7. *Spectrophotometry in the Far-ultraviolet Region. Part II.* Absorption Spectra of Steroids and Triterpenoids.*

By D. W. TURNER.

Thirty-six spectra of steroids and triterpenoids in hexane are presented together with those of simpler model compounds. The necessity for introducing a correction for hydrocarbon skeletal absorption when determining $\lambda_{max.}$ of the ethylene band is noted. Exceptions to a correlation of $\lambda_{max.}$ with the number of ethylene substituents are discussed and a relationship is postulated between steric strain and certain features of far-ultraviolet absorption.

ABSORPTION by the ethylene chromophore in the far-ultraviolet region, the result of excitation to two upper states of similar energy ($N \longrightarrow V$ and $N \longrightarrow R$, separately distinguished in only the simplest compounds), is sensitive to replacement of ethylenic hydrogen atoms by alkyl radicals. The resultant bathochromic shift of the broad intense absorption band has been described in terms of a dipole-moment vector effect [1,2] (the result of loss of symmetry of the environs of the ethylenic double bond), or simply as an additive result of progressive substitution.[3] We now describe a series of spectra in which both effects can be discerned and show the effect of steric strain to be of comparable importance.

Attempts to use the alkylation shift diagnostically in the field of steroids and triterpenoids have been limited to measurements of the long-wavelength edge of this band [4, 5, 6] (above 2050 Å) and if intensity changes here are to be taken as reflecting the changes in the position of the maximum it must be assumed that the shape of the band is not altered. There is no experimental justification for this assumption; indeed relatively small changes in structure can cause marked alterations in appearance of the spectra of simpler compounds,[7] and the present investigation was undertaken partly to examine to what extent " end absorption " truly reflected the position of the maximum and the shape of the whole band.

RESULTS AND DISCUSSION

In many of the examples studied (Table 1) the experimental absorption curve corrected for absorption by the solvent (Figs. 1 and 2*C*) showed no maximum and further absorption arising presumably from the complex carbon skeleton must overlie the falling edge of the ethylenic band at shorter wavelengths (none of the functional groupings present except carbonyl gives rise to appreciable absorption in this region). Examination of the spectra of the corresponding saturated materials (Fig. 2*D*) confirmed this; high-intensity absorption is exhibited (ε approaching 10^4) at 1760 Å related to the number of quaternary carbon centres present in the molecule.[8] The ethylenic spectra were corrected for this skeletal absorption either by subtraction of the curve for the exactly corresponding dihydro-compound, or of that of one having essentially the same carbon skeleton, number of quaternary carbon centres, and substituent groups. The resultant corrected curves (broken line) show maxima which, in many cases, resemble in shape and $\lambda_{max.}$ those of simpler olefins [compare

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* Part I, *J.*, 1957, 4555.

[1] Gary and Pickett, *J. Chem. Phys.*, 1954, **22**, 599, 1266.

[2] Semenow, Harrison, and Carr, *ibid.*, p. 638.

[3] See, for example, Potts, *ibid.*, 1955, **23**, 73.

[4] Bateman and Koch, *J.*, 1944, 600.

[5] Halsall, *Chem. and Ind.*, 1951, 867.

[6] Bladon, Henbest, and Wood, *J.*, 1952, 2737.

[7] See, for example, Carr and Stücklen, *J. Chem. Phys.*, 1936, **4**, 760.

[8] Turner, *Chem. and Ind.*, 1958, 626.

TABLE 1.

