

145. *The Ultraviolet Absorption of Isolated Ethylenic Bonds.*

By P. S. ELLINGTON and G. D. MEAKINS.

The ultraviolet spectra of forty-seven steroids and triterpenes containing isolated ethylenic bonds have been examined in the range 192—250 $m\mu$. With one exception ethanolic solutions of these compounds gave absorption bands centred between 193 and 205 $m\mu$. The widths and intensities of the bands were also measured.

Correlations between the structural type of a double bond and its spectrographic properties are discussed.

THE absorption of isolated ethylenic bonds near the end of the conventional ultraviolet range ($\sim 200 m\mu$) has been used by Henbest and his co-workers¹ and by Halsall² for detecting and characterising olefinic centres in steroids and triterpenes. With the apparatus in use at that time the region below 205 $m\mu$ could not be investigated; consequently measurements were limited to the long-wavelength edge of the bands (the so-called "end absorption") and it was recognised that the intrusion of scattered light led to certain inaccuracies in the absorption intensities at wavelengths approaching 205 $m\mu$. More recently Turner³ examined solutions of olefins in hexane between 210 and 160 $m\mu$ with a vacuum-spectrophotometer and located the positions of the absorption maxima. While few such spectrophotometers are available several conventional instruments in current use are capable of accurate operation down to about 190 $m\mu$.

The object of the present work was to see whether the maxima could be observed with a routine spectrophotometer, and whether the information obtained could be used to distinguish between various types of double bond. The fifty-two steroids and triterpenes examined were chosen to provide examples of various structural types, and each compound was purified until satisfactory physical constants were obtained. Although ethanol's transmission below 190 $m\mu$ is somewhat inferior to that of hexane, ethanol is a much more powerful solvent for the majority of polycyclic compounds containing oxygenated substituents and was therefore used in this survey.

EXPERIMENTAL

Spectroscopy.—Spectra were recorded on a Cary spectrophotometer (model 14-M) with dynode setting 5 and a scanning speed of 50 sec./ $m\mu$. The wavelength scale of the instrument was checked by using the emission lines from a mercury-vapour lamp. The spectrometer was flushed with "white spot" cylinder nitrogen through the five inlet nozzles for 48 hr. at 250

¹ Bladon, Henbest, and Wood, *J.*, 1952, 2737.

² Halsall, *Chem. and Ind.*, 1951, 867.

³ Turner, *J.*, 1959, 30.

ml./min. before use and during operation. While cells were being introduced into the spectrometer the supply of nitrogen to the cell wells was increased by using an auxiliary cylinder. One pair of matched cells (path-length 0.1 cm.) was used throughout, with "clinical absolute alcohol" as solvent. In some cases spectra were repeated using "B.D.H. spectroscopic hexane." A background run (solvent in both beams) was recorded immediately before the examination of each compound. The programmed slits were found to open fully (3 mm.) at 192 $m\mu$ when ethanol was used as solvent, and at 188 $m\mu$ when hexane was used. Results obtained at wavelengths lower than these are not quoted.

Materials.—Except for new compounds (see below) the materials were prepared by published procedures. In the following list the m. p. and $[\alpha]_D$ (in chloroform) values found in this work are quoted after the number of the compound. (For the names of compounds corresponding to the numbers see Tables 1 and 3.) Thus "1, 80—81, +25" indicates "Number 1, Cholestane, m. p. 80—81°, $[\alpha]_D$ +25°." References to compounds which are not described in Elsevier's "Encyclopædia of Organic Chemistry," Vol. 14 and Supplements, are given after the physical constants.

