253. *Infrared Spectra of Natural Products. Part VII.** The Identi-
fication and Location of Ethylenic Double Bonds in Pentacyclic Triter-
penoids.*

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Frequencies and peak intensities of infrared bands in the regions of $C=C$
stretching, C–H stretching, and C–H bending absorption are given for
a number of different locations of ethylenic double bonds (both isolated
and conjugated) in compounds based on oleanane, ursane, and lupane.
Differences in ring strain account for differences in $C=C$ stretching fre-
quencies compared with those for comparable positions in steroids. The
use of " adjacent methylene " absorption near 1435 cm.$^{-1}$ in the detection
of tetrasubstituted double bonds is described.

THREE types of infrared absorption band are commonly investigated for the identification
and location of ethylenic double bonds in organic compounds,[1-3] *viz.,* that due to the $C=C$

* Part VI, *J.,* 1956, 4868.
[1] Bellamy, " The Infrared Spectra of Complex Molecules," Methuen, London, 1954.
[2] Jones, Humphries, Packard, and Dobriner, *J. Amer. Chem. Soc.,* 1950, **72**, 86.
[3] Bladon, Fabian, Henbest, Koch, and Wood, *J.,* 1951, 2402; Henbest, Meakins, and Wood, *J.,*
1954, 800.

stretching vibration (1580—1680 cm.$^{-1}$) and the bands in the regions of stretching (3000—3080 cm.$^{-1}$) and bending (680—1000 cm.$^{-1}$) vibrations of the C–H bonds attached to the trigonal carbon atoms. A fourth type of band, due to a bending vibration of methylene groups adjacent to double bonds, has been identified in work on steroids.[4] The present work is part of an investigation of the relations between the structures of triterpenoids and their infrared spectra.[5]

The compounds described here are based on the hydrocarbons oleanane (I), ursane (II), and lupane (III) and contain double bonds in a variety of positions, mostly isolated but occasionally conjugated with other ethylenic bonds or carbonyl groups. While the structures of oleanane and lupane have been completely established, controversy exists over the structure of the ursane–α-amyrin series,[6] but the numbering and location of the double bonds in these compounds is unambiguous.[7, 8]

(I)   (II)   (III)
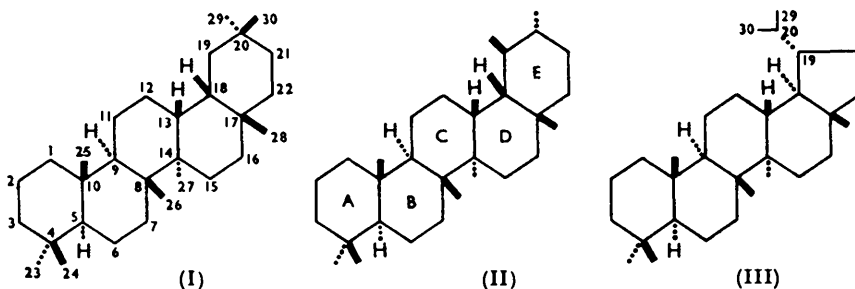
(*A*) *Non-conjugated Double Bonds.*—(1) C=C *Stretching absorption.* Since the C=C system is relatively non-polar the absorption due to its stretching vibration is very weak, and its detection by single-beam spectroscopy is made difficult by the water-vapour absorption of the atmosphere. If the air in the spectrometer is dried and a background spectrum is recorded on each chart, quite weak bands can be found, but double-beam instruments are preferred for work in this region.

The double-bond stretching frequencies of the individual compounds are given in Table 1 and characteristic frequencies for the different structures are summarised in Table 3. Representative compounds have been studied quantitatively so that in work on new substances the required concentration of solution for a given cell length can be readily calculated. The peak intensity is of the order of 0·1—0·02 of that of a carbonyl band. Intensity values have not been given where the relevant bands occur on the side of over-lapping intense carbonyl bands. The exact frequencies of the olean-18-ene compounds are not quite as certain as the others because of their low intensity. This low intensity is brought about by the presence of the *gem*-dimethyl group on $C_{(20)}$ which makes its environment much more nearly symmetrical than that of double bonds in most other positions. A few compounds were studied in chloroform solution, but there is virtually no shift in C=C absorption frequency in this solvent compared with that in carbon tetrachloride.

