

**210.** *Infrared Spectra of Natural Products. Part V.\* The Characterisation of Carbonyl Groups in Pentacyclic Triterpenoids.*

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The carbonyl frequencies of a large number of pentacyclic triterpenoids based on oleanane, lupane, and ursane have been measured in carbon tetrachloride and chloroform, and characteristic frequencies for 18 types of carbonyl function are given. Some six-membered ring ketones cannot be distinguished by carbonyl absorption alone, but bands due to bending vibrations of adjacent methylene groups assist in their characterisation.

THE use of infrared spectra has proved valuable in solving problems of steroid structure, and the results obtained in that field have been summarised by R. N. Jones and Herling<sup>1</sup> and by Cole.<sup>2</sup> Compounds containing fused *cyclohexane* systems are particularly suitable for infrared work since a very large number of compounds are available based on a fairly constant molecular skeleton, and differing mainly in the number and positions of substituents. Furthermore, these compounds being for the most part saturated and relatively non-polar, electronic effects are rarely transferred beyond neighbouring carbon atoms, and the change in spectrum brought about by altering a particular substituent can usually be predicted fairly accurately.

Recently emphasis in this type of structural chemistry has shifted from steroids to

\* Part IV, *J.*, 1955, 2624.

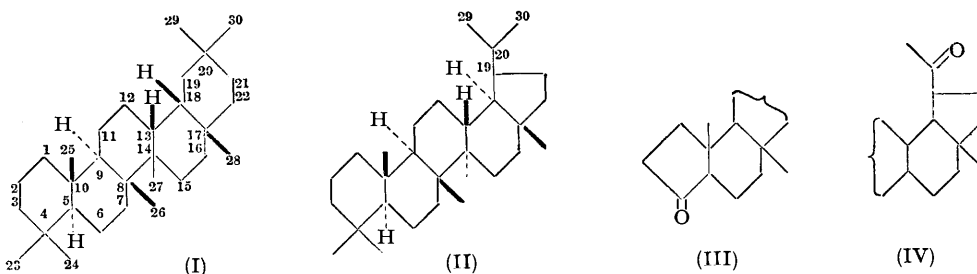
<sup>1</sup> R. N. Jones and Herling, *J. Org. Chem.*, 1954, **19**, 1252.

<sup>2</sup> Cole, *Rev. Pure Appl. Chem. (Australia)*, 1954, **4**, 111.

triterpenoids, and it has been usual to apply steroid infrared results to the latter compounds. While in many cases this practice has given valuable information, it would be preferable to know the infrared frequencies for groups in triterpenoid molecules themselves, since the environments at each substituent position are not identical in the two types of ring system. For instance, the presence of the  $C_{(4)}$ -gem-dimethyl group might well influence a  $C_{(3)}$ -substituent, and the amount of strain in ring c which is fused to two six-membered rings in the pentacyclic triterpenoids will be considerably different from that in the steroids where the adjacent D-ring is five-membered. Also the large number of angular methyl groups will alter the appearance of the spectra, especially in the regions of C-H stretching and bending absorption.

In this paper carbonyl groups in the pentacyclic triterpenoids are considered and it is hoped later to present results covering ethylenic double bonds, hydroxyl groups, C-H groups, carboxylic acids and their methyl esters, and some aspects of stereochemistry. Similar results for many tetracyclic triterpenoids will also be given later.

The compounds considered below are derivatives of oleanane (I), lupane (II), and ursane. There is still some doubt about the structure of the last hydrocarbon<sup>3</sup> but the numbered positions of carbonyl groups are the same as in the oleanane and lupane series.



The types of carbonyl group encountered include cyclic ketones at positions 3, 11, 12, and 19, carboxylic acids and their methyl esters, aldehydes, lactones, acetates, formates benzoates, and various conjugated ketones. Other possible types are the A-trisnor- $C_{(3)}$ -ketone (III) formed from  $3\beta$ -hydroxy-compounds by dehydration with phosphorus pentachloride and subsequent oxidation, and the methyl ketone (IV) from lupeol by oxidation of the side chain.

Primarily, the absorption due to the carbonyl stretching vibration is used to distinguish between these types, but certain ambiguities exist in that region. Therefore absorption bands in other regions which are useful in identifying certain groups are also given below.

#### EXPERIMENTAL

The infrared spectrometer employed in this work consists of a Grubb-Parsons S.3.A. monochromator used in conjunction with a Perkin-Elmer thermocouple, light chopper, and No. 81 amplifier. A calcium fluoride prism is used for all measurements between 1300 and 3800  $\text{cm}^{-1}$  and a double-pass sodium chloride system<sup>4</sup> between 670 and 1300  $\text{cm}^{-1}$ . The instrument was calibrated by using data summarised by Downie, Magoon, Purcell, and Crawford,<sup>5</sup> and band positions can be measured with an accuracy of  $\pm 0.5 \text{ cm}^{-1}$  between 1300 and 1900  $\text{cm}^{-1}$ . The spectrometer is controlled by thermostat at  $30^\circ \pm 0.5^\circ$  and the air inside the case is continuously circulated through a Burnett and Lewis "Humidryer" to reduce the amount of atmospheric water vapour absorption. A string-type automatic slit drive<sup>6</sup> was employed to compensate for the fall-off in energy of the source.