1, 80—81, +25.	18, 148—149, 0.	36, 175—177, +66.
2, 141.5—142, +34.	19, 111—112, +29 (ref. 7).	37, 125.5—127.5, +43 (ref. 10).
3, 192.5—193, -6.	20, 187—191, +84.	38, 127—129, +113.
4, 206—207, -16.	22, 165—166, +98.	39, 185.5—187, +115.
6, 69—70, +13 (ref. 4).	23, 198—202, +99.	40, 203—205, +221 (ref. 11).
7, 75—76, +67.	25, 177—178, -32 (ref. 7).	41, 106—109, +130 (ref. 10).
8, 84—85, -84 (ref. 5).	26, 146—147, +62.	42, 164—166, +57.
9, 163—164, +31.	27, 121—122, +58.	43, 116—118, +135.
10, 207—210, +37.	28, 123—124, +36.	44, 148.5—150, +140.
11, 216—217, +42.	29, 208—211, -16.	45, 142—143, +33 (ref. 7).
12, 83—84, +76.	30, 129—130, +12.	48, 147—148, -61 (ref. 7).
13, 131—132, +45 (ref. 6).	31, 109—111, +2 (ref. 8).	49, 129—130, -5 (ref. 7).
14, 87—88, +10.	32, 60—61, +5.	50, 173—175, +25.
15, 94—95, -56.	33, 129—130, +44 (ref. 9).	51, 134—136, +118.
16, 150—151, -40.	34, 213—214, +19.	52, 165—170, +120.
17, 86—87, +12 (ref. 5).	35, 176—177.5, +105.	

The trisnor-hydrocarbons nos. 5, 21, 24 [derived respectively from lupanol (no. 4), α -amyrin (no. 20), and β -amyrin (no. 23) by modifying ring A to the form shown] * were prepared by Huang-Minlon reduction of the corresponding 3-oxo-compounds [(5 β H)4,23,24-trisnor-5(4 \rightarrow 3)abeo-lupan-3-one (no. 35), -urs-12-en-3-one,¹² and -olean-12-en-3-one (no. 40)]. The *abeolupane* (no. 5) crystallised from ethyl acetate-ethanol as rods, m. p. 166—167°, $[\alpha]_D$ +4° (c 1.2) (Found: C, 87.3; H, 12.2. C₂₇H₄₆ requires C, 87.5; H, 12.5%). The *abeours-12-ene* (no. 21) crystallised from ethyl acetate-methanol as plates, m. p. 90—91°, $[\alpha]_D$ +116° (c 1.1) (Found: C, 87.7; H, 11.9. C₂₇H₄₄ requires C, 88.0; H, 12.0%). The *abeo-olean-12-ene* (no. 24) crystallised from ethyl acetate-methanol as plates, m. p. 149—150°, $[\alpha]_D$ +120° (c 1.1) (Found: C, 87.8; H, 12.1. C₂₇H₄₄ requires C, 88.0; H, 12.0%).

Ergosta-7,22-diene-3 β ,11 β -diol (no. 46). A solution of 3 β -acetoxyergosta-7,22-dien-11-one¹³ (3.1 g.) in ether (250 c.c.) was refluxed with lithium aluminium hydride (1.5 g.) for 2 hr. Standard manipulation gave the *diol* (2.1 g.), m. p. 157—161° after crystallisation from methanol, $[\alpha]_D$ -32° (c 1.0) (Found: C, 80.9; H, 11.0. C₂₈H₄₆O₂ requires C, 81.1; H, 11.2%).

* The prefix "abeo" and the accompanying numerals indicate a bond migration in the molecule named as parent. Thus 5(4 \rightarrow 3)abeolupane is lupane in which the 5,4-bond has been replaced by a 5,3-bond (giving a five-membered ring A). This usage and related nomenclature proposals are being actively considered by the Society.—Ed.

⁴ Henbest and Wilson, *J.*, 1956, 3289.

⁵ Turner, Meador, and Winkler, *J. Amer. Chem. Soc.*, 1957, **79**, 4122.

⁶ Plattner, Heusser, and Kulkarni, *Helv. Chim. Acta*, 1949, **32**, 265.

⁷ Castells, Jones, Meakins, and Williams, *J.*, 1959, 1159, and unpublished work.

⁸ Laubach and Brunings, *J. Amer. Chem. Soc.*, 1952, **74**, 705.

⁹ Dauben, Micheli, and Eastham, *ibid.*, p. 3852.

¹⁰ Jones, Meakins, and Stephenson, *J.*, 1958, 2156.

¹¹ Allan, Favez, Spring, and Stevenson, *J.*, 1956, 456.