The stretching frequencies of the isolated endocyclic double bonds studied here do not vary significantly from one another, indicating that they are subject to approximately equal amounts of ring-strain. The data are useful for indicating the presence of trisubstituted ethylenic systems, but, apart from the low intensity of the Δ^{18}-type, the C=C stretching absorption does not assist much in fixing the position of this type of double bond

[4] Jones and Cole, *J. Amer. Chem. Soc.*, 1952, **74**, 5648; Jones, Cole, and Nolin, *ibid.*, p. 5662.
[5] Cole and Thornton, *J.*, 1956, 1007.
[6] Meisels, Jeger, and Ruzicka, *Helv. Chim. Acta*, 1949, **32**, 1075; Melera, Arigoni, Eschenmoser, Jeger, and Ruzicka, *ibid.*, 1956, **39**, 441; Beaton, Spring, Stevenson, and Strachan, *J.*, 1955, 2610; Meakins, *Chem. and Ind.*, 1955, 1353; Corey and Ursprung, *J. Amer. Chem. Soc.*, 1956, **78**, 183; Phillips and Tuites, *Chem. and Ind.*, 1956, R 29; Cole, Thornton, and White, *Chem. and Ind.*, 1956, 795.
[7] Guider, Halsall, and Jones, *J.*, 1953, 3024.
[8] *J.*, 1953, 4203.

in a new compound. The vinylidene group in the side-chain of the lupeol series can be easily identified by the relatively strong band ($\varepsilon \sim 60$) at 1640—1642 cm.[-1].

The C=C stretching frequency of the very common Δ^{12}-compounds varies over rather a wide range, the few very high results being given by compounds containing 3- and 19-carbonyl groups. While it is quite likely that the presence of a trigonal carbon atom in the E ring could influence the Δ^{12}-C=C stretching frequency, the same group at $C_{(3)}$ seems rather too remote to have any similar effect. The " normal " Δ^{12}-frequency may be taken as 1654—1657.cm.[-1], as exhibited by α- and β-amyrin and urs-12-ene.

Also it seems unlikely that the carbonyl group in methyl 3-oxo-olean-18-en-28-oate (methyl moronate, C=C 1661 cm.[-1]) could be responsible for the high C=C stretching frequency compared with those of methyl morolate (1656 cm.[-1]) and morene (1647 cm.[-1]).

Not many of the ethylenic double bonds in the pentacyclic triterpenoids can be directly compared with corresponding positions in the steroids,[2,3,9] but it is interesting that while the Δ^2-C=C frequency (1653—1661 cm.[-1]) is practically the same in both series, the $\Delta^{9(11)}$-type has a significantly higher frequency in the triterpenoids (1660 cm.[-1]; cf. steroids 1643—1648 cm.[-1]). This is related to the decrease in ring strain on increasing the size of the neighbouring D-ring from five to six members, since ring strain is known[3] to cause a lowering of endocyclic double-bond stretching frequency. The lower strain in the $\Delta^{9(11)}$-triterpenoids is also reflected in the absence of an ethylenic C-H stretching band near 3042 cm.[-1] which is easily detected in the spectra of the $\Delta^{9(11)}$-steroids (see below).

(2) =C-H *Stretching absorption.* Usually the absorption of an ethylenic C-H group appears as a shoulder or weak band on the high-frequency side of the main C-H band, which is made up of overlapping absorption bands of methyl (2872 and 2962 cm.[-1]) and methylene (2853 and 2926 cm.[-1]) groups. In the steroids, confirmatory information on the presence and amount of strain in most types of double bonds can readily be obtained from this region,[2,3] but the large number of methyl groups in the triterpenoids means that the absorption at 2962 cm.[-1] is greatly intensified. The overlap of this absorption often prevents detection of the ethylenic C-H absorption. In the trisubstituted systems it is, at best, only just discernible as an unresolved shoulder and often not visible.

