ULTRAVIOLET ABSORPTION OF STEROIDS

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CONTENTS

I. INTRODUCTION AND SCOPE

In recent years ultraviolet absorption analysis has found wide application in the elucidation and corroboration of the structure of organic molecules. This may be ascribed to the commercial development of instruments which require no special skill to operate and which give the results quickly and accurately. Workers in the field of natural products, among others, soon found such instruments indispensable. This has been especially true of investigations in steroid chemistry, and it is with this field of organic chemistry that this review is concerned.

By 1939 the data in the steroid field were so extensive that Dannenberg (83) was able to write a comprehensive review, in which he tabulated the various chromophore systems and the range and the intensity of absorption that were characteristic of steroids which had been isolated or prepared up to that time. Subsequent publications (47, 48, 48a, 86, 120, 129, 235, 464, 465, 466) in the

field of steroids and aliphatic compounds have amplified these initial observations. The present review is an extension to include steroids through 1951. The emphasis will be placed on a correlation between ultraviolet absorption and molecular structure rather than on theoretical considerations.

A. Definition of terms

Chromophore = a group containing multiple bonds which are fundamentally responsible for the light absorption or color of molecules,

Auxochrome = a group which does not confer color upon an otherwise colorless substance but does increase the coloring power of a chromophore,

Bathochrome = a group which produces a shift of an absorption band toward longer wave lengths,

Hypsochrome = a group which produces a shift of an absorption band toward shorter wave lengths,

Hyperchrome = a group which causes an increase in the molecular extinction coefficient of an absorption band,

Hypochrome = a group which produces a decrease in the molecular extinction coefficient of an absorption band,

Optical density = $D = \log (I_0/I)$, where I_0 is the intensity of the incident light and I is the intensity of the transmitted light,

Molecular extinction coefficient = $E = D/lc$, where D is the optical density, l is the cell path in centimeters, and c is the concentration in moles per liter,

Extinction coefficient = $E^{1\%}_{1\,cm.} = D/lc$, where c is now expressed in grams per 100 cc. of solvent.

The ultraviolet absorption is characteristic of certain chromophore systems rather than of the molecule as a whole. It has been established (47, 48a) that this absorption is related to valence-bond resonance and that for maximum resonance a coplanar configuration of the chromophore system is required. The chromophore concept (47, 121, 380) is based upon the idea of the covalently unsaturated atom or molecule. There are two important types of electron states in the unsaturated molecule: the π-electrons, sometimes referred to as the unsaturation electrons, and the unpaired or lone electrons of free radicals. The ordinary bonding electrons are designated as σ-electrons and absorb in the far ultraviolet region. This absorption is relatively unaffected by an accumulation of σ-electrons. Covalently unsaturated atoms or molecules absorb at 150–200 mμ, a region that is difficult to measure with quartz spectrophotometers. However, the conjugation of two or more such chromophores causes a displacement of the absorption to the near ultraviolet (200–400 mμ) and to the visible. It is with these systems that this review is mainly concerned.

A number of important facts have been established (47) about chromophores.

1. The various absorption ranges in any molecule belong to the various elec-

tronically excited states of the same chromophore, and the intensity of absorption is a measure of the probability of those excited states.

2. The individual absorption bands may be correlated with certain different molecular components and will recur in all molecules containing these components. (*a*) Several chromophores or chromophore systems in one molecule are relatively independent of each other if they are separated by at least two single —C—C— bonds, and the intensity of absorption is nearly additive for the individual components. (*b*) In the conjugation of several chromophores, an interaction of the electronic systems will occur to produce a new uniform chromophore system.

3. Electronic interaction (47) can occur between σ- and π-electrons. This phenomenon is known as hyperconjugation or the second-order conjugation effect, and is observed for alkyl groups which, when linked to a chromophore system, cause a bathochromic shift. This effect has also been observed when a cyclopropyl (231, 253) or ethylene oxide moiety is adjacent to a ketone group or a double bond.

It is at times difficult to attribute a specific absorption to a particular chromophore system, because in a number of examples molecules with different conjugated chromophores have similar absorption characteristics. In these instances the following comparisons are helpful.

1. The ratio (47) of $\epsilon_{max.}/\epsilon_{\lambda}$, where ϵ_{λ} is the extinction coefficient at wave length λ on another part of the curve. The ratio (391) of $D_{max.}/D_{min.}$, where $D_{max.}$ is the optical density at the maximum and $D_{min.}$ is the density at the nearest minimum of shorter wave length. The latter relationship is independent of the concentration and thickness of the solution used for measurement and thus can be used in assessing the purity of substances of unknown constitution.

