239. *Infrared Spectra of Natural Products. Part VIII.* The Characterization of Carbonyl Groups and Ethylenic Double Bonds in Tetracyclic Triterpenoids.*

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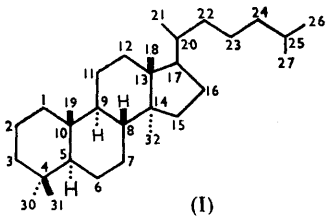
Absorption bands related to carbonyl and ethylenic double bonds in compounds based on lanosterol have been studied with emphasis on the patterns of infrared absorption due to conjugated ketone systems formed by oxidation of centres near the 8 : 9-double bond. These patterns, with their associated ultraviolet absorption, are useful in structural investigations, and additional structural information may be obtained from bands due to adjacent methylene groups. The regions of ethylenic C–H stretching and bending vibrations have also been studied for some of the compounds.

The tetracyclic triterpenoids [1] form a useful bridge in extending the well-known steroid infrared data [2] to the more complex pentacyclic triterpenoids.[1a,3,4] The absorption frequencies of functional groups would be expected to depend on position in the molecule as in the cholestane series. However, small but significant shifts might occur due to the altered mass relations caused by the additional methyl groups, and the absorption of these groups will alter the appearance of the spectra in the regions of C–H stretching and bending absorption.



(I)

The common triterpenoids differ from the common steroid derivatives notably in including compounds which contain complex conjugated ketone systems in rings B and C. The ultraviolet absorption due to these systems [5] is useful for identification and in the present work particular attention is paid to their characteristic infrared patterns.

The compounds studied here are nearly all based on lanostane (I) (a preliminary account of some of the results has been published [2c]). Most of the results will be readily applicable to similar triterpenoids based on eburicane and euphane.[5]

Experimental

To minimise the effects of intermolecular interaction,[6] all compounds were studied in dilute solution in carbon tetrachloride, chloroform (2·5—8 μ, calcium fluoride prism, single pass), or carbon disulphide (8—15 μ, sodium chloride prism, double pass). For the short-wavelength region carbon tetrachloride is preferred (and most of the ensuing discussion is based on measurements in this solvent), but representative compounds were studied in chloroform since many natural acids and polyhydroxy-compounds are insufficiently soluble in carbon tetrachloride. Carbonyl frequencies are between 3 and 20 cm.$^{-1}$ lower in chloroform,[2a] the corresponding solvent shift for ethylenic double-bond frequencies being 1—5 cm.$^{-1}$ and often not significant. The infrared spectrometer and general experimental conditions have been described.[4] Spectral slit widths were approximately 5 cm.$^{-1}$ at 3000 cm.$^{-1}$, 3 at 1700 cm.$^{-1}$ and 2 at 800 cm.$^{-1}$ and apparent molar extinction coefficients are accurate within about 5%.

Results and Discussion

The band frequencies for the individual compounds are listed in Tables 1—4 and characteristic frequencies for different structures are summarised in Tables 5 and 6. Apart

* Part VII, *J.*, 1957, 1332.

[1] (*a*) Jeger, *Fortschr. Chem. org. Naturstoffe*, 1950, **7**, 1; (*b*) Jones and Halsall, *ibid.*, 1955, **12**, 44; Gascoigne and Simes, *Quart. Rev.*, 1955, **9**, 328.

[2] (*a*) Jones and Herling, *J. Org. Chem.*, 1954, **19**, 1252; (*b*) Cole, *Rev. Pure Appl. Chem.* (*Australia*), 1954, **4**, 111; (*c*) Cole, *Fortschr. Chem. org. Naturstoffe*, 1956, **13**, 1.

[3] White, *Rev. Pure Appl. Chem.* (*Australia*), 1956, **6**, 191.

[4] Cole and Thornton, *J.*, 1956, 1007.

[5] For a summary, see Jones and Halsall, ref. 1.