Ring strain causes an increase in the frequency of this absorption, taking it away from the methyl absorption, and it occurs as a distinct band at 3037 cm.[-1] in the spectrum of ursa-9(11) : 12-diene[10] where the presence of two double bonds in the same ring considerably raises the strain. Conjugation of the double bonds may also contribute to this effect.

The vinylidene group in the side chain of the lupeol series has a very characteristic C-H stretching band at 3070 cm.[-1], which is raised to 3080, but lowered in intensity, when conjugated with a carbonyl group.

The spectra of the two $\Delta^{2:12}$-dienes studied have well-defined shoulders at 3000 and 3010 cm.[-1] respectively. This is most probably due to the *cis*-disubstituted Δ^2-system since the corresponding absorption of 2 : 3- and 6 : 7-double bonds in the steroids[9] occurs near this position and is slightly more intense than that of a trisubstituted double bond.

A similar type of absorption, near 3045 cm.[-1], found in the spectra of triterpenoids containing a CH_2 group in a 3-membered ring (*e.g.*, in phyllanthol) has been described in an earlier paper of this series.[11]

(3) =C-H *Bending absorption.* Tables 1 and 3 include the frequencies and some intensities of bands due to bending vibrations of ethylenic C-H groups. Most of the double bonds studied here are trisubstituted and give rise to one or more relatively weak bands[12] in the range 800—840 cm.[-1]. It is not clear why more than one band in this

[9] For summaries, see Cole, *Rev. Pure Appl. Chem.* (*Australia*), 1954, **4**, 111; *Fortschr. Chem. org. Naturstoffe*, 1956, **13**, 1.
[10] Newton and White, unpublished results.
[11] Cole, *J.*, 1954, 3810.
[12] Thompson and Torkington, *Proc. Roy. Soc.*, 1945, *A*, **184**, 3; *Trans. Faraday Soc.*, 1945, **41**, 246; Rasmussen and Brattain, *J. Chem. Phys.*, 1947, **15**, 120; Rasmussen, Brattain, and Zucco, *ibid.*, p. 135.

region is described as being due to a bending vibration of a lone C–H bond, but a pattern of bands is in many cases characteristic of the position of the unsaturated group in the steroid ring system.[9] The trisubstituted 12 : 13-double bonds in the triterpenoids mostly give three bands in this region, near 804, 818, and 828 cm.[-1] respectively, although occasionally the second of these is missing. The absorption of the Δ^{18}-compounds is rather erratic, while conjugation of the 12 : 13-double bond with a carbonyl group results in usually only two bands (~806, ~828). The 9(11)-double bond produces only one band, of slightly greater intensity than the other types. The C–H bending frequencies given in the summary in Table 3 have been selected to give an indication of the pattern of absorption but cannot be taken as characteristic of all compounds.

The out-of-plane C–H bending vibration of the vinylidene group of the lupeol side chain causes intense absorption at 882—885 cm.[-1] and this is the most characteristic frequency of this group (cf. 1640 and 3070 cm.[-1] above).

The *cis*-disubstituted 2:3-double bond is characterised[3] by absorption near 700 cm.[-1], due to an out-of-plane C–H bending vibration.