2. The intensity of absorption (47) can also be expressed in terms of the area under the curve.

The theory of absorption spectra has been discussed in a number of excellent reviews (121, 380) and in references cited therein.

B. Solvent effect

It has been difficult to correlate the effect of solvents on the ultraviolet absorption spectra. Spectra taken in hexane solution closely resemble those observed in the gas phase. A change in solvent usually affects $\lambda_{max.}$ more than $\epsilon_{max.}$; in the use of polar solvents this has been attributed (380) to an inductive effect, where the dipoles of the solvent reinforce the polar character of the dissolved chromophore. A displacement to shorter or longer wave lengths may occur, depending on the state in which the molecule was before the influence of the solvent occurred. With respect to the steroids, solvents exert almost no effect on the absorption characteristics of conjugated dienes and polyenes containing no polar substituents. However, the effect of the solvent has not been determined in cases where a polar group is present.

Corrections for solvents (129) have been made on the α,β-unsaturated ketosteroids, as shown in table 1.

II. ULTRAVIOLET ABSORPTION OF ISOLATED CHROMOPHORES OCCURRING IN STEROIDS

The single chromophore groups that commonly occur in steroids are the ethylene, carbonyl, and carboxyl groups, all of which exhibit strong absorption at 170–200 mμ, a region which is beyond the range of most spectrophotometers. However, carbonyl groups have an additional well-defined band at approximately 280 mμ, and a recent publication (41) describes the extension of the useful range of the spectrophotometer to 200 mμ, in which region alkylated double bonds absorb. Therefore, these two groups may be easily detected.

TABLE 1

Comparison of the effect of solvent on the ultraviolet absorption of testosterone

SOLVENT*	$\lambda_{max.}$	FACTOR FOR CORRECTION TO ALCOHOL
	mμ	
Hexane	230	+11
Ether	234	+7
Dioxane	236	+5
Chloroform	240	+1
Ethanol	241	0

* The solvent is ethanol for the data presented in the subsequent sections and tables 1–20, unless otherwise specified.

TABLE 2

Ultraviolet absorption of isolated ketone groups

POSITION OF KETONE GROUP	AVERAGE		RANGE	
	$\lambda_{max.}$	$\epsilon_{max.}$	$\lambda_{max.}$	$\epsilon_{max.}$
	mμ		mμ	
C_3	282	31	280–286	16–50
C_6	288	45	280–300	40–50
C_7	290	40	287–292	40
C_{11}	287	75	285–290	50–107
C_{12}	287	50	285–288	25–70
C_{16}	297	35		
C_{17}	293	46	293–294	43–48
C_{20}	284	56	282–285	40–75

A. Absorption of steroid ketones

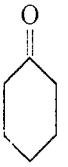
Table 2 summarizes the values of $\lambda_{max.}$ and $\epsilon_{max.}$ for the various steroid ketones. The average values cannot be taken with certainty, as there are an insufficient number of examples in each group. It should be pointed out that there are a number of these compounds that do not show selective absorption in the ultraviolet, a fact difficult to explain, since closely related substances do exhibit a ketone band.

Since the extinction coefficient of the carbonyl band is quite low, it is best to characterize it by a highly absorbing derivative such as a semicarbazone

($\epsilon_{226-230}$ = 12,100–13,600) or a 2,4-dinitrophenylhydrazone ($\epsilon_{367-371}$ = 17,000–30,000).

It is interesting to note that the absorption of ketone groups in the cyclopentano ring D of steroids is at a longer wave length than for those on a six-membered ring, a fact which has been previously observed (253) with cyclopentanone and cyclohexanone. The bathochromic displacement is undoubtedly due to the more highly strained five-membered ring. The degree of

ϵ_{299} = 30



ϵ_{292} = 17

alkylation of the carbon atoms alpha to the ketone group also influences the region of absorption. For C_6, C_7, C_{11}, and C_{12} steroid ketones, one of the α-carbons is disubstituted or trisubstituted and they absorb at a longer wave length than those in which the α-carbon atoms are monosubstituted, as in the C_3 ketones.