[6] Cole, *Chem. and Ind.*, 1954, 661.

from carbonyl and C=C stretching frequencies, the Tables include representative measurements in the regions of ethylenic C–H stretching and bending vibrations and " adjacent methylene " vibrations,[7] all of which give valuable information in structural investigations. For example, in the non-conjugated ketones the frequency of the 3-carbonyl group (1708 cm.$^{-1}$) is hardly significantly higher than that of the 11-carbonyl group (1703—1706 cm.$^{-1}$), but with the high dispersion of a calcium fluoride prism near its long-wave cut-off there is no difficulty in distinguishing the adjacent methylene groups ($C_{(2)}$ at 1426—1427 cm.$^{-1}$, $C_{(12)}$ at 1432—1433 cm.$^{-1}$). It is interesting that the frequency of the 2-methylene group in the tetracyclic triterpenoid 3-ketones is intermediate between those found for the pentacyclic triterpenoid 3-ketones [4] (1429 cm.$^{-1}$) and the steroid 3-ketones [7] (1422 cm.$^{-1}$).

In the presence of a Δ^8-7-ketone grouping, the frequency of the 3-carbonyl group is raised to 1713—1715 cm.$^{-1}$. This must be due to extra strain in ring A because of the flattening of ring B by the conjugated system.

TABLE 1. *Frequencies (cm.$^{-1}$), with some peak intensities (in parentheses), of bands characteristic of non-conjugated carbonyl groups. In this and subsequent Tables, a blank space indicates that the region was not examined while a dash indicates that no band was found.*

C=O (CCl_4)	Compound	C=O ($CHCl_3$)	CH_2 adjacent to C=O (CCl_4)
	3-Ketones		
1708	Lanost-8-en-3-one	1700(490)	1427
1708(590)	9 : 19-*cyclo*Lanost-24-en-3-one (*cyclo*Artenone)	1697	
1713(550)	Lanost-8-ene-3 : 7-dione *	1705	1427
1715	Lanost-8-ene-3 : 7 : 11-trione *		1426
	11-Ketones		
1703(510)	3β-Acetoxylanostan-11-one *		1432
1704(500)	3β-Acetoxylanost-5-en-7 : 11-dione *	1703	1432
1706	3β-Hydroxylanost-5-en-7 : 11-dione *		1433
	7 : 11-Diketones		
1705	3β-Hydroxylanostane-7 : 11-dione		1432
1707(800)	Me 3β-acetoxy-7 : 11-dioxo-25 : 26 : 27-trisnorlanostan-24-oate *	1703	
1708(820)	3β-Acetoxylanostane-7 : 11-dione *	1703	1433
1712(1180) [a]	3β-Benzoyloxy-4 : 4 : 14-trimethyl-5α-pregnane-7 : 11 : 20-trione		1432, 1357
1712(1450) [c] / 1760(170) [d]	3β-Benzoyloxy-7 : 11-dioxo-25 : 26 : 27-trisnorlanostan-24-oic acid		1431
	3 : 7 : 11-Triketone		
1711(1040)	Lanostane-3 : 7 : 11-trione	1703	1430
	Five-membered ring ketones		
1741	A-Nor-30 : 31-bisnorlanost-8-en-3-one		1407(67)
1747 [e]	3β : 7β : 11α-Tribenzoyloxy-4 : 4 : 14-trimethyl-5α-androstan-17-one *		1411
	3β : 7β : 11α-Triacetoxy-4 : 4 : 14-trimethyl-5α-androstan-17-one		1412

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

[a] Includes C=O absorption of BzO and AcO groups. [b] Methyl bending frequency of COMe. [c] Includes C=O absorption of BzO group and dimeric acid. [d] Monomeric acid. [e] Sodium chloride prism.

For non-conjugated 7 : 11-diones and the 3 : 7 : 11-triones the individual carbonyl and adjacent methylene bands are not resolved, but the high carbonyl intensity indicates the presence of more than one group. Although the true measure of intensity is the integrated band area,[8] the peak heights given here may be useful as giving an idea of the expected

[7] Jones and Cole, *J. Amer. Chem. Soc.*, 1952, **74**, 5648; Jones, Cole, and Nolin, *ibid.*, pp. 5662, 6321.

[8] Ramsay, *J. Amer. Chem. Soc.*, 1952, **74**, 72; Jones, Ramsay, Keir, and Dobriner, *ibid.*, p. 80.

