## **395.** *The Ultraviolet Absorption of Isolated Double Bonds.*

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The ultraviolet absorptions of thirty substances, mostly steroids and triterpenes, containing isolated double bonds have been measured at wavelengths down to 187 mμ.

Structural correlations are discussed in the light of these and other workers' results.

RECENTLY several workers have reported measurements of absorption spectra in the ultraviolet region below 205 mμ, made principally on steroids and triterpenes, with the purpose of distinguishing between isolated double bonds having various degrees of substitution. Turner,[1] using a vacuum spectrometer with fluorite optics, concluded that, with few exceptions, di-, tri-, and tetra-substituted double bonds could be differentiated satisfactorily by such measurements. Ellington and Meakins [2] have since reported their examination of a similar collection of compounds in a commercial instrument with silica optics and came to much less favourable conclusions. Stich *et al.*[3] made similar measurements on another commercial instrument and came to substantially the same conclusions as Turner.

We were interested in the possibility of applying the results of measurements in this region on a standard commercial spectrophotometer to the determination of structure and have therefore attempted to clarify this situation by examining a smaller but representative group of compounds, including those examined by earlier workers as far as they were available.

### EXPERIMENTAL

The spectra were measured on a standard Hilger Uvispek model 308 spectrophotometer fitted with a silica prism and flushed before use with " white spot " nitrogen until the energy at 187 mμ reached a constant (maximum) value. The percentage of stray light under these conditions was determined by means of a Vycor filter.[4] The figures in Table 1 therefore refer to stray light of wavelengths greater than 220 mμ. These figures are so low (cf. ref. 3) that we considered it unnecessary to correct our observations for stray light, particularly as solutions were used that in general had a transmission greater than 50% at $\lambda_{max.}$; it was thought that the

TABLE 1.

| | | | |
|---|---|---|---|
| λ (mμ) | 185 | 190 | 195 |
| Stray light (%) | 1·2 | 0·12 | 0·06 |

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[1] Turner, *J.*, 1959, 30, where reference are given to earlier papers.
[2] Ellington and Meakins, *J.*, 1960, 697.
[3] Stich, Rotzler, and Reichstein, *Helv. Chim. Acta*, 1959, **42**, 1480.
[4] Gibson in Mellon's " Analytical Absorption Spectroscopy," Wiley, New York, 1950, p. 247.

TABLE 2.*

| | This work | | Ellington & Meakins [2] | | Stich *et al.*[3] | | Turner [1] | | Other workers | |
|---|---|---|---|---|---|---|---|---|---|---|
| Compound | λ (mμ) | ε | λ (mμ) | ε | λ (mμ) | ε | λ (mμ) | ε | λ (mμ) | ε |
| *Disubstituted* | | | | | | | | | | |
| Cyclohexene | <187 | (6000) | | | <190 | 7200 | | | 183·5 [d] | 7400 [d] |
| 11α-Acetoxy-3β-hydroxy-5α-ergost-22-ene | <187 | (14,000) | | | | | | | | |
| 3β-Acetoxy-5α-ergost-22-ene | | | | | | | 186 | 11,600 | | |
| 5α-Cholest-2-ene [a] | <187 | (7000) | 189 | 5100 | 189·5 | 5600 | 182 | 7500 | | |
| 3β-Acetoxy-5α-cholest-6-ene [b] | <188 | (8000) | | | | | | | | |
| 5α-Cholest-6-ene | | | *195* | *7500* | 190·5 | 7800 | | | | |
| 5α,22α-Spirost-2-ene | <187 | (7000) | | | | | | | | |
| 3β-Hydroxy-5α,22α-spirost-11-ene | <187 | (6000) | | | | | | | | |
| Lupeol acetate | 195 | 9000 | 194 | 9300 | | | 196 | 8450 | | |
| Lupeol [a] | *197* | *8000* | *195* | *8900* | | | | | | |
| *Trisubstituted* | | | | | | | | | | |
| 2,4,4-Trimethylpent-1-ene | 193 | 7000 | | | | | | | | |
| 2,4,4-Trimethylpent-2-ene | 193·5 | 8000 | | | | | | | | |
| Cholest-5-ene [a] | 190 | 9000 | 191 | 8200 | 193 | 8100 | 190 | 7820 | | |
| 3β-Hydroxycholest-5-ene | | | | | | | | | 187 [d]<br>191 [e] | 15,800 [d]<br>10,200 [e] |
| 3β-Acetoxycholest-5-ene | 189 | 8000 | 195 | 8100 | 193 | 8900 | | | | |
| 3β,24-Diacetoxycholest-5-ene [b] | 190 | 12,000 | | | | | | | | |
| 5α-Cholest-4-ene [b] | 192 | 10,000 | *196* | *9700* | 194 | 10,700 | 190 | 8860 | | |
| 3β,5α-Diacetoxyergost-7-en-11-one | 187 | 12,000 | | | | | | | | |
| *Tetrasubstituted* | | | | | | | | | | |
| 3β-Acetoxylanost-8-ene | 202 | 9000 | 197 | 7500 | | | 202 | 7000 | | |
| 3β-Hydroxylanost-8-ene | *201* | *7000* | *198* | *7300* | | | | | | |
| 3β-Acetoxy-5α-ergost-8(14)-ene | *200* | *11,000* | *204* | *12,200* | *205* | *11,800* | | | 206 [e] | 11,200 [e] |
| 3β-Acetoxy-5α-hydroxy-ergost-8(9)-ene | *200* | *9000* | | | | | | | | |
| 3β-Acetoxy-11-methyl-5α,25β-spirost-9(11)-ene | 200 | 7000 | | | | | | | | |
| Euphenyl acetate [c] | 197 | 10,000 | 197 | 8400 | | | 200 | 10,400 | | |
| *Saturated steroids and ketones* | | | | | | | | | | |
| 3β-Acetoxy-5α-cholestane | ⩽187 | 300 † | | | | | | | | |
| 3β-Hydroxy-5α-cholestane | | | No max. | 300 † | | | | | | |
| Acetone | 186—187 | 2000 | | | 191 | 1000 | | | 186 [d] | 5800 [d] |
| 2,4,6-Trimethylcyclohexanone | <187 | (1000) | | | | | | | | |
| 2,2,6,6-Tetramethylcyclohexanone | <187 | (1000) | | | | | | | | |
| Cholestan-3-one | <187 | (2500) | *194* | *1600* | 188·5 | 2000 | | | | |
| 3β-Acetoxy-5α-ergostan-11-one | <187 | (3000) | | | | | | | | |
| 3β-Acetoxy-5α,9β-ergostan-11-one | <187 | | | | | | | | | |
| 3β-Acetoxy-5α-pregnan-12-one | <187 | (3000) | | | | | | | | |
| 3β-Acetoxy-5α-pregnan-20-one | <187 | (4000) | | | | | | | | |