All compounds were studied as dilute solutions (approximately 0.01M) to minimise the effects

<sup>3</sup> Cf. Jeger, *Fortschr. Chem. org. Naturstoffe*, 1950, **7**, 47; Corey and Ursprung, *Chem. and Ind.*, 1954, 1387; Beton and Halsall, *ibid.*, p. 1560; Allan, Beaton, Shaw, Spring, Stevenson, Stewart, and Strachan, *ibid.*, 1955, 281.

<sup>4</sup> Walsh, *Nature*, 1951, **167**, 810; Rochester and Martin, *Nature*, 1951, **168**, 785.

<sup>5</sup> Downie, Magoon, Purcell, and Crawford, *J. Opt. Soc. Amer.*, 1953, **43**, 941.

<sup>6</sup> Blount and Cole, *J. Sci. Inst.*, 1955, **32**, 471.

of intermolecular interaction. The advisability of using dilute solutions instead of solid samples for this type of work has often been stressed.<sup>7</sup>

Most triterpenoids are sufficiently soluble in carbon tetrachloride to permit that solvent to be used in cells of about 1 mm. thickness, but for dihydroxy-compounds or carboxylic acids it is necessary to use cells 3 mm., and occasionally up to 10 mm., in thickness. Since many natural products are more soluble in chloroform, representative compounds have also been studied in this solvent. However, if the sample is sufficiently soluble, carbon tetrachloride is much to be preferred since the same solution may be used for studying the regions of C-H absorption which are obscured by chloroform absorption. Moreover chloroform, as usually supplied, contains a small amount of ethanol to inhibit oxidation to carbonyl chloride and, while this does not affect its use as a solvent in the carbonyl region, it must, of course, be removed if the same solution is to be used for the study of hydroxyl absorption. This may be done in small batches by pouring the chloroform through silica gel prepared by heating it at 140° under vacuum. Alcohol-free chloroform prepared in this manner will keep for about 1 week, oxidation being readily detected by the appearance of carbonyl absorption at 1810 cm.<sup>-1</sup>.

The absorption in the regions of C-H (2800—3100 cm.<sup>-1</sup>) and C=O (1650—1800 cm.<sup>-1</sup>) stretching vibrations is between two and three times as intense as that in the C-H bending region (1350—1500 cm.<sup>-1</sup>). We have found it convenient to weigh out only one solution containing about 5 mg. per ml. (~0.01M) and to use a 1.3 mm. cell for the former regions and a 3.3 mm. cell for the latter and also for the O-H stretching (~3630 cm.<sup>-1</sup>) and C=C stretching (1570—1680 cm.<sup>-1</sup>) regions.

### RESULTS AND DISCUSSION

The carbonyl frequencies of individual compounds are given in Tables 1 and 2 while the average values for the various types are summarised in Table 3. These Tables and Table 4 include the frequencies of other bands which may be used to distinguish or confirm doubtful types of carbonyl group. The values given in Table 3 are based on compounds listed under A in Tables 1 and 2, and it must be remembered that the frequency ranges might be wider when the particular absorption band is overlapped by that due to another group.

With the exception of the carboxylic acids, which are complicated by hydrogen bonding, the carbonyl frequencies are always lower (and the bands slightly broader) in chloroform solution than in carbon tetrachloride, the mean difference varying from 3 cm.<sup>-1</sup> for the C<sub>(11)</sub>-ketones to 20 cm.<sup>-1</sup> for the  $\gamma$ -lactones. The greater part of the following discussion is based on the results for carbon tetrachloride. Although carbon disulphide has not been used in this work its solutions are known to give approximately the same absorption frequencies as carbon tetrachloride.

The various types listed in Table 3 fall into a number of groups which cannot be identified unequivocally by the carbonyl frequency alone. Such a group includes aldehydes, acetates, formates, and methyl esters which all absorb between 1723 and 1737 cm.<sup>-1</sup>. The presence of these will sometimes be known from the chemistry of the compound but in any case they often can be distinguished from one another by observing bands in other regions. For example, acetates absorb<sup>8</sup> at 1240 cm.<sup>-1</sup> and<sup>9</sup> at 1375 and 1368 cm.<sup>-1</sup>. Methyl esters have characteristic bands<sup>9</sup> near 1438, at<sup>10</sup> 1135 and 1155, and near 760—790 cm.<sup>-1</sup> while formates absorb at 1176 cm.<sup>-1</sup>.