TABLE 2. *Frequencies (cm.$^{-1}$), with some peak intensities (in parentheses), of bands characteristic of conjugated carbonyl groups.*‡

C=C (CCl_4)	C=O (CCl_4)	Compound	C=O ($CHCl_3$)	C=C ($CHCl_3$)	CH_2 adjacent to C=O (CCl_4)	CH_2 adjacent to C=C (CCl_4)	Ethylenic CH bend (CS_2)
		Δ^5-7-Ketones					
1609	1667	3β-Hydroxylanost-5-ene-7 : 11-dione *			1433		
1610(90)	1668(640)	3β-Acetoxylanost-5-ene-7 : 11-dione *	1663				803, 794
		Δ^8-7-Ketones					
†	1665	3β-Hydroxylanost-8-en-7-one			1417	1425	
†	1666(620)	3β-Acetoxylanost-8-en-7-one *	1653	1583	1420	1420	
†	1670(510)	Lanost-8-ene-3 : 7-dione *	1660	1585	1418	1427	
		Δ^8-11-Ketone					
†	1657(550)	3β-Acetoxylanost-8-en-11-one *	1646	1584	1418	1428	
		Δ^8-7 : 11-Diketones					
—	1676(770) 1685(sh)	3β-Acetoxylanost-8-ene-7 : 11-dione *	1673	—	1428		
—	1676 1690	Lanost-8-ene-3 : 7 : 11-trione *			1426		
—	1677 1685(sh)	3β-Hydroxylanost-8-ene-7 : 11-dione			1427		
—	1677(700) 1684(sh)	3β-Benzoyloxylanost-8-ene-7 : 11-dione *	1673	—	1428		
—	1677(790) 1685(sh)	Methyl 3β-benzoyloxy-7 : 11-dioxo-25 : 26 : 27-trisnorlanost-8-en-24-oate *	1673	—			
		$\Delta^{5:8}$-7 : 11-Diketone					
1623(110)	1673(510) 1654(905)	3β-Acetoxylanosta-5 : 8-diene-7 : 11-dione *	1668 1648	1620	1426		813
		$\Delta^{5:8}$-7 : 11 : 12-Triketones					
1620(100)	1737(315) 1685(590) 1650(960)	Lanosta-5 : 8-diene-7 : 11 : 12-trione	1736 1681 1646	1615	(ethylenic CH str 3075 cm.$^{-1}$)	—	820, 790, 768, 730
1619(100)	1738(320) 1686(560) 1655(980)	3β-Hydroxylanosta-5:8-diene-7 : 11 : 12-trione	1735 1682 1648	1618		—	820, 788, 769, (34) (64) (24) 731 (30)
1622(95)	1740(770)[a] 1684(570) 1656(940)	3β-Acetoxylanosta-5 : 8-diene-7 : 11 : 12-trione	1732 1682 1650	1620		—	820, 793, 769, 734
1631(130)	1737(315) 1685(500) 1656(940)	Lanosta-2 : 5 : 8-triene-7 : 11 : 12-trione	1733 1681 1646	1627	(ethylenic CH str 3075 cm.$^{-1}$)	1412 [b]	821, 795, 772, (30) (22) (33) 748,[b] 730 (80) (48)
		$\Delta^{5:8:11}$-7-Ketone					
1615(~400)	1647(900)	Lanosta-5 : 8 : 11-trien-7-one			(ethylenic CH str 3047, 3010 cm.$^{-1}$)		830, 749,[b] 729
		$\Delta^{8:5:8}$-7 : 11 : 12-Triketone (iso)					
1631(710)	1735(390) 1682(630) 1645(880)	3-*iso*Propylidene-A-nor-30 : 31-bisnorlanosta-5 : 8-diene-7 : 11 : 12-trione (*iso*lanostatrienetrione)					
		Δ^{24}-26-Aldehyde					
1650(85)	1692(750)	3β-Acetoxylanosta-8 : 24-dien-26-al *	1681	1645	1420	1434	817

* See footnote to Table 1. † Obscured by solvent absorption. ‡ A blank space indicates that the region was not investigated; a dash indicates that the region was investigated but no absorption band found. sh = unresolved shoulder.

[a] Includes C=O absorption of OAc group. [b] Attributed to the *cis*-disubstituted double bond.