(4) *Fully substituted double bonds and adjacent methylene absorption.* When an ethylenic double bond is fully and symmetrically substituted, as in oleanol (IV), its high symmetry means that the C=C stretching vibration is inactive and the absence of ethylenic C–H bonds prevents the appearance of the characteristic C–H stretching or bending absorption bands. Its detection by infrared spectroscopy is therefore quite difficult, although Bladon, Henbest, and Wood[13] and Halsall[14] have pointed out that it can be detected by its ultraviolet absorption.
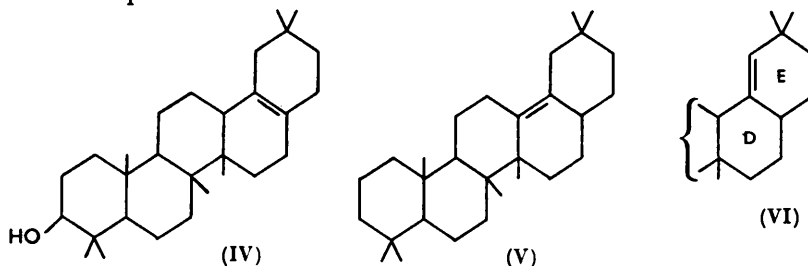
Jones and Cole[4,9] have shown that in the steroids this and other types of double bond cause a lowering of the bending frequency of adjacent methylene vibrations from 1450 cm.[-1] to near 1435 cm.[-1], and similar absorption is found in the spectra of unsaturated triterpenoids (Table 2). Thus, oleanol (IV) absorbs at 1437 cm.[-1] and 28-norolean-13(18)-ene (V) at 1435 cm.[-1]. While this absorption will not distinguish between the two types of tetrasubstituted double bond, it does, at least, show that the unsaturated groups are present. Methyl ester groups, methylene groups adjacent to trisubstituted double bonds (Table 2), and those adjacent to some types of carbonyl groups[4,5] also absorb near 1435 cm.[-1] and these must be taken into account when looking for symmetrically substituted double bonds.

Compounds in the oleanane series, containing an 18 : 19-double bond (VI), have no adjacent methylene group and have no band near 1435 cm.[-1] (Table 2), and oxidation of Δ^{12}-compounds to the corresponding Δ^{12}-$C_{(11)}$-ketones is, of course, accompanied by a disappearance of this band.

It has been reported[15] that an in-plane deformation vibration of the =CH_2 system gives rise to a band at 1410—1420 cm.[-1], but no such absorption has been found in the spectra of the lupeol derivatives studied here.

(*B*) *Conjugated Dienes.*—Conjugation of double bonds leads to a lowering of frequency of the C=C stretching absorption (Table 1*B*) and frequently causes a splitting into two

[13] Bladon, Henbest, and Wood, *Chem. and Ind.*, 1951, 866.
[14] Halsall, *ibid.*, p. 867.
[15] For summary, see ref. 1, p. 46.

TABLE 1. *Frequencies (cm.⁻¹) with some peak intensities (in parentheses) of bands characteristic of ethylenic double bonds in pentacyclic triterpenoids.*

A blank space in this or subsequent tables means that the region has not been investigated, a dash that no absorption peak is present.