The benzoate frequency (1719 cm.<sup>-1</sup>) is relatively unambiguous but, if necessary, confirmation of its presence can be obtained from the strong bands<sup>1</sup> at 1273 and 710 cm.<sup>-1</sup>. It should be noted that, if it is necessary to esterify a hydroxyl group before carrying out a reaction, or in order to facilitate chromatography, and if subsequently infrared measurements are to be made, it is preferable to use acetates of compounds containing six-membered ring carbonyl groups and benzoates of those containing five-membered ring carbonyls. In this way, the interference of the ester carbonyl absorption with that of the group being studied is kept at a minimum.

<sup>7</sup> Jones and Dobriner, *Vitamins and Hormones*, 1949, **7**, 293; Cole, *Chem. and Ind.*, 1954, 661; Dickson, Page, and Rogers, *J.*, 1955, 443.

<sup>8</sup> Jones, Humphries, Herling, and Dobriner, *J. Amer. Chem. Soc.*, 1951, **73**, 3215.

<sup>9</sup> Jones and Cole, *ibid.*, 1952, **74**, 5648.

<sup>10</sup> Cole and Thornton, unpublished results.

TABLE 1. *Non-conjugated carbonyl frequencies (cm.<sup>-1</sup>).*

In each section, compounds without completely overlapping carbonyl absorption in carbon tetrachloride solution are given under *A* and those in which bands are not resolved, under *B*. Because of frequency shifts and band broadening in chloroform solution some bands of compounds listed under *A* might not be completely resolved in this solvent. Compounds given under 1C and 12C show interaction effects which are discussed in the text.

CCl <sub>4</sub> soln.	Compound	CHCl <sub>3</sub> soln.	Ester C=O <sup>a</sup>	Adjacent- CH <sub>2</sub> <sup>b</sup>
<i>1 A γ-Lactones</i>				
1772	3β:13β-Dihydroxyursan-28-oic 13(28)-lactone (ursolic acid lactone)	1754	—	—
1773	3β:13β-Dihydroxy-18α-oleanan-28-oic 13(28)-lactone	1755	—	—
1774	3β-Acetoxy-13β-hydroxyoleanan-28-oic 13(28)-lactone *	1754	—	—
1774	3β-Acetoxy-13β-hydroxy-18α-oleanan-28-oic 13(28)-lactone *	1756	—	—
1775	3β:13β-Dihydroxyoleanan-28-oic 13(28)-lactone (oleanolic acid lactone)	1751	—	—
<i>1 C</i>				
1782	3β:12α-Diacetoxy-13β-hydroxyoleanan-28-oic 13(28)-lactone *	1766	—	—
1779	12α-Bromo-3β:13β-dihydroxyoleanan-28-oic 13(28)-lactone	1763	—	—
1779	3β-Acetoxy-12α:13β-dihydroxyoleanan-28-oic 13(28)-lactone *	1760	—	—
1791	3β-Acetoxy-13β-hydroxy-12-oxo-oleanan-28-oic 13(28)-lactone *	1772	—	—
<i>2 A Five-membered ring ketone</i>				
1740	Methyl 3-oxo-A-trisnorlupan-28-oate * <sup>c</sup>	—	—	1413
<i>3 A Acetates</i>				
1732	Urs-12-en-3β-yl acetate (α-amyrin acetate)	—	—	—
1732	Lup-20(29)-en-3β-yl acetate (lupenyl acetate)	1719	—	—
1732	3β-Acetoxy-lup-20(29)-en-30-al *	1718	—	—
1732	3β-Acetoxy-13β-hydroxy-12-oxo-oleanan-28-oic 13(28)-lactone *	1722	—	—
1733	3β-Acetoxyurs-12-en-11-one *	1717	—	—
1733	3β:12α-Diacetoxy-13β-hydroxyoleanan-28-oic 13(28)-lactone *	1725	—	—
1733	3β-Acetoxy-12α:13β-dihydroxyoleanan-28-oic 13(28)-lactone *	1722	—	—
1734	3β-Acetoxy-13β-hydroxyoleanan-28-oic 13(28)-lactone *	1721	—	—
1734	3β-Acetoxy-13β-hydroxy-18α-oleanan-28-oic 13(28)-lactone *	1721	—	—
1735	3β-Acetoxyoleanan-12-one *	1721	—	—
1737	3β:28-Diacetoxyoleanan-19-one *	—	—	—
<i>3 C</i>				
1747	3β:12α-Diacetoxy-13β-hydroxyoleanan-28-oic 13(28)-lactone *	1741	—	—
<i>4 B Aldehyde</i>				
1732	3β-Acetoxyolean-18-en-28-al	—	—	—
<i>5 A Methyl esters</i>				
1723	Methyl 3β:19α-dihydroxy-12-oxo-oleanan-28-oate *	1714	—	—
1725	Methyl 3-oxours-12-en-28-oate *	1714	—	—
1725	Methyl urs-12-en-28-oate	—	—	—
1725	Methyl 3β-hydroxy-12-oxo-oleanan-28-oate *	1715	—	—
1726	Methyl 3β-hydroxyurs-12-en-28-oate (methyl ursolate)	—	—	—
1726	Methyl 3-oxo-olean-18-en-28-oate *	1716	—	—
1727	Methyl 3β-hydroxyolean-18-en-28-oate (methyl morolate)	—	—	—
1727	Methyl 3β:19α-dihydroxyolean-12-en-28-oate (methyl siaresin-olate)	—	—	—
1728	Methyl 3-oxolupan-28-oate *	1719	—	—
1729	Methyl 3β-hydroxyolean-12-en-28-oate (methyl oleanolate)	—	—	—
1729	Methyl 3β-hydroxylup-20(29)-en-28-oate (methyl betulate)	—	—	—
1730	Methyl lupan-28-oate	—	—	—
1730	Methyl 3-oxo-A-trisnorlupan-28-oate * <sup>c</sup>	—	—	—
1731	Methyl 3:19-dioxo-olean-13(18)-en-28-oate *	1721	—	—
1732	Methyl 3:12:19-trioxo-olean-13(18)-en-28-oate *	1725	—	—
1733	Methyl 3:19-dioxo-olean-12-en-28-oate *	1721	—	—
<i>6 A Formates</i>				
1723	alloBetulin formate	1714	—	—
1726	Olean-18-en-3β:28-diol diformate	1714	—	—
<i>7 A Benzoates</i>				
1717	3β-Benzoyloxylup-20(29)-en-30-al *	1707	—	—
1719	3β-Benzoyloxyoleanan-12-one *	1708	—	—
1720	Urs-12-en-3β-yl benzoate (α-amyrin benzoate)	—	—	—
1720	Olean-12-en-3β-yl benzoate (β-amyrin benzoate)	—	—	—