TABLE 3. *Frequencies (cm.$^{-1}$), with some peak intensities (in parentheses), of bands characteristic of ethylenic double bonds.**

	Ethylenic CH stretch (CCl_4)	C=C (CCl_4)	CH_2 adjacent to C=C (CCl_4)	Ethylenic CH bend (CS_2)
(*A*) *Non-conjugated* C=C.				
Δ^7-*Compound*				
Lanost-7-en-3β-yl acetate	3030	(1662) [a]	1435	822
Δ^8-*Compounds*				
Lanost-8-ene	—	—	1434	—
Lanost-8-en-3β-yl acetate	—	—	1434	—
3β-Acetoxylanosta-8 : 24-dien-26-al	—	—	1434	—
Lanost-8-en-3β-ol	—	—	1435	—
Lanost-8-en-3-one	—	—	1435	—
Lanosta-8 : 24-diene	—	—	1435	—
Lanosta-8 : 24-dien-3β-yl acetate	—	—	1435	—
A-Nor-30 : 31-bisnorlanost-8-en-3-one	—	—	1435	—
3-*iso*Propylidene-A-nor-30 : 31-bisnorlanost-8-ene (*iso*lanostadiene)	—	—	1435	—
$\Delta^{9(11)}$-*Compounds*				
Lanost-9(11)-en-3β-ol	3053	—	1435	815
Lanost-9(11)-en-3β-yl acetate	3053	—	1435	815
Δ^{24}-*Compounds*				
Lanosta-8 : 24-diene		1673(15)		
Lanosta-8 : 24-dien-3β-yl acetate				829
9 : 19-*cyclo*Lanost-24-en-3-one		1673		836(35)
Δ^{25}-*Compounds*				
9 : 19-*cyclo*Eburic-25-en-3β-ol (*cyclo*Laudenol)	3040,[b] 3071			887
9 : 19-*cyclo*Eburic-25-en-3β-yl acetate	3040,[b] 3071			887
9 : 19-*cyclo*Eburican-3β-yl acetate	3040,[b] —			—
(*B*) *Conjugated* C=C.				
$\Delta^{7:9(11)}$-*Dienes*				
Lanosta-7 : 9(11)-diene	3030(45)	1629	1432	814, 800
Lanosta-7 : 9(11)-dien-3β-ol	3032	1629	1432	814, 800
Lanosta-7 : 9(11)-dien-3β-yl acetate	3028		1432	814, 800
$\Delta^{3:7:9(11)}$-*Triene* (iso)				
3-*iso*Propylidene-A-nor-30 : 31-bisnorlanosta-7 : 9(11)-diene (γ-lanostatriene)	3015		1430	810

* A blank space indicates that the region was not investigated; a dash indicates that the region was investigated but no absorption found.

[a] Very weak band; frequency uncertain because of water-vapour absorption in background. [b] *cyclo*Propyl ring absorption (ref. 11).

TABLE 4. *Miscellaneous ester carbonyl frequencies (cm.$^{-1}$) and benzoate* CH *frequencies.*

Compound	No. of compounds	C=O (CCl_4)	C=O ($CHCl_3$)	Aromatic CH stretch	Aromatic CH out-of-plane
Acetates	15	1733—1741	1720—1730		
Benzoates	4	1718—1720	1709—1713	3066—3071	711
Me esters	2	1740			

intensity, partly for identification and partly as an aid in deciding solution concentrations and cell lengths when recording spectra.

The five-membered ring ketones, obtained as oxidation products, have characteristic carbonyl frequencies near 1740 cm.$^{-1}$ which would not be confused with that of a normal six-membered ring carbonyl, but one of the bands of the $\Delta^{5:8}$-7 : 11 : 12-trione system (see below) lies as high as 1737—1740 cm.$^{-1}$. Also the acetate-carbonyl absorption (1733—1741 cm.$^{-1}$) usually obscures part or all of the five-membered carbonyl band and when looking for this type of group it is preferable to use benzoates (1718—1720 cm.$^{-1}$) if esterification of hydroxyl groups is necessary to increase solubility or to prevent hydrogen-bonding. In the presence of acetates, however, positive identification of the five-membered ring carbonyl can usually be obtained from the adjacent methylene absorption near 1407—1410 cm.$^{-1}$. Intensity measurements on this band have been used to determine the

number of CH_2 groups adjacent to a five-membered ring-carbonyl group in compounds related to lanosterol [9] and phyllocladene.[10]

TABLE 5. *Average* C=O *and double-bond characteristic frequencies* (*cm.*$^{-1}$).