Compound	C=C stretching (CCl₄ or CHCl₃)	C–H stretching (CCl₄)	C–H bending (CS₂)		
(A) Non-conjugated double bonds.					
Δ¹²-Compounds.					
Me 3 : 19-dioxo-olean-12-en-28-oate	1667	—			
Urs-12-en-3-one	1666		806(30)	—	828(30)
Me 3-oxours-12-en-28-oate	1665	3030(sh) *			
Me 3β-acetoxy-18-*iso*olean-12-en-28-oate	1663				
Me 3β-hydroxyolean-12-en-28-oate (oleanolate)	1661(15)		802(15)	816(30)	826(30)
Ursa-2 : 12-diene	1660	3000(sh)			
Me 3β-acetoxyurs-12-en-28-oate	1659	—			
Me ursa-2 : 12-dien-28-oate	1659	3010(sh)			
3β-Acetoxyolean-12-en-28-oyl chloride	1658		802(22)	816(48)	827(41)
Me 3β-acetoxyolean-12-en-28-oate	1658	—			
Me 3β-hydroxyurs-12-en-28-oate (ursolate)	1657	—	807(30)	819(19)	829(30)
Me urs-12-en-28-oate	1657	—	808(35)	819(22)	828(35)
Urs-12-ene	1657(15)	3025(sh) 3035	805(25)	—	827(35)
Urs-12-en-3β-yl benzoate	1656	3066 } † 3090			
Olean-12-en-3β-yl benzoate	1655	3035 3066 } † 3090	802	819	828
Urs-12-en-3β-yl acetate	1655	3025(sh)	806(35)	820(20)	828(35)
Urs-12-en-3β-ol (α-amyrin)	1654(20)	—	806(30)	—	829(30)
Olean-12-en-3β-ol (β-amyrin)	1654(15)	—	—	815(30)	828(22)
Me 3β : 19α-dihydroxyolean-12-en-28-oate	1650	3030(sh)	802(35)	817(15)	828(15)
Me 3β-acetoxy-19α-hydroxyolean-12-en-28-oate	1650(18)	3023(sh)	802(30)	817(15)	831(10)
Δ²-Compounds.					
Me lup-2-en-28-oate	1661(20)	3005(sh)	729		
Ursa-2 : 12-diene	1660	3000(sh)			
Me ursa-2 : 12-dien-28-oate	1659	3010(sh)			
Δ¹⁸-Compounds.					
Me 3-oxo-olean-18-en-28-oate	1661	3028(sh)	—	—	840(20)
Me 3β-hydroxyolean-18-en-28-oate	1656		802(20)	—	—
Me 3β-acetoxyolean-18-en-28-oate	1656		802(10)	—	—
Me 3β-benzoyloxyolean-18-en-28-oate	1656	3030 } † 3065	802(20)	—	—
3β-Acetoxyolean-18-en-28-al	1653(8)	3030(sh)			
Olean-18-ene-3β : 28-diol diacetate	1650		—	—	—
Olean-18-ene-3β : 28-diol diformate	1649	—			
Olean-18-ene (germanicene, morene)	1647(10)	—			
Olean-18-ene-3β : 28-diol 3-acetate	1646		—	—	—
Olean-18-en-3β-yl benzoate	1645		802(30)	819(25)	—
Δ⁹⁽¹¹⁾-Compound.					
Olean-9(11)-ene-3β : 28-diol diacetate	1660	—	—	819(40)	—
Δ²⁰⁽²⁹⁾-Compounds.					
Lup-20(29)-en-3β-ol (lupeol)	1640(60)	3073(40)	883(180)		
Lup-20(29)-en-3β-yl acetate	1640(70)	3071	883(210)		
Lup-20(29)-en-3α-ol	1641(60)	3070(45)	882		
Lup-20(29)-en-28-ol	1641(55)	3073	883(190)		
Lup-20(29)-en-3-one	1641(65)	3070(40)			
Lup-20(29)-en-3α-yl acetate	1641(58)	3070(35)	882(220)		
Lup-20(29)-ene-3β : 28-diol 3-acetate	1641(55)	3070(37)	883(200)		
Lup-20(29)-ene-3β : 28-diol diacetate	1641(65)	3071	884(210)		
Me 3β-hydroxylup-20(29)-en-28-oate (betulate)	1641	3072	885(200)		
Me 3β-acetoxylup-20(29)-en-28-oate	1641(70)	3072(36)	884(170)		
Me 3α-acetoxylup-20(29)-en-28-oate			884		
Me 3α-hydroxylup-20(29)-en-28-oate	1642	3073(40)	885(170)		
Me 3-oxolup-20(29)-en-28-oate	1642	3073(40)			
Lup-20(29)-ene-3β : 28-diol (betulin)	1642(60)	3071			

TABLE 1. (*Continued.*)