TABLE I. (Continued.)

CCl <sub>4</sub> soln.	Compound	CHCl <sub>3</sub> soln.	Ester C=O <sup>a</sup>	Adjacent- CH <sub>2</sub> <sup>b</sup>
	7 B			
1721	Methyl 3β-benzoyloxyolean-18-en-28-oate	—	—	—
	8 A C <sub>(19)</sub> -Ketone			
1712	3β : 28-Diacetoxyoleanan-19-one *	not resolved	—	—
	8 B			
1705	Methyl 3β-acetoxy-12 : 19-dioxo-oleanan-28-oate *	1695	1730 (1721)	—
1708	Methyl 3 : 19-dioxo-olean-12-en-28-oate *	1703	—	—
1715	Methyl 3β-acetoxy-19-oxo-oleanan-28-oate *	1714	1730 (1714)	—
1717	Methyl 3β-acetoxy-19-oxo-18α-olean-12-en-28-oate *	1714	1735 (1721)	—
1720	Methyl 3β-acetoxy-19-oxo-18α-oleanan-28-oate *	—	1738	—
	9 A 30-nor-C <sub>(20)</sub> -ketone			
1712	3β-Hydroxy-30-norlupan-20-one	1700	—	1354 <sup>d</sup>
	10 A C <sub>(3)</sub> -Ketones			
1706	Urs-12-en-3-one	1698	—	1430 <sup>e</sup>
1707	Methyl 3-oxours-12-en-28-oate *	1698	—	—
1707	Urs-12-en-3 : 11-dione * <sup>c</sup>	—	—	1428
1708	Methyl 3-oxolupan-28-oate *	1699	—	—
1708	Methyl 3-oxo-olean-18-en-28-oate *	1700	—	—
1708	28-Norolean-17-en-3-one	1698	—	1431
1708	Phyllanth-3-one <sup>f</sup>	1699	—	1427
1709	Methyl 3 : 19-dioxo-olean-13(18)-en-28-oate *	1698	—	—
	10 B			
1708	Methyl 3 : 19-dioxo-olean-12-en-28-oate *	1703	—	—
1709	Methyl 3 : 12 : 19-trioxo-olean-13(18)-en-28-oate *	1698	—	—
	11 A C <sub>(11)</sub> -Ketones			
1706	Methyl 3β-acetoxy-11-oxo-oleanan-28-oate *	1703	1727 (1715)	—
1707	Ursan-11-one <sup>c</sup>	—	—	1430 <sup>e</sup>
	12 A C <sub>(12)</sub> -Ketones			
1698	Methyl 3β : 19α-dihydroxy-12-oxo-oleanan-28-oate *	1692	—	—
1699	Methyl 3β-acetoxy-19α-hydroxy-12-oxo-oleanan-28-oate *	1692	1725 (1714)	1422 <sup>e</sup>
1700	3β-Hydroxyoleanan-12-one	1692	—	1420
1701	3β-Acetoxyoleanan-12-one *	1692	—	1420
1701	3β-Benzoyloxyoleanan-12-one *	1696	—	1419
1701	Methyl 3β-hydroxy-12-oxo-oleanan-28-oate *	1696	—	1419
1703	Methyl 3β-acetoxy-12-oxo-oleanan-28-oate *	1696	1727 (1717)	1420
	12 B			
1705	Methyl 3β-acetoxy-12 : 19-dioxo-oleanan-28-oate *	1695	1730 (1721)	1415
	12 C			
1718	3β-Acetoxy-13β-hydroxy-12-oxo-oleanan-28-oic 13(28)-lactone *	1715	—	1426
	13 A Carboxylic acids			
1744 <sup>g</sup>	} 3β-Hydroxyurs-12-en-28-oic acid (ursolic acid)	1714	—	—
1687				
1742 <sup>g</sup>	} 3β-Hydroxyolean-18-en-28-oic acid (morolic acid)	1714	—	—
1696				
1745 <sup>g</sup>	} 3β-Hydroxyolean-12-en-28-oic acid (oleanolic acid)	1714	—	—
1696				