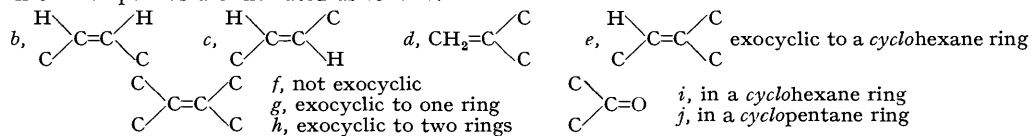
¹² Allan, Spring, Stevenson, and Strachan, *J.*, 1955, 3371.

¹³ Bladon, Henbest, Jones, Lovell, Wood, Woods, Elks, Evans, Hathway, Oughton, and Thomas, *J.*, 1953, 2921.

TABLE 1. *Ultraviolet absorption of compounds containing one ethylenic bond.*

Compounds 1—5 (not containing double bonds) are included for comparison. λ_{\max} figures are in μ . ϵ_{\max} values are molecular extinction coefficients (mole⁻¹ l. cm.⁻¹ units). ϵ_x is ϵ at $x \mu$. $\Delta\lambda_i$ is twice the difference between λ_{\max} and the wavelength (on the high-wavelength side of the band) at which $\epsilon = \frac{1}{2}\epsilon_{\max}$.

Compounds containing no C=C or C=O bonds are denoted by *a*. Types of ethylenic bond present in the compounds are indicated as follows:



No.	Name	Structural type	Ethanol as solvent				Hexane as solvent				
			Present work			ϵ_{210}	Previous work ¹	Present work		Previous work ³	
			λ_{\max}	ϵ_{\max}	$\Delta\lambda_i$			λ_{\max}	ϵ_{\max}	λ_{\max}	ϵ_{\max}
1	Cholestane	<i>a</i>	no max.	$\epsilon_{195} = 90$	$\epsilon_{200} = 50$						
2	Cholestan-3 β -ol	<i>a</i>	"	$\epsilon_{195} = 300$	$\epsilon_{200} = 120$		~150				
3	Lupane	<i>a</i>	"	$\epsilon_{195} = 240$	$\epsilon_{200} = 80$						
4	Lupen-3 β -ol	<i>a</i>	"	$\epsilon_{195} = 350$	$\epsilon_{200} = 160$						
5	(5 β H)4,23,24-Trisnor-5(4 \rightarrow 3)abeo-lupane	<i>a</i>	"	$\epsilon_{195} = 350$	$\epsilon_{200} = 210$						
6	Cholest-1-ene	<i>b</i>	194	6200	12	500					
7	Cholest-2-ene	<i>b</i>	<193			200	200	189	5100	182	7500
8	Cholest-6-ene	<i>b</i>	195	7500	18	1900					
9	Lup-20(29)-ene	<i>d</i>	195	8700	20	2200					
10	Lup-20(29)-en-3 β -ol	<i>d</i>	195	8900	22	2200					
11	3 β -Acetoxylup-20(29)-ene	<i>d</i>	196	9300	22	2500		194	9300	196	8450
12	Cholest-4-ene	<i>e</i>	196	9700	18	2600	3000			190	8860
13	Cholest-4-en-3 β -ol	<i>e</i>	197	9000	21	3100					
14	3 β -Acetoxycholest-4-ene	<i>e</i>	197	12,400	18	3300					
15	Cholest-5-ene	<i>e</i>	195	8100	21	2500	2700	191	8200	190	7820
16	3 β -Acetoxycholest-5-ene	<i>e</i>	195	8100	18	1400	1500				
17	Cholest-7-ene	<i>e</i>	197	5800	34	4300					
18	3 β -Acetoxyergost-7-ene	<i>e</i>	197	6000	34	4500	4700				
19	3 β -Acetoxy-5 β -lumist-7-ene	<i>e</i>	196	7500	32	4700					
20	Urs-12-en-3 β -ol	<i>e</i>	196	8200	21	2400					
21	(5 β H)4,23,24-Trisnor-5(4 \rightarrow 3)abeours-12-ene	<i>e</i>	195	8200	22	2400					
22	Olean-12-ene	<i>e</i>	195	9000	25	3200					
23	Olean-12-en-3 β -ol	<i>e</i>	195	8500	24	3100					
24	(5 β H)4,23,24-Trisnor-5(4 \rightarrow 3)abeo-olean-12-ene	<i>e</i>	195	9400	23	3100					
25	3 β -Acetoxy-5 α -lumist-8-ene	<i>f</i>	196	9000	24	3400					
26	Lanost-8-en-3 β -ol	<i>f</i>	198	7300	29	4700					
27	3 β -Acetoxylanost-8-ene	<i>f</i>	198	7300	30	4400		197	7500	202	7000
28	3 β -Acetoxy-(13 α ,14 β ,17 β H)lanost-8-ene	<i>f</i>	197	8400	28	4300				200	10,400
29	5(4 \rightarrow 3)Abeo-lup-3-ene	<i>g</i>	195	9700	29	4800					
30	Ergost-8(14)-en-3 β -ol	<i>h</i>	204	11,400	29	10,300					
31	3 β -Acetoxyergost-8(14)-ene	<i>h</i>	204	12,200	29	10,700	10,500				
32	3 β -Methoxyergost-8(14)-ene	<i>h</i>	204	11,300	30	10,000					