CCl_4 Soln.			$CHCl_3$ Soln.	
C=C	C=O	Compound	C=O	C=C
	1708	3-Ketone	1699	
	1714	Δ^8-3 : 7-Diketone	1705	
	1704	11-Ketone	1703	
	1709	7 : 11-Diketone	1703	
	1711	3 : 7 : 11-Triketone	1703	
	1741	A-Nor-3-ketone		
	1747	17-Ketone		
1610	1668	Δ^5-7-Ketone	1663	
	1667	Δ^8-7-Ketone	1657	1584
	1657	Δ^8-11-Ketone	1646	1584
—	1677, 1686	Δ^8-7 : 11-Diketone	1673	—
1623	1673, 1654	$\Delta^{5:8}$-7 : 11-Diketone	1668, 1648	1620
1620	1738, 1685, 1655	$\Delta^{5:8}$-7 : 11 : 12-Triketone	1734, 1682, 1648	1618
1615	1647	$\Delta^{5:8:11}$-7-Ketone		
1631	1735, 1682, 1645	$\Delta^{3:5:8}$-7 : 11 : 12-Triketone		
1650	1692	Δ^{24}-26-Aldehyde	1681	1645
1673		24 : 25-C=C		
1629		$\Delta^{7:9(11)}$-Diene		

TABLE 6. *Frequencies* (*cm.*$^{-1}$) *of methylene groups adjacent to* C=O *and* C=C *centres* (CCl_4 *solution*). *The position of the absorbing group is given in parentheses.*

	CH_2 adjacent to C=O	CH_2 adjacent to C=C
3-Ketone	1426—1427 (C_2)	
11-Ketone	1432—1433 (C_{12})	
7 : 11-Diketone	1431—1433 (C_6, C_{12})	
A-Nor-3-ketone	1407 (C_2)	
Δ^8-7-Ketone	1417—1420 (C_6)	1425—1427 (C_{11})
Δ^8-11-Ketone	1418 (C_{12})	1428 (C_7)
Δ^8-7 : 11-Diketone ...	1426—1428 (C_6, C_{12})	
$\Delta^{5:8}$-7 : 11-Diketone	1426 (C_{12})	

	CH_2 adjacent to C=C
Δ^{24}-26-Aldehyde	1420 (C_{23})
2 : 3-C=C	1412 (C_1)
7 : 8-C=C	1435 (C_6)
8 : 9-C=C	1434—1435 (C_7, C_{11})
9 : 11-C=C	1435 (C_{12})
$\Delta^{7:9(11)}$-Diene	1432 (C_6, C_{12})
$\Delta^{3:7:9(11)}$-Triene ((iso)	1430 (C_2, C_6, C_{12})

The carbonyl absorption of the carboxylic acid included in section 3 of Table 1 is considered in more detail in Part XII of this series (below).

The identification of isolated ethylenic centres (Table 3*A*) is not easy by single-beam infrared spectroscopy since their stretching absorption is very weak and is partly obscured by absorption by atmospheric water-vapour. Such a band was found with certainty only in the case of the Δ^{24}-compounds, but with the other types assistance in identification is obtained in other regions of the spectrum. The adjacent methylene band at 1435 cm.$^{-1}$ is particularly useful in telling the presence of the 8 : 9-double bond which, being symmetrical, has no C=C stretching absorption and, since it is fully substituted, can give no ethylenic C–H stretching or bending absorption. Ring strain due to the neighbouring five-membered D-ring raises the ethylenic C–H stretching frequency of the $\Delta^{9(11)}$-compounds to 3053 cm.$^{-1}$, while in the *cyclo*laudenol derivatives bands due to both the vinylidene group (3071 cm.$^{-1}$) and the *cyclo*propane ring [11] (3040 cm.$^{-1}$) are well resolved.

For conjugated diones and ketones the frequencies of both the carbonyl and the ethylenic centre are lowered and their intensities increased with respect to the corresponding non-conjugated compounds. Some of the C=C bands (*e.g.*, for Δ^8-7- and Δ^8-11-ketones) fall at too low a frequency to be studied in carbon tetrachloride but can be easily found in

[9] Barnes, Barton, Cole, Fawcett, and Thomas, *J.*, 1953, 571.
[10] Bottomley, Cole, and White, *J.*, 1955, 2624.
[11] Cole, *J.*, 1954, 3807.

chloroform solution. The 8 : 9-ethylenic centre is no longer symmetrical in these conjugated ketones and its stretching absorption shows up clearly near 1584 cm.$^{-1}$ (in chloroform). *trans*-Fusion of the five-membered D-ring with the C-ring tends to flatten the latter, making the ethylenic bond and the 11-carbonyl group more nearly coplanar and facilitating conjugation. This is reflected in its carbonyl frequency (1657 cm.$^{-1}$), which is lower than that for the Δ^8-7-carbonyl group (1665—1670 cm.$^{-1}$), and this difference suffices to distinguish the two in oxidation products.