\* These compounds have one or more additional carbonyl bands, the frequencies of which are given in other sections.

<sup>a</sup> Composite bands of methyl ester and acetate carbonyl groups which are not given in sections 3 and 5 (value for chloroform solution in parentheses). <sup>b</sup> Carbon tetrachloride solution. <sup>c</sup> Prepared in this department. <sup>d</sup> Methyl absorption of -CO-CH<sub>3</sub> group. <sup>e</sup> Partly-resolved shoulder only. <sup>f</sup> Hexacyclic triterpenoid, included because of close relation to α-amyrin series. <sup>g</sup> Monomer frequency—see text.

The six-membered ring ketones at positions 3, 11, 12, and 19 and the 30-nor-C<sub>(20)</sub>-ketone (IV) which absorb between 1698 and 1712 cm.<sup>-1</sup> cannot all be distinguished with certainty, but a study of the region of C-H bending absorption will usually allow a distinction to be made (see below). By careful measurements a C<sub>(12)</sub>-ketone group can be distinguished from the others, but if only a sodium chloride prism is available this might not be possible.

TABLE 2.† Conjugated carbonyl frequencies (cm.<sup>-1</sup>).

CCl <sub>4</sub> soln.	Compound	CHCl <sub>3</sub> soln.	Ester C=O.
	14 A $\Delta^{20(29)}\text{-C}_{(30)}$ -aldehydes		
1696	3 $\beta$ -Acetoxyup-20(29)-en-30-al *	1689	—
1696	3 $\beta$ -Benzoyloxyup-20(29)-en-30-al *	1691	—
	15 A $\Delta^{13(18)}\text{-C}_{(12)}\text{:C}_{(19)}$ -Diketone		
1692 1709	} Methyl 3 : 12 : 19-trioxo-olean-13(18)-en-28-oate *	—	—
		16 A $\Delta^{13(18)}\text{-C}_{(19)}$ -Ketone	
1689	Methyl 3 : 19-dioxo-olean-13(18)-en-28-oate *	1684	—
	17 A $\Delta^{12}\text{-C}_{(11)}$ -Ketones		
1665	Methyl 3 $\beta$ -acetoxy-11-oxo-olean-12-en-28-oate *	1649	1729 (1721)
1665	Methyl 3 $\beta$ -acetoxy-11-oxours-12-en-28-oate *	1656	1731 (1721)
1665	Methyl 3 $\beta$ -acetoxy-11-oxo-olean-12-en-29-oate *	1652	1731 (1721)
1665	Methyl 3 $\beta$ -acetoxy-11-oxo-18 $\alpha$ -olean-12-en-28-oate *	1656	1734 (1721)
1666	Urs-12-en-11-one <sup>c</sup>	1650	—
1666	Urs-12-en-3 : 11-dione * <sup>c</sup>	—	—
1666	3 $\beta$ -Acetoxyurs-12-en-11-one *	1649	—
	18 A $\Delta^{12:18}$ -Diene-C <sub>(11)</sub> -ketone		
1663	Methyl 3 $\beta$ -acetoxy-11-oxo-oleana-12 : 18-dien-28-oate *	1649	1732 (1719)

† See heading and footnotes to Table 1.

TABLE 3. Summary of carbonyl frequencies (cm.<sup>-1</sup>).