It is difficult to evaluate the influence of an isolated double bond on the ketone absorption because of insufficient data. However, there is an indication that an ethylenic bond in the vicinity of a carbonyl group has a hypsochromic effect. The carbonyl band of 3β-hydroxy-5,14-androstadien-17-one (77) is at 285 mμ, and 3β-acetoxy-13-iso-5,14-androstadien-17-one (39) absorbs at approximately 275 mμ. The hypsochromic shift of 8 mμ in the first example is caused by the Δ^{14} double bond, since the Δ^5 bond is without influence. In the C_{13} iso compound the effect is larger, probably owing to a steric factor.

The presence of a $C_{16,17}$-epoxy or a C_{17}-hydroxyl group causes a bathochromic displacement of 6–15 mμ in the absorption of C_{20} ketones. The three-membered ring in both 3β-acetoxy-16,17-methylene-5-pregnen-20-one (373) and 3,5-cyclocholestan-6-one (373) causes a hypsochromic shift of 8–10 mμ in the absorption of the respective ketones.

It was observed (21) that bromine atoms alpha to the carbonyl group cause varichromic effects in the low-intensity absorption band of the carbonyl group depending on the stereochemical configuration of the halogen atom, as is indicated in the following compounds:

COMPOUND	$\lambda_{max.}$	$\epsilon_{max.}$	$\Delta m\mu$
	$m\mu$		
7-Ketocholestanyl acetate	287	40	
6α-bromo	282	40	−5
6β-bromo	313	160	+26
6-Ketocholestanyl acetate	280	40	
5-bromo	308	126	+28
7β-bromo	310	160	+28
5,7β-dibromo	340	160	+60
5′,7β-dibromo	305	126	+25

It is evident in this series that the 5′- and 6α-bromine atoms cause a hypsochromic shift of 5 mμ and that the average bathochromic shift for the other bromine atoms is 28 mμ. Compounds containing 2-iodo-3-keto elements absorb at $\epsilon_{258} = 900$.

Compounds containing isolated diketone groups that involve the 6-, 7-, 11-, 12-, and 17-positions absorb at 288–293 mμ, $\epsilon_{max.} = 61–100$; these values are comparable to those for the respective monoketones with approximately twice the intensity.

B. Absorption of isolated double bonds

The isolated double bond has a strong absorption band below 200 mμ which is shifted toward longer wave lengths on replacement of ethylenic hydrogens by

TABLE 3

Ultraviolet absorption of isolated double bonds in steroids

POSITION OF DOUBLE BOND	EXOCYCLIC DOUBLE BOND	λ"max."	$\epsilon_{max.}$	ϵ_{210}	ϵ_{215}	ϵ_{220}	ϵ_{223}
		mμ					
Disubstituted:							
Δ^{2}	0	203	600	200	—	—	
Δ^{6}	0	204	1500	750	225	100	
Δ^{11}	0	204	2450	900	275	75	
Trisubstituted:							
Δ^{4}	1	203	4000	3000	1500	850	
Δ^{5}	1	204	3300	1950	780	410	
Δ^{7}	1	207	4500	4300	3100	1600	
$\Delta^{9(11)}$	1	206	3550	2650	1450	500	
Δ^{14}	1	204	4100	2600	900	200	
Tetrasubstituted:							
$\Delta^{8(9)}$	0	207	4670	4470	3970	3470	2830
$\Delta^{8(14)}$	2	208	10100	9900	8350	6100	3700
$\Delta^{9(10)}$	2	205	9000	7450	4900	2600	

alkyl groups or alkyl residues. The absorption spectra of a number of unsaturated steroids were determined (41) in the 200–225 mμ region, and the average values are presented in table 3. The maxima reported in the table are "apparent maxima" and are not the true positions or extinction coefficients of the absorption band. This is due to the varying amount of false energy or scattered light at these short wave lengths, which is inherent in the instrument design and in the intensity of the light source. The values at ϵ_{210}, ϵ_{215}, ϵ_{220}, and ϵ_{223} indicate the slope of the absorption curve. Regardless of the recorded absorption errors, pertinent information is obtained.

From the data in table 3 the authors (41) observed the following factors which influence the absorption of a steroid ethylenic bond: The extinction coefficient increases with increasing substitution at the double bond. The effect is probably

due to the bathochromic displacement of the absorption band, which results in an increasing area of end absorption. In the tetrasubstituted group, the absorption curve of the $\Delta^{8(14)}$ and $\Delta^{9(10)}$ bond is much steeper than that of the $\Delta^{8(9)}$ bond. The greater absorption of the former two ethylenic bonds is due to their double exocyclic position as compared to the endocyclic $\Delta^{8(9)}$ bond. This fact has already been observed for conjugated dienes and ketones.

To account for the fact that Δ^7 compounds have an appreciably higher extinction coefficient than the other trisubstituted double bonds, it was suggested that the absorption of any particular ethylenic bond is influenced by the absorption of the potentially unsaturated centers adjacent to it. Thus a Δ^5 bond has a potentially trisubstituted (Δ^4) and a disubstituted (Δ^6) double bond as immediate neighbors, whereas a Δ^7 bond is adjacent to a tetrasubstituted bond ($\Delta^{8(9)}$ or $\Delta^{8(14)}$) and a disubstituted bond (Δ^6). Support of these ideas is evidenced by the very similar absorptions of Δ^4 and Δ^5 bonds, the bathochromic shift of the apparent maximum of a $\Delta^{9(11)}$ bond relative to a Δ^5 bond, and the increased intensity of absorption of a Δ^{11} bond when compared to a Δ^2 bond.

The influence of neighboring groups is observed in the Δ^5 series. A C_3-hydroxyl group lowers the intensity of absorption of a Δ^5 bond and a further reduction is effected by the respective acetate. However, when the acetate group is further removed from the double bond, a slight increase in absorption intensity is observed. Replacement of the C_3-hydroxyl group by chlorine in the Δ^5 compounds is accompanied by an increase in absorption which is further increased by a bromine atom.

The application (41) of ultraviolet absorption in the 200–225 mμ region has been successful in elucidating the structure of Westphalen's diol. The spectrum clearly indicates the presence of a doubly exocyclic tetrasubstituted olefinic bond; thus it must be at the $\Delta^{9(10)}$-position and not at the $\Delta^{8(9)}$-position as previously accepted. This conclusion is further substantiated by the fact that the corresponding diketone is unaffected by alcoholic sodium ethoxide, a reagent that would isomerize the double bond to the $\Delta^{7(8)}$-position in conjugation with the C_6-keto group if the bond were originally situated at $\Delta^{8(9)}$.

C. Absorption of hyperconjugated chromophore systems

It has been shown (121, 231) that the cyclopropyl and the epoxy groups have chromophoric powers approaching that of an ethylene bond, but weaker, since the three-membered ring is under less strain than a double bond. When these groups are alpha to a double bond or a carbonyl group, absorption occurs which is intermediate between that of a monoene and a conjugated diene. The hyperconjugated system probably absorbs near 200 mμ. Though the peak cannot be measured because of the limitations of the present spectrophotometers, a strong end absorption can be observed which is fairly characteristic of the above group combinations. The isolated cyclopropyl, epoxy, and carbonyl groups and disubstituted double bonds have an end extinction coefficient which at 220 mμ is below 100.

NAME	ϵ_{220}	REFERENCE
3,5-Cyclo-6-cholestene	8000	(231)
3,5-Cyclo-6-cholestanone	1600	(231)
3β-Acetoxy-16,17-methylene-5-pregnen-20-one	6300	(373)
3β,17β-Diacetoxy-9,11α-oxido-7-androstene	320	(182)
3β-Acetoxy-9,11α-oxido-7-cholestene	400	(182)
3β-Acetoxy-9,11α-oxido-7,22-ergostadiene	200	(175)
3β,17β-Diacetoxy-8,9α-oxidoandrostane-7,11-dione	2000	(175)
3β-Acetoxy-8,9α-oxidocholestane-7,11-dione	1600	(175)
3β-Acetoxy-16,17-oxidoallopregnan-20-one	3200	(307)
3β,21-Diacetoxy-16,17-oxidoallopregnan-20-one	2500	(307)

The unusually low end absorption of the 9,11α-oxido-7-ene compounds is probably due to steric inhibition of resonance.

The hyperconjugation effect is readily observed in conjugated systems. The bathochromic shift of the cyclopropane ring in 3,5-cyclo-6,8,22-ergostatriene (134a) is approximately 15 mμ.

III. ULTRAVIOLET ABSORPTION OF CONJUGATED DIENE AND POLYENE STEROIDS

The ultraviolet absorption spectra of conjugated diene and polyene steroids closely resembles that of their aliphatic analogs containing the corresponding number of alkyl substituents. Two ethylene bonds in conjugation give rise to a chromophore system in which the principal band has shifted 30–40 mμ toward longer wave lengths and whose extinction coefficient has increased with respect to that of an isolated ethylene bond.

Early investigators (31, 45, 74, 128) classified the dienes into two broad groups.

1. The two double bonds may be distributed between two adjoining rings (heteroannular dienes), in which case they absorb in the region 220–250 mμ, $\epsilon_{max.}$ = 14,000–28,000. This region of absorption also includes those dienes whose double bonds are distributed between a hydroaromatic ring and a side chain or are solely in the C_{17} side chain.

2. The two ethylene bonds may be in the same ring (homoannular dienes); they then absorb at 260–285 mμ, $\epsilon_{max.}$ = 5,000–15,000.

The linearly conjugated steroid trienes and tetraenes can be treated as dienes in which the additional double bonds extend the conjugation, which results in a bathochromic shift of approximately 30 mμ for each ethylene group.

The ultraviolet absorption of the steroid dienes and polyenes is summarized in tables 4, 5, and 6. The wide range of $\epsilon_{max.}$ values may be attributed to the difficulty in purifying conjugated olefins. It has been shown (194) that, unless care is taken, successive recrystallization of ergosterol and 7-dehydrocholesterol lowers their extinction coefficients. Compounds which were reported with too high or low an extinction coefficient or whose absorption bands do not follow the average were excluded from these tables but are listed in the tables of compounds (see page 103). The conjugated dienes in the C_{17} side chain were also excluded, since their absorption depends on the number of alkyl substituents on the double bonds and can be predicted with fair agreement by calculation.

TABLE 4

Ultraviolet absorption of conjugated steroid dienes

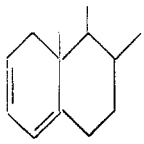
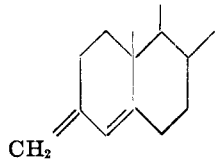
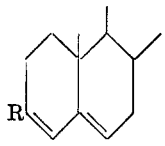
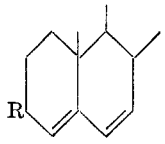
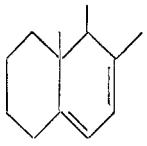
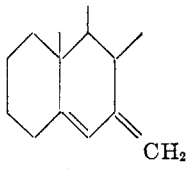
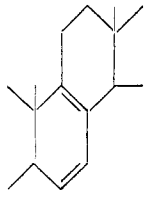
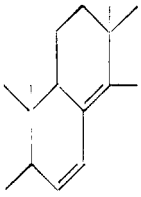
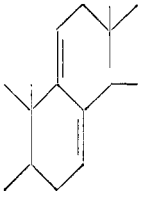
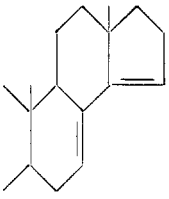
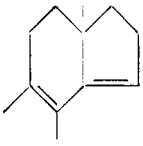
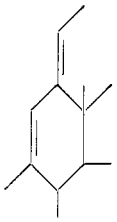
COMPOUND	AVERAGE		RANGE		$\lambda_{max.}$ CALCULATED
	$\lambda_{max.}$	$\epsilon_{max.}$	$\lambda_{max.}$	$\epsilon_{max.}$	
	$m\mu$		$m\mu$		$m\mu$
 $\Delta^{2,4}$	~266 275 ~287			6,300–15,000 6,300–20,000 13,500	273
 $\Delta^{3',4}$	233 239	16,200 17,300			239
 $\Delta^{3,5}$ (R = H, CH_3COO†)	228 235 243(i)*	18,600 19,000 13,600	228 234–239 243(i)	18,600 16,800–20,000 13,600	234
 $\Delta^{4,6}$ (R = OH, CH_3COO)	232 239 248	21,500 23,500 16,000	232 238–240 248	17,800–24,000 20,100–28,200 12,700–19,500	234
 $\Delta^{5,7}$	262(i) 271 282 293	7,700 11,400 11,900 6,900	262(i) 270–273 280–283 292–294	7,400–8,000 9,500–15,500 10,000–15,900 5,700–9,780	283
 $\Delta^{5,7'}$	236	20,000			239
 $\Delta^{6,8(9)}$	275	5,000	275	4,700–5,300	273

TABLE 4—*Concluded*

COMPOUND	AVERAGE		RANGE		$\lambda_{max.}$ CALCULATED
	$\lambda_{max.}$	$\epsilon_{max.}$	$\lambda_{max.}$	$\epsilon_{max.}$	
	$m\mu$		$m\mu$		$m\mu$
 $\Delta^{6,8(14)}$	253	17,000	245–253		244
 $\Delta^{7,9(11)}$	236 243 251	12,800 14,500 10,100	235–236 242–245 250–252	10,000–15,400 10,700–17,000 9,000–11,400	244
 $\Delta^{7,14}$	242	10,000	242–250	9,900–15,000	244
 $\Delta^{8,14}$	248	18,500	245–250	16,100–20,000	244
 $\Delta^{9,12(23)}$	242	19,500			244
C=C—  $\Delta^{16,20}$	238	15,000			224

* (i) signifies an inflection.