9 α -Methylergosta-7,22-diene-3 β ,11 β -diol (no. 47). 3 β -Hydroxy-9 α -methylergosta-7,22-dien-11-one¹⁰ (1 g.) in ether (150 c.c.) was reduced with lithium aluminium hydride (0.5 g.) as above. Crystallisation of the product from methanol gave the diol (705 mg.), m. p. 132—134°, $[\alpha]_D -55^\circ$ (c 0.9) (Found: C, 81.4; H, 11.25. C₂₉H₄₈O₂ requires C, 81.25; H, 11.3%).

DISCUSSION

The results are recorded in Tables 1 and 3 and illustrated in the Figures. With one exception (compound 7 in ethanol) all the compounds containing one or more C=C bonds and/or a C=O group give absorption bands between 189 and 205 m μ . That these bands are true absorption maxima and not due to instrumental factors (cf. the discussion by

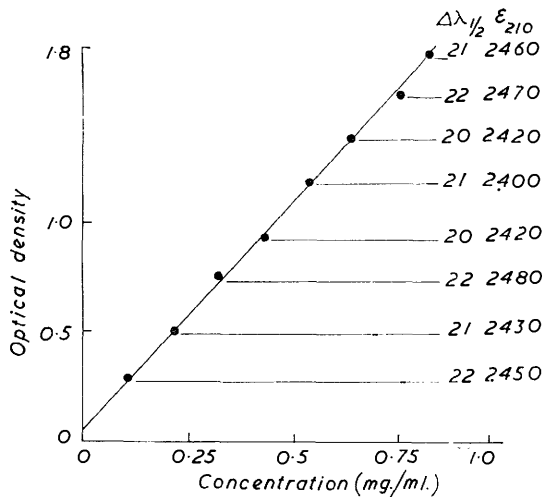
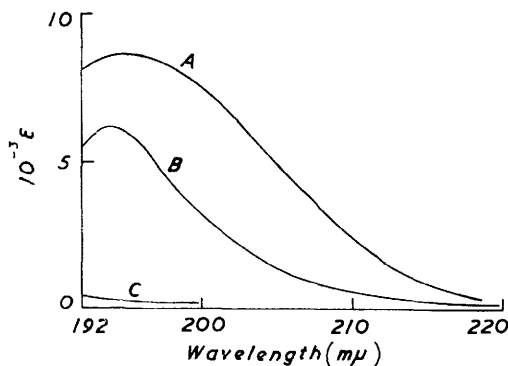


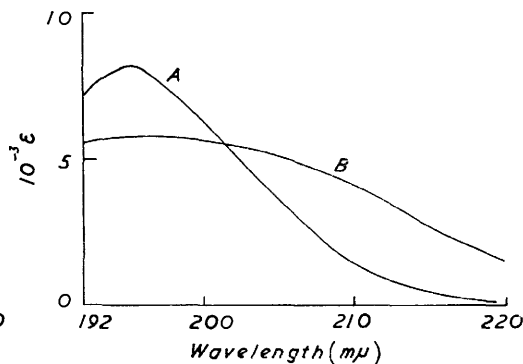
FIG. 1. Examination of cholest-5-ene, no. 15, at different concentrations.