CCl <sub>4</sub> soln.			CHCl <sub>3</sub> soln.	
Mean	Range		Mean	Range
1774 (5) †	1772—1775	$\gamma$ -Lactone	1754 (5)	1751—1756
1740 (1)	—	A-Tris-nor-C <sub>(3)</sub> -ketone (five-membered ring)	—	—
1733 (11)	1732—1737	Acetate	1721 (9)	1717—1725
1732 (1)	—	Aldehyde	—	—
1728 (16)	1723—1733	Methyl ester	1718 (8)	1714—1725
1725 (2)	1723—1726	Formate	1714 (2)	—
1719 (4)	1717—1720	Benzoate	1708 (2)	1707—1708
1712 (1)	—	C <sub>(19)</sub> -Ketone (oleanane series)	—	—
1712 (1)	—	C <sub>(20)</sub> -Ketone (30-norlupane series)	1700 (1)	—
1708 (8)	1706—1709	C <sub>(3)</sub> -Ketone	1699 (7)	1698—1700
1706 (2)	1706—1707	C <sub>(3)</sub> -Ketone	1703 (1)	—
1700 (7)	1698—1703	C <sub>(12)</sub> -Ketone	1694 (7)	1692—1696
1744 } (3)	1742—1745 }	Carboxylic acid	1714 (3)	—
1693 }	1687—1696 }			
1696 (2)	—	Conjugated aldehyde	1690 (2)	1689—1691
1709 } (1)	—	$\Delta^{13(18)}\text{-C}_{(12)}\text{:C}_{(19)}$ -Diketone (oleanane series)	—	—
1692 }				
1689 (1)	—	$\Delta^{13(18)}\text{-C}_{(19)}$ -Ketone (oleanane series)	1684 (1)	—
1665 (7)	1665—1666	$\Delta^{12}\text{-C}_{(11)}$ -Ketone	1652 (6)	1649—1656
1663 (1)	—	$\Delta^{12:18}$ -Diene-C <sub>(11)</sub> -ketone	1649 (1)	—

† No. of compounds studied.

TABLE 4. Frequencies of "adjacent methyl or methylene" groups (cm.<sup>-1</sup>, in carbon tetrachloride solutions).

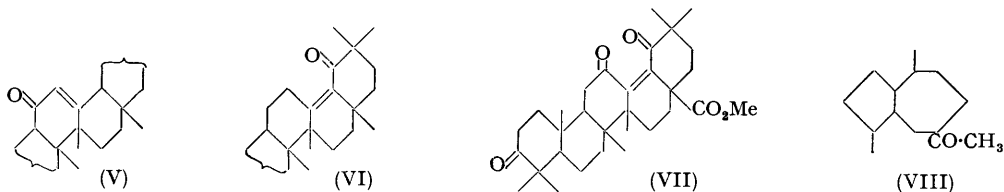
	Mean	Range
C <sub>(11)</sub> -Ketone	1430 (1) †	—
C <sub>(3)</sub> -Ketone	1429 (4)	1427—1431
C <sub>(12)</sub> -Ketone	1420 (6)	1419—1422
A-Nor-C <sub>(3)</sub> -ketone	1413 (1)	—
30-Nor-C <sub>(20)</sub> -ketone	1354 (1)	—

† No. compounds of studied.

The frequency of  $1712\text{ cm.}^{-1}$  for the  $C_{(19)}$ -ketone should be regarded as a tentative assignment only, since in all compounds available the absorption of this group was overlapped to some extent by neighbouring bands.

The carboxylic acids exist in carbon tetrachloride solution mostly in the dimeric form with the carboxyl groups hydrogen-bonded, and this system absorbs near  $1693\text{ cm.}^{-1}$ . The small amount of monomer present has its carbonyl frequency at  $1744\text{ cm.}^{-1}$  which usually appears as a weak shoulder at the side of the dimer absorption. The acids are anomalous in chloroform solution where their carbonyl bands are extremely broad with the peak near  $1714\text{ cm.}^{-1}$ . This broadening must be related to solvent-solute hydrogen bonding, and further work on these compounds is in progress.

The well-known lowering of carbonyl frequency (which is accompanied by an increase in intensity) with conjugation is clearly illustrated by the triterpenoids listed in Table 2. The drop in frequency from that of the saturated compound is proportional to the efficiency of the conjugation but the effect may be opposed to some extent by the stiffening of the ring system caused by the introduction of the double bonds. Thus the lowering is much greater in the  $\Delta^{12}C_{(11)}$ -ketones (V;  $41\text{ cm.}^{-1}$ ) than in the  $\Delta^{13(18)}C_{(19)}$ -ketone (VI;  $23\text{ cm.}^{-1}$ ).



In the only  $\Delta^{13(18)}C_{(12)}:C_{(19)}$ -diketone (VII) studied neither carbonyl group conjugates completely with the double bond. The total carbonyl absorption consists of bands at  $1732$  (ester),  $1709$ , and  $1692\text{ cm.}^{-1}$ , with the middle peak approximately twice as intense as the other two. Part of this intensity belongs to the  $C_{(3)}$ -ketone while the rest of it and the band at  $1692\text{ cm.}^{-1}$  must be due to the components of the conjugated system.