* Entries in italics indicate the use of ethanol as solvent; otherwise hydrocarbon solvents were used. † Relates to $\varepsilon_{195}$.

*a, b, c.* We are indebted to Prof. D. H. R. Barton for specimens marked *a*, to Prof. H. B. Henbest for those marked *b*, and to Dr. G. D. Meakins for those marked *c*.

*d, e.* These figures are quoted by Stich *et al.*[3] from measurements made by (*d*) Klevens and Platt, (*e*) the Shell Development Laboratories, Wood River, Ill., U.S.A.

slight loss of accuracy occasioned by the measurement of small $E$ values would be more than offset by consequently minimising the effect of stray light.

All measurements were made in 1-mm. demountable silica cells (Hilger and Watts). Below 220 mμ these were not accurately matched. Determinations of the correction necessary showed this to be variable but fortunately small: it depended on the position in which the silica components were reassembled, and perhaps also on surface contamination, and would therefore have been difficult to apply when a demountable cell was in use. Also slight evaporation could not be avoided when hexane was used, and for these reasons the values of $\varepsilon$ are given to one significant figure only.

A commercial " spectroscopic " grade of n-hexane and absolute ethanol were used. With these solvents readings could be made to 187 and 195 mμ, respectively.

## RESULTS AND DISCUSSION

The values found for $\lambda_{\text{max.}}$ and $\varepsilon_{\text{max.}}$ are given in Table 2. When no maximum was reached within the range of the present series of measurements, the values of $\varepsilon$ at 188 and 195 mμ (for hexane and ethanol, respectively) are given in parentheses. When available, the values obtained by other workers for the same or closely related compounds are included for comparison.

Also included in Table 2 are several saturated ketones and 3β-acetoxycholestane, none of which showed a maximum at wavelengths $\geqslant$187 mμ in n-hexane.

Our results, like Turner's, clearly fall into three groups that coincide with the three degrees of substitution of the double bonds in the compounds concerned (Table 3). We find also the same exceptions, *viz.*, a bathochromic shift associated with the geminally disubstituted double bond in lupeol, and a shift from the expected position for a $\Delta^7$-bond: here we agree with Stich *et al.* in finding this to be to a shorter wavelength.

TABLE 3.

| | | | |
|---|---|---|---|
| No. of substituents | 2 | 3 | 4 |
| $\lambda_{\text{max.}}$ (mμ) | 187 | 187—193 | 199—202 |

In seeking to explain the discrepancy between the results obtained by Turner and by ourselves (and to a considerable extent, by Stich, Rotzler, and Reichstein) on the one hand, and, on the other, by Ellington and Meakins (a discrepancy clearly in the instrumental results and not in their interpretation), we conclude that the last workers have underestimated the effect of stray light on measurements made in ethanol. The transmission of 1 mm. of absolute ethanol at 195 mμ is less than 10% and drops to 1% at 192 mμ. In this way a situation can readily be envisaged in which, despite the linearity up to an optical density of 1·8 at 195 mμ, artificial maxima will be produced between 190 and 195 mμ, with corresponding shifts to longer wavelengths of true maxima in this region. The spurious effects produced by scattered light are dependent on its intensity relative to that of the transmitted light being measured, *i.e.*, the $E$ of the solution being examined. Thus the assertion that the compounds containing neither C=C nor C=O bonds showed no bands has little significance for the apparent spectra of the substances we are interested in.

The Swiss group have examined more closely the effect of stray light in their measurements and have made a correction for it, and, in their tables, indicate corrected wavelengths. Nevertheless, discrepancies exist between their reported values of $\lambda_{\text{max.}}$ and those given by Turner and ourselves for similar groupings; in particular, those for disubstituted olefins tend to be at longer wavelengths. Though claiming reasonable agreement of their results with those from the Shell Development Laboratories, they note the much poorer agreement with Platt, Klevens, and Price,[5] but do not attempt to explain this.

We conclude that measurements made with an instrument having a low level of intrinsic scattered light down to 187 mμ, on solutions of low (*ca.* 0·3) optical density, for

[5] Platt, Klevens, and Price, *J. Chem. Phys.*, 1949, **17**, 466.

classification of double bonds according to the degree of substitution, give results in close agreement with those obtained on a vacuum-fluorite instrument. This procedure, moreover, would seem to give rather better results than that of applying a correction to measurements involving a larger contribution from scattered light.

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