence of *cis*-bonds (*cyclo*pentene derivatives have not been considered in this work, but see the spectra published by Roberts and Gorham, *J. Amer. Chem. Soc.*, 1952, **74**, 2278).

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