With the exception of some 13(28)-lactones with  $C_{(12)}$ -substituents all the polycarbonyl compounds studied absorb at the same frequencies as the respective monocarbonyl compounds, and the bands are resolved if they differ in frequency by about  $10\text{ cm.}^{-1}$ . When their centres are closer than this they appear as one band, which may or may not be asymmetrical, and intensity measurements<sup>11</sup> must be used to determine the number of groups present.

*Interaction of Groups.*—The overlapping of independent absorption bands should not be confused with interaction of neighbouring groups which causes them to absorb at frequencies displaced from their normal positions. A number of lactones listed in Table 1 (1C) show this type of interaction. Thus  $3\beta$ -acetoxy-12-oxo-oleanolic lactone, which might be expected to absorb at  $1774$  (lactone),  $1732$  (acetate), and  $1700\text{ cm.}^{-1}$  ( $C_{(12)}$ -ketone), has its carbonyl bands at  $1791$ ,  $1732$ , and  $1718\text{ cm.}^{-1}$ . A hydroxy- or bromo-substituent at  $C_{(12)}$  raises the lactone carbonyl frequency to  $1779\text{ cm.}^{-1}$ . The spectrum of  $3\beta:12\alpha$ -diacetoxy-oleanolic lactone illustrates the differentiation of two types of acetate group, since the  $C_{(12)}$ -acetoxy-carbonyl frequency is raised to  $1747\text{ cm.}^{-1}$  while the  $C_{(3)}$ -acetate absorbs at the expected position ( $1733\text{ cm.}^{-1}$ ). The lactone absorption is at  $1782\text{ cm.}^{-1}$ .

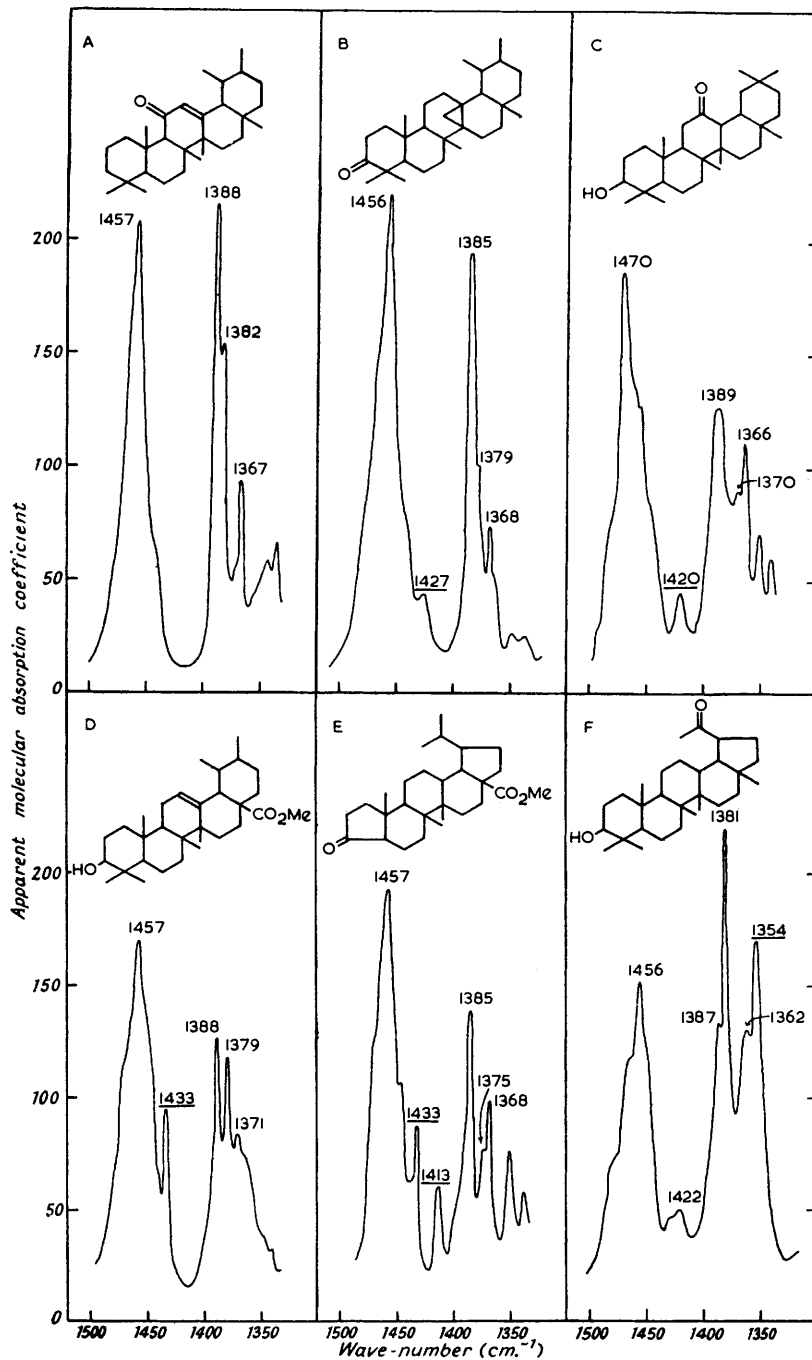
*Adjacent-methylene Absorption.*—Jones and Cole<sup>9</sup> have shown how the absorption of methyl and methylene groups can supply useful additional information about the carbonyl groups in steroids. The results of similar measurements on the pentacyclic triterpenoids are presented in Tables 1 and 4. The Fig. \* illustrates typical spectra in this region for compounds containing respectively no adjacent methylene group, methylene groups next to  $C_{(3)}$ - and  $C_{(12)}$ -carbonyl groups, and five-membered ring carbonyl groups.