For these conjugated ketones the hyperconjugative effect on the adjacent methylene groups is enhanced, and usually two bands can be resolved, *viz.*, 1417—1420 cm.$^{-1}$ for the CH_2 next to the carbonyl and 1425—1428 cm.$^{-1}$ for that next to the ethylenic bond.

In the Δ^8-7 : 11-diones the two carbonyl groups act in opposition in conjugating with the double bond. Two resolved peaks (1676, 1690 cm.$^{-1}$) are found in the spectrum of lanost-8-ene-3 : 7 : 11-trione (apart from the 3-ketone absorption at 1715 cm.$^{-1}$), and the lower of these we assign to the 11-carbonyl group since this appears to conjugate more effectively (see above). A similar effect has been reported [4] for $\Delta^{13(18)}$-pentacyclic triterpenoid 12 : 19-diketones. The other compounds in this class have an unsymmetrical carbonyl band with its peak near 1677 cm.$^{-1}$ and an unresolved shoulder near 1685 cm.$^{-1}$. In chloroform the absorption (1673 cm.$^{-1}$) is slightly broader than in carbon tetrachloride, and for the compounds studied here the asymmetry was not observed. A carbonyl frequency of 1671 cm.$^{-1}$ has been reported [12] for this system, but the medium was not named.

The relatively high carbonyl frequencies of these compounds support the view that conjugation is incomplete, and further evidence is found in the higher adjacent methylene frequency (1426—1428 cm.$^{-1}$) compared with the singly conjugated 7- and 11-ketones (1417—1420 cm.$^{-1}$). The 8 : 9-ethylenic centre in these diones is again symmetrical, and no stretching absorption could be found.

As the conjugated system becomes longer the pattern of infrared absorption becomes more complex. 3β-Acetoxylanosta-5 : 8-diene-7 : 11-dione shows, apart from its acetate-carbonyl absorption (1741 cm.$^{-1}$), bands at 1673 cm.$^{-1}$ (singly conjugated 11-ketone) and 1654 cm.$^{-1}$ (doubly conjugated 7-ketone), and a relatively intense 5 : 6-double-bond band at 1623 cm.$^{-1}$. In this compound also the conjugation of the two carbonyl groups is somewhat mutually opposed and the 11-carbonyl frequency is not as low as that of the simple Δ^8-11-ketones.

The carbonyl pattern is even more characteristic in the case of the $\Delta^{5:8}$-7 : 11 : 12-triketones. The bands should properly be considered to belong to the system as a whole, but those at 1650—1655 and 1684—1686 cm.$^{-1}$ can be attributed to the $\Delta^{5:8}$-7-ketone and the Δ^8-11-ketone respectively, while the high-frequency absorption (1737—1740 cm.$^{-1}$) is due to the 12-carbonyl group. This kind of frequency increase has been noted previously for 11 : 12-dioxo-steroids [13] and appears to be due to the increase in ring strain since the 12-carbonyl group cannot be said to be conjugated in the usual sense. The C=C stretching band near 1620 cm.$^{-1}$ is quite intense. For lanosta-2 : 5 : 8-triene-7 : 11 : 12-trione the 2 : 3-double bond must absorb on the high-frequency side of the conjugated double-bond absorption since only one band (1631 cm.$^{-1}$) is found. The adjacent methylene peak at 1412 cm.$^{-1}$ must be attributed to the 1-methylene group since the conjugated system has none of these groups.

The spectrum of lanosta-5 : 8 : 11-trien-7-one is notable for the very low frequency (1647 cm.$^{-1}$) and high intensity of the triply conjugated carbonyl group and the intense band at 1615 cm.$^{-1}$ due to the double bonds.

*iso*Lanostatrienetrione has its two higher carbonyl frequencies at much the same frequencies as the $\Delta^{5:8}$-7 : 11 : 12-triketones, but the increased conjugation leads to a further lowering of the 7-ketone frequency. The extremely intense band at 1631 cm.$^{-1}$

[12] Warren and Watling, *J.*, 1958, 179.
[13] Jones and Dobriner, *Vitamins and Hormones*, 1949, **7**, 293.

cannot be attributed to any particular ethylenic bond, but must belong to the system as a whole.

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