FIG. 2.



A, No. 9 (type d). B, No. 6 (type b).
C, No. 3 (type a).

FIG. 3.



A, Δ^5 -Steroid, no. 16 (type e).
B, Δ^7 -Steroid, no. 17 (type e).

Henbest and his co-workers¹¹ is supported by several pieces of evidence. The I_0 lines (solvent in both beams) were flat, and the required light energy was reaching the detector in the ranges studied (193—250 m μ and 188—250 m μ for ethanol and hexane solutions respectively). With compounds containing neither C=C nor C=O bonds (nos. 1—5) no bands were observed. In these cases the absorption increased towards 190 m μ but the ϵ values were below 500 (Table 1 and Fig. 2): this absorption probably represents the long-wavelength edge of bands below 180 m μ associated with the saturated hydrocarbon

centres.³ Inspection of Fig. 1 shows that in several runs with cholest-5-ene (no. 15) at different concentrations Beer's law was obeyed. This result and the consistency of the values found for ϵ_{210} and $\Delta\lambda_{\frac{1}{2}}$ (a measure of the band width) indicate that the results are not appreciably affected by using concentrations leading to different optical densities at the absorption maximum.

Some results of previous work^{1,3} are included in Table 1. The values of ϵ_{210} recorded by Henbest and his collaborators¹ agree well with those of the present study (compounds 2, 7, 12, 15, 16, 18, and 31). Results with compounds 11, 15, and 27 show that, while the ϵ_{max} values are not affected by using hexane rather than ethanol as solvent, the λ_{max} figures are somewhat lower for hexane solutions. With two of these compounds (nos. 7 and 27) there is disagreement between the present work and Turner's recent study.³ (The figures shown in the penultimate column of Table 1 were read from the published curves and are not quoted in ref. 3.) Although the results with cholest-5-ene (Fig. 1) show that there is little or no error due to stray light at 195 $m\mu$ in the present work, it is possible that the effect of stray light is appreciable at lower wavelengths. This may be the cause of the difference in appearance between Turner's curves and those recorded in the present investigation. Thus, while in all the cases reported here the ethylenic maximum is clearly discernible several of Turner's spectra show the ethylenic absorption as a shoulder or inflexion on a rising background (due to the absorption of saturated centres at lower wavelengths), and in these cases the ethylenic maximum was obtained by subtracting the absorption of a related saturated compound. A second, and probably more important, consideration in comparing the two studies is that the absorption bands are very broad, thus causing inherent uncertainty in the λ_{max} figures. For example, with compound 17 (Fig. 3) with an extremely broad band, the point of maximal absorption could be reasonably taken as anywhere between 195 and 199 $m\mu$.

The results of the present work (with ethanolic solutions) are summarised in Table 2. There is a general increase in the values of the four characteristics of the bands on passing down the Table. However, the divisions between the values for various types of double bond are not sharp: the considerable overlap in many cases severely limits the usefulness of the method in determining the type of double bond present. Only when a doubly exocyclic tetrasubstituted ethylenic linkage is present (the Δ^8 -compounds, nos. 30, 31, and 32, see Fig. 4) does the λ_{max} value allow unequivocal identification. This type of linkage is also characterised by high values for ϵ_{max} and ϵ_{210} . Conversely the 1,2-disubstituted *cis*-ethylenic bond (Fig. 2) gives significantly low intensity values.

TABLE 2.