The effect of a carbonyl group is to lower the bending frequency of an adjacent methyl or methylene group. It should be noted particularly that the effects in the triterpenoids

\* Formulæ based on ursane in the figure are shown with the usual six-membered E-ring, but are not intended to support this structure rather than another (see above).

<sup>11</sup> Ramsay, *J. Amer. Chem. Soc.*, 1952, **74**, 72; Jones, Ramsay, Keir, and Dobriner, *ibid.*, p. 80.

Infrared spectra in the region of methyl and methylene bending absorption.



A. Urs-12-en-11-one.

B. Phyllanth-3-one.

C. 3β-Hydroxyoleanan-12-one.

D. Methyl 3β-hydroxyurs-12-en-28-oate (methyl ursolate).

E. Methyl 3-oxo-Δ-trisnorlupan-28-oate.

F. 3β-Hydroxy-30-norlupan-20-one.



are not identical with those found in steroid spectra for comparable positions. In steroids,  $C_{(2)}$ - and  $C_{(4)}$ -methylene groups ( $C_{(3)}$ -ketone) absorb near  $1420\text{ cm.}^{-1}$  while in the 3-oxotriterpenoids the  $C_{(2)}$ -methylene group absorbs near  $1430\text{ cm.}^{-1}$ ; a  $C_{(11)}$ -methylene in 12-oxosteroids absorbs at  $1434\text{ cm.}^{-1}$  while the same group in 12-oxotriterpenoids absorbs close to  $1420\text{ cm.}^{-1}$ . The only five-membered ring ketone studied here, an A-nor- $C_{(3)}$ -ketone (III), has its adjacent methylene absorption at  $1413\text{ cm.}^{-1}$ , which is close to the range found for 17-oxosteroids and tetracyclic triterpenoids.<sup>12</sup>

The absorption in this region of the spectrum is slightly complicated by the fact that methyl esters have a band near  $1435\text{ cm.}^{-1}$  (see Fig. ; D) and this will interfere with measurements on  $C_{(3)}$ -ketones. However, the carbonyl frequencies of these two types are easily distinguished.  $C_{(12)}$ -Ketones and those on five-membered rings may be positively identified even in the presence of methyl esters (see Fig. ; E). This is important particularly when dealing with five-membered ring ketones, whose carbonyl absorption is very close to that of esters and may not be resolved, especially if a sodium chloride prism is used. The  $C_{(19)}$ -ketones (oleanane series) have no adjacent methylene groups.

The methyl ketone (IV) prepared from lupeol may be identified by the well-defined band at  $1354\text{ cm.}^{-1}$  due to the bending vibration of the side-chain methyl group (see Fig. ; F). The carbonyl and methyl bending frequencies of this compound are similar to those described by Jones and Cole<sup>9</sup> for the 20-oxosteroids of the pregnane series, except that an additional small band is present at  $1422\text{ cm.}^{-1}$ . This might be due to the antisymmetrical methyl bending vibration lowered by the influence of the carbonyl group from its usual position near  $1450\text{ cm.}^{-1}$  (always obscured by ring methylene absorption) but such an effect was not found in the 20-oxosteroids. However, in the sesquiterpene field the methyl ketone (VIII) prepared from guaiol<sup>13</sup> shows, besides its carbonyl band at  $1712$  and "adjacent methyl" band at  $1352\text{ cm.}^{-1}$ , a small band at  $1426\text{ cm.}^{-1}$  similar to that described above for the lupeol derivative.

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<sup>12</sup> Barnes, Barton, Cole, Fawcett, and Thomas, *J.*, 1953, 571.

<sup>13</sup> Cole, Melrose, and White, unpublished results.

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