Spectrum no.	Compound (in hexane unless stated)	Spectrum no.	Compound (in hexane unless stated)
1	*cyclo*Hexene	24	Euph-8-en-3-yl acetate
2	Cholest-2-ene	25	Ergost-8(14)-en-3-ol
3	Pregn-2-en-20-one	26	*iso*Lanost-3-ene
4	Cholest-6-en-3-yl acetate [d]	27	Δ^9-Octalin [b]
5	2-Methylene*cyclo*hexan-1-ol [a]	28	12-Oxo-β-amyran-3-yl acetate
6	2-Methylene*cyclo*pentan-1-ol [a]	29	Moradiol diacetate oxide
7	Lupeol acetate	30	Lupan-3-yl acetate
8	2 : 4 : 4-Trimethylpent-1-ene	31	Coprostigmastan-3-yl acetate
9	Stigmast-22-en-3-yl acetate	32	3-Methoxycholestane
10	Ergost-22-en-3-yl acetate	33	Cholestane
11	Cholesterol	34	5β-Androstane [c]
12	3-Methylcholest-2-ene	35	Noroleana-16 : 18-dien-3β-ol
13	Cholest-5-ene	36	5α-Androstan-3β-yl acetate [c]
14	17-Hydroxy-17-methylandrost-5-en-3-yl acetate	37	5α-Androstane [c]
		38	5α-Androstan-3α-ol [c]
15	Androst-5-en-17β-yl acetate	39	*iso*Bornyl acetate *
16	Cholest-5-en-3α-ol [e]	40	2 : 2-Dimethylbutane *
17	Cholest-4-ene	41	*cis*-Pinane
18	3-Hydroxyandrost-9(11)en-17-one	42	*iso*Bornyl acetate
19	Lanost-7-en-3-yl acetate	43	α-Amyrin acetate
20	Androst-7-en-3β : 17β-diol diacetate	44	α-Pinene
21	Lanost-7-en-3-one	45	Ergost-9(11)-en-3β-yl acetate [d]
22	Cholest-7-en-3-ol	46	β-Ergosten-3-ol [d]
23	Lanost-8(9)-en-3-yl acetate	47	1-Methyl*cyclo*hexene [d]

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* In perfluoro*cyclo*hexane.

FIG. 1.

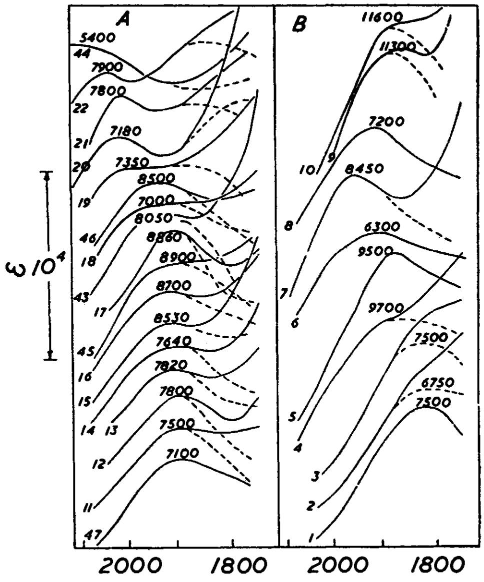
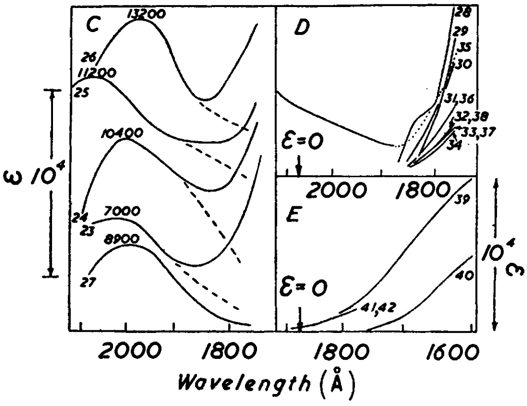


FIG. 2.



*Absorption spectra of trisubstituted olefins (A), disubstituted olefins (B), tetrasubstituted olefins (C), and saturated hydrocarbons (D) in hexane, and of some saturated compounds in perfluoromethyl*cyclo*hexane (E).*

The spectra are at arbitrary intervals on the ε axis, the $\varepsilon_{\max.}$ value only being indicated on each curve. All are to the same scale of ε except in *E* where the curves are plotted to half-scale. The arrows on the vertical axis represent 10^4 units of ε.