Compound	C=C stretching (CCl₄ or CHCl₃)	C–H stretching (CCl₄)	C–H bending (CS₂)		
Δ¹³⁽¹⁸⁾-Compound.					
28-Norolean-13(18)-ene	—	—	—	—	—
Δ¹⁷-Compounds.					
28-Norolean-17-en-3β-ol (oleanol)	—	—	—	—	—
28-Norolean-17-ene	—	=	=	=	=
28-Norolean-17-en-3-one	—	—	—	—	—
(B) *Conjugated dienes.*					
Δ¹²:¹⁸-Compound.					
Me 3β-acetoxyoleana-12 : 18-dien-28-oate	1650		808	819	834
Δ⁹⁽¹¹⁾:¹²-Compounds.					
Me 3β-acetoxyoleana-9(11) : 12-dien-28-oate	1635		—	824(130)	838(33)
Ursa-9(11) : 12-diene	1635	3037			
Oleana-9(11) : 12-diene-3 : 28-diol diacetate	1635		—	820(47)	—
Δ¹¹:¹³⁽¹⁸⁾-Compounds.					
Me 3β-hydroxyoleana-11 : 13(18)-dien-28-oate	1626		808(12)	816(10)	—
Me 3β-acetoxyoleana-11 : 13(18)-dien-28-oate	1627		808	817	—
Oleana-11 : 13(18)-diene-3 : 28-diol diacetate	1621		—	814	—
(C) *Conjugated ketones.*					
Δ¹²-C₍₁₁₎-Ketones.					
Me 3β-acetoxy-11-oxo-18-isoolean-12-en-28-oate	1626(80)	3023(sh)	809	—	826
Me 3β-acetoxy-11-oxo-olean-12-en-28-oate	1623(70)	—	809	—	—
Urs-12-en-11-one	1622	3025(sh)			
Me 3β-acetoxy-11-oxours-12-en-28-oate	1621(80)	3023(sh)	802(20)	817(20)	826(12)
Me 3β-acetoxy-11-oxo-olean-12-en-30-oate	1621(70)	—	806(16)	824(28)	833(28)
3β-Acetoxyurs-12-en-11-one	1619	3030(sh)			
Urs-12-ene-3 : 11-dione	1618(70)	3023(sh)			
Δ¹³⁽¹⁸⁾-C₍₁₂₎ : C₍₁₉₎-Diketone.					
Me 3 : 12 : 19-trioxo-olean-13(18)-en-28-oate	1622(70)	—			
Δ²⁰⁽²⁹⁾-C₍₃₀₎-Aldehydes.					
3β-Acetoxylup-20(29)-en-30-al	1618	3080(30) 3030			
3β-Benzoyloxylup-20(29)-en-30-al	1617	3065 ⎫ † 3088 ⎭			

* Weak, incompletely resolved shoulder.   † Absorption of benzenoid C–H groups of benzoate.

TABLE 2.   *Frequencies (cm.⁻¹) of bending vibrations of methylene groups adjacent to ethylenic double bonds in pentacyclic triterpenoids (CCl₄ solution).*

Compound		Compound	
Δ¹²-C=C, CH₂ at C₍₁₁₎.		Δ¹³⁽¹⁸⁾-C=C, CH₂ at C₍₁₂₎ and C₍₁₉₎.	
Olean-12-en-3β-yl benzoate	1436	28-Norolean-13(18)-ene	1435
Urs-12-en-3β-ol (α-amyrin)	1435		
Olean-12-en-3β-ol (β-amyrin)	1435	Δ¹⁸-C=C, no adjacent CH₂.	
Urs-12-en-3β-yl acetate	1435 *	No peak between 1400 and 1445 cm.⁻¹.	
Urs-12-en-3β-yl benzoate	1435 *	Olean-18-ene	
Urs-12-ene	— †	Olean-18-en-3β-ol	
Urs-12-en-3-one	1440 ‡	Olean-18-en-3β-yl benzoate	
		Olean-18-ene-3β : 28-diol 3-acetate	
Δ⁹⁽¹¹⁾-C=C, CH₂ at C₍₁₂₎.		Olean-18-en-3β : 28 diol diacetate	
Olean-9(11)-ene-3β : 28-diol diacetate ...	1437		
		* Incompletely resolved shoulder.	
Δ¹⁷-C=C, CH₂ at C₍₁₆₎ and C₍₁₉₎.		† See heading of Table 1.	
28-Norolean-17-en-3β-ol (oleanol)	1437	‡ Composite band due to methylene groups	
28-Norolean-17-ene	1437 *	adjacent to double bond and carbonyl group;	
28-Norolean-17-ene-3-one	1436 ‡	see ref. 5	