	λ_{max}	$\Delta\lambda_{\frac{1}{2}}$	ϵ_{max}	ϵ_{210}
-HC=CH-	< 196	12—18	6200—7500	200—1900
CH ₂ =C<	195—196	20—22	8700—9300	2200—2500
-HC=C< (exocyclic)	195—196	18—25	8100—9700	1400—3200
Δ^7 -Steroids	196—197	32—34	5700—7500	4300—4700
>C=C< (not exocyclic).....	196—198	24—30	7300—9000	3400—4700
>C=C< (doubly exocyclic)	204	29—30	11,300—12,200	10,000—10,700

It is clear that the degree of substitution is not the only factor influencing the characteristics of the olefinic absorption bands.¹ The effect of environment is illustrated by comparing Δ^4 - and Δ^5 -steroids and Δ^{12} -triterpenes, which give a fairly compact set of results for exocyclic trisubstituted double bonds, with the formally similar Δ^7 -steroids which have much broader bands with lower ϵ_{max} and higher ϵ_{210} values. [The ϵ_{210} values are at least as useful as the ϵ_{max} values in distinguishing between different types of double bonds. While the ϵ_{210} figures are generally in line with the corresponding ϵ_{max} values, change in band shape (as in the Δ^7 -steroids) can upset this relationship.] The presence of certain substituents near the double bond can also cause marked changes. Thus the

allylic acetoxy group in no. 14 leads to unusually high intensity values, whereas the corresponding alcohol, no. 13, gives normal results.

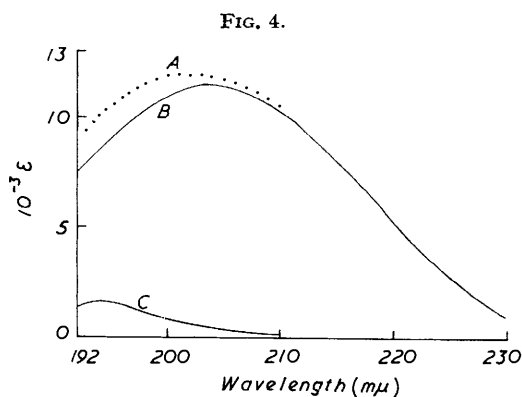


FIG. 4.
A, λ_{\max} . 201, ϵ_{\max} . 12,000. B, No. 30 (type h). C, No. 33 (type i). The dotted line is the sum of the curves for nos. 30 and 33 [cf. no. 41 (types h + i) with λ_{\max} . 200, ϵ_{\max} . 12,500].

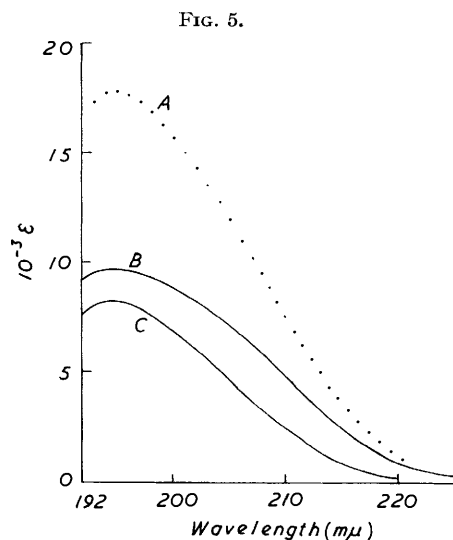


FIG. 5.
A, λ_{\max} . 195, ϵ_{\max} . 18,000. B, No. 29 (type g). C, No. 21 (type e). The dotted line is the sum of the curves for nos. 21 and 29 [cf. no. 51 (types e + g) with λ_{\max} . 196, ϵ_{\max} . 19,500].

TABLE 3. *Compounds containing two ethylenic bonds, or an ethylenic bond and a carbonyl group.*

Compounds nos. 33, 34, and 35 (containing one carbonyl group) are included for comparison.