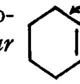
for example 3-methylcholest-2-ene (12) with 1-methyl*cyclo*hexene (47)]. In such cases a clear correlation exists between $\lambda_{max.}$ and the degree of double-bond substitution:

$\lambda_{max.}$ (Å.)	2000—1960	1930—1880	1880—1820
Number of substituents	4 (Fig. 2*C*)	3 (Fig. 1*A*)	2 (Fig. 1*B*)

Two classes of exception to this grouping can be distinguished: (1) The geminally disubstituted olefins absorb at abnormally long wavelengths (lupeol acetate particularly so, $\lambda_{max.}$ ~1950 Å) attributable to a dipole-moment vector effect; a bathochromic shift of ~100 Å is also observed on comparing the vicinally disubstituted butenes, pentenes, and hexenes with their geminally disubstituted isomers.[1, 2] The shift in such cases is not accompanied by increased absorption in the 1700—1800 Å region. (2) By contrast, a bathochromic shift most marked in certain of the trisubstituted group—particularly in Δ^7 compounds—is accompanied by a marked increase of absorption between 1700 Å and 1800 Å. Unusually high end-absorption by ergost-7-ene has been reported, and ascribed to the influence of the neighbouring 8(14) tetrasubstituted position.[6] A similar effect though less marked can be seen in those tetrasubstituted olefins where steric strain may be expected to be present; ergost-8(14)-enol ($\lambda_{max.}$ 2080 Å) in particular shows evidence of additional absorption near 1850 Å. The same association of bathochromic shift with fresh absorption in the far ultraviolet region is shown to the highest degree by α-pinene where considerable strain (entirely in-plane double-bond deformation) is present. It is suggested therefore that spectral abnormalities of the second type are to be ascribed to steric strain and that in the steroids this strain increases in the order Δ^4, Δ^5, $\Delta^{9(11)}$, Δ^{14}, Δ^7 for trisubstituted and $\Delta^{8(9)}$, $\Delta^{8(14)}$ for tetrasubstituted olefins. The corresponding position in the triterpenes shows little spectral abnormality (α-amyrin acetate for example), evidently owing to the replacement by a more flexible six-membered ring of the five-membered ring D, the principal source of rigidity in the steroid molecule.

The difference between spectra of Δ^7- and $\Delta^{9(11)}$-compounds is striking, since it indicates that the magnitude of the strain in the two cases is in the reverse order of that which has been inferred from a study of the C=C stretching frequency.[9] Barton-type models of the various carbon skeletons were constructed and showed a clear difference only in that the terminal ethylene bonds suffered most in-plane distortion in Δ^7-compounds; indeed the spectral abnormality could be related to the angular distortion in the models (Table 2). The magnitude of twisting deformation of the double bond could not, however, be clearly distinguished, and no systematic variation was found.

TABLE 2. *Distortion of the ethylenic terminal-bond angle (referred to 1-methyl*cyclo*hexene) in trisubstituted olefinic steroids estimated from Barton-type molecular models.*



Order of increasing bathochromic shift	Δ^2, Δ^3, Δ^4, Δ^5	$\Delta^{9(11)}$	Δ^{14}	Δ^7	α-Pinene
Bond angle distortion	—	+1½°	+3½°	−6°	+6½°

We conclude that whilst the C=C stretching frequency, determined principally by the C=C stretching force constant, may be most sensitive to twisting deformation (not clearly revealed by models) as a result of π-orbital overlap changes, the $N \longrightarrow V$ transition is less so, being more sensitive to in-plane deformation through changes in *sp*-hybridization ratio.

EXPERIMENTAL

The spectrophotometer and technique were described in Part I.

Solvents.—Unless otherwise indicated hexane (Spectrosol) further purified by passage through activated (350° C) silica gel (200 mesh) was used. Perfluoromethyl*cyclo*hexane was purified by repeated extraction with methanol followed by passage through silica gel.

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[9] Bladon, *J.*, 1951, 2402.

cyclo*Hexene* (1).—A commercial sample was redistilled from sodium immediately before use, n_D^{20} 1·4460 (lit.,[10] n_D^{22} 1·44507).

α-*Pinene*.—A commercial sample was redistilled before use, and had b. p. 155°/760 mm., n_D^{22} 1·4654.

cis-*Pinane* (41).—α-Pinene in ethanol was hydrogenated at room temperature and pressure with Adams catalyst; hydrogen uptake was quantitative. The product was distilled and a fraction, b. p. 166°/760 mm., n_D^{24} 1·4612, collected (Waterman [11] gives b. p. 166°/755 mm., n_D^{20} 1·4616).

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[10] "Dictionary of Organic Compounds," Ed. Heilbron and Bunbury, Eyre and Spottiswoode. London, 1953.

[11] Waterman, *Rec. Trav. chim.*, 1929, **48**, 1191.