TABLE 3. *Summary of frequencies* $(cm.^{-1})$ *characteristic of ethylenic double bonds in pentacyclic triterpenoids (peak intensities in parentheses).*

| Position of unsaturation	C=C stretching	C–H stretching	C–H bending *	Adjacent CH₂
12 : 13	1650—1667(15—20)	3023—3030(sh)	804(30), 818(25), 828(30)	1435—1436
2 : 3	1659—1661(20)	3000—3010(sh)	729	
18 : 19	1645—1661(8—10)	3028—3030(sh)	802, variable	—†
9 : 11	1660	—	819(40)	1437
20 : 29	1640—1642(55—70)	3070—3072(35—45)	883(195)	—
13 : 18	—	—	—	1435
17 : 18	—	—	—	1436—1437
$\Delta^{12:18}$-Diene	1650		808, 819, 834	
$\Delta^{9(11):12}$-Diene	1635	3037	variable	—
$\Delta^{11:13(18)}$-Diene	1621—1627		808(12), 816(10)	
Δ^{12}-$C_{(11)}$-Ketone	1618—1626(70—80)	3023—3030(sh)	806, 820(?), 828	—
$\Delta^{13(18)}$-$C_{(12)}$: $C_{(19)}$-Diketone	1622(70)	—		

* Mean values, see text. † See heading of Table 1.

or more bands due to in-phase and out-of-phase vibrations of the system.[2] In the few conjugated dienes investigated here, only one band could be detected, although they were all measured in chloroform down to 1550 cm.⁻¹. This is not surprising in the case of the $\Delta^{11:13(18)}$-compounds where one of the double bonds is fully substituted, but a second band of lower frequency might be expected in the spectra of the other types. However, the intensity of the absorption could be very low.

The ethylenic C–H stretching band of the 9(11) : 12-diene system has been mentioned above.

(C) Conjugated Ketones.—The carbon–carbon double-bond stretching absorption of a conjugated ketone also occurs at a lower frequency than that of the non-conjugated type, and is approximately three times as intense (Table 1C). The degree of lowering of frequency varies from one type to another, being about 36 cm.⁻¹ for the Δ^{12}-$C_{(11)}$-ketones and 23 cm.⁻¹ for $\Delta^{20(29)}$-$C_{(30)}$-aldehydes. This lowering will be increased the more effective the conjugation, and also in the case of an endocyclic double bond if the presence of three trigonal carbon atoms leads to increased ring strain.

The spectrum of methyl 3 : 12 : 19-trioxo-olean-13(18)-en-28-oate (VII) is interesting since it illustrates that double-bond stretching absorption can be exhibited by a fully (but not symmetrically) substituted ethylenic system. This compound, of course, has no adjacent methylene group absorption related to the ethylenic double bond.
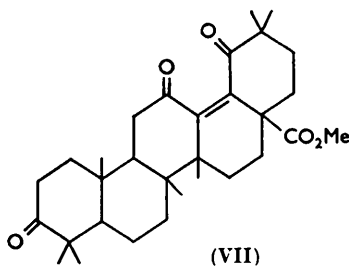
(VII)

EXPERIMENTAL

The infrared spectrometer has been· previously described.[5] Compounds were studied as carbon tetrachloride (1350—3700 cm.⁻¹, calcium fluoride prism, single-pass) and carbon disulphide (680—1350 cm.⁻¹, sodium chloride prism, double-pass) solutions at approx. 0·02M concentrations in cells of 1·2 and 3 mm. thickness. Intensities, measured as peak apparent molar extinction coefficient $[\varepsilon = (\log_{10} I_0/I)/cl]$, are accurate to approx. 5%, and have not been corrected for finite slit width.[16]

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¹⁶ Ramsay, *J. Amer. Chem. Soc.*, 1952, **74**, 72.