† The bands or inflections at 228 and 243 mμ do not appear when a C_3-acetate group or C_3-halogen is present.

TABLE 5

Ultraviolet absorption of conjugated steroid trienes

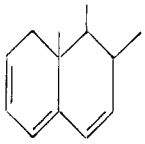
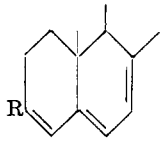
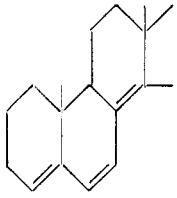
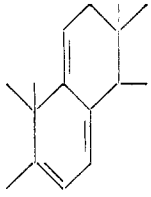
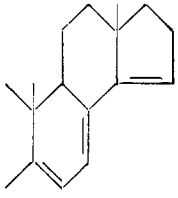
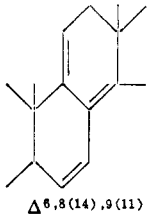
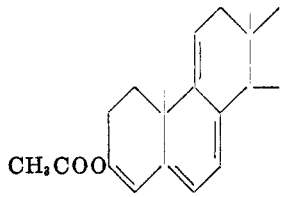
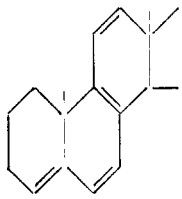
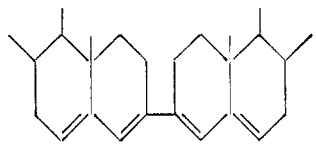
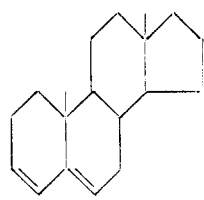
COMPOUND	AVERAGE		RANGE		$\lambda_{max.}$ CALCULATED
	$\lambda_{max.}$	$\epsilon_{max.}$	$\lambda_{max.}$	$\epsilon_{max.}$	
	$m\mu$		$m\mu$		$m\mu$
 $\Delta^{2,4,6}$	296 306 320	14,500	296 304–307 320	12,600–16,600	303
 $\Delta^{3,5,7}$ (R = H, CH_3COO)	302 315 331	16,800 19,800 13,400	301–305 314–317 330–332	12,500–20,000 15,700–23,400 11,100–17,400	313
 $\Delta^{4,6,8(14)}$	283	33,000			284
 $\Delta^{5,7,9(11)}$	312 324 339	10,400 11,800 7,400	310–312 322–325 338–340	9,100–11,500 10,300–14,500 6,400–7,950	323
 $\Delta^{5,7,14}$	319	16,200	319	15,000–17,500	323
 $\Delta^{6,8(14),9(11)}$	~243 285	~12,000 9,100			

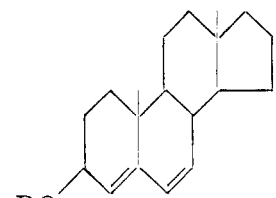
TABLE 6

Ultraviolet absorption of conjugated steroid tetraenes

COMPOUND	AVERAGE		RANGE		$\lambda_{max.}$ CALCULATED
	$\lambda_{max.}$	$\epsilon_{max.}$	$\lambda_{max.}$	$\epsilon_{max.}$	
	$m\mu$		$m\mu$		$m\mu$
 CH_3COO $\Delta^{3,5,7,9(11)}$	338	16,400	336–339	15,000–17,800	
	355	19,700	354–356	17,400–21,900	353
	374	14,600	372–375	13,000–16,200	
 $\Delta^{4,6,8(9),11}$	355	13,500			343
 $\Delta^{5,3,3',5'}$	298	41,000	298	37,000–47,900	
	313	55,400	312–313	50,000–63,100	314
	323	46,800	323	46,800	

Many dienes exhibit three absorption bands, with one on each side of the principal band and almost equidistant from it. The band at the longest wave length has the lowest extinction coefficient. The two secondary bands are approximately