No.	Name	Structural type	Ethanol as solvent			
			λ_{\max} .	ϵ_{\max} .	$\Delta\lambda_{\dagger}$	ϵ_{210}
33	Cholestan-3-one	<i>i</i>	194	1600	13	200
34	Lupan-3-one	<i>i</i>	193	1400	17	200
35	(5 β H)4,23,24-Trisnor-5(4 \rightarrow 3)abeolupan-3-one	<i>j</i>	193	900	16	200
36	Lup-20(29)-en-3-one	<i>d, i</i>	195	10,000	20	2400
37	3 β -Acetoxy-9 α -methylergost-7-en-11-one	<i>e, i</i>	195	10,100	16	2100
38	Urs-12-en-3-one	<i>e, i</i>	195	11,000	23	3300
39	Olean-12-en-3-one	<i>e, i</i>	195	10,000	22	3400
40	(5 β H)4,23,24-Trisnor-5(4 \rightarrow 3)abeo-olean-12-en-3-one	<i>e, j</i>	195	9300	24	3000
41	3 β -Hydroxy-9 α -methylergost-8(14)-en-11-one	<i>h, i</i>	200	12,500	28	10,000
42	Lupa-2,20(29)-diene	<i>b, d</i>	195	13,700	17	2600
43	Ursa-2,12-diene	<i>b, e</i>	194	14,900	18	3500
44	Oleane-2,12-diene	<i>b, e</i>	195	13,100	19	3300
45	5 β -Lumista-7,22-dien-3 β -ol	<i>c, e</i>	196	12,000	21	4300
46	Ergosta-7,22-diene-3 β ,11 β -diol	<i>c, e</i>	195	12,900	20	4400
47	9 α -Methylergosta-7,22-diene-3 β ,11 β -diol	<i>c, e</i>	197	14,000	17	4000
48	5 β -Lumista-8,22-dien-3 β -ol	<i>c, f</i>	195	16,200	20	5700
49	5 β ,14 β -Lumista-8,22-dien-3 β -ol	<i>c, f</i>	195	14,900	23	5600
50	5(4 \rightarrow 3)Abeolupa-3,20(29)-diene	<i>d, g</i>	195	21,500	25	8500
51	5(4 \rightarrow 3)Abeoursa-3,12-diene	<i>e, g</i>	196	19,500	26	8300
52	5(4 \rightarrow 3)Abeo-oleane-3,12-diene	<i>e, g</i>	196	20,400	25	9200

The three non-conjugated ketones (nos. 33, 34, and 35) shown in Table 3 have low-intensity maxima near 193 $m\mu$, the ϵ_{210} figures being similar to those found in a comprehensive study of oxo-steroids.¹⁴ The other compounds in Table 3 contain a C=C bond well separated from a C=O group (nos. 36—41), or two isolated C=C bonds (nos. 42—52).

¹⁴ Bird, Norymberski, and Woods, *J.*, 1957, 4149.

Generally the figures agree well with those obtained by summation of the curves for the individual chromophores. The ϵ_{\max} of an ethylenic bond is somewhat increased by the presence of a carbonyl group in the same molecule, while the λ_{\max} is usually unaffected or slightly decreased. In a compound containing a double exocyclic tetrasubstituted double bond and a carbonyl group the separation between the λ_{\max} values of the individual groups is greatest, and the carbonyl group therefore causes an appreciable shift (see Fig. 4).

The diolefins studied have ethylenic bonds whose λ_{\max} figures vary only slightly, all being in the range 193—198 $m\mu$. Consequently the bands observed are close to 196 $m\mu$, and their intensities are approximately equal to the sum of the individual ϵ_{\max} values. This additivity is illustrated in Fig. 5 for a compound (no. 51) containing a tri- and a tetra-substituted double bond. Although no compound with only a 1,2-disubstituted *trans*-ethylenic centre was studied the results with compounds 46—50 show that such a bond (type *c*) has $\lambda_{\max} \sim 196 m\mu$, $\epsilon_{\max} \sim 6000$.

It is concluded that structural diagnosis by this method requires examination of band widths and intensities as well as the wavelengths of maximal absorption. In *favourable* cases these values *taken together* allow identification of the type of double bond present, but in other cases the method does not lead to a clear distinction between two or more possibilities.*

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THE DYSON PERRINS LABORATORY, OXFORD.

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* Since the preparation of this paper a somewhat similar survey of the ultraviolet spectra of olefinic bonds has been published by Stich, Rötzel, and Reichstein (*Helv. Chim. Acta*, 1959, **42**, 1480) whose findings are in general agreement with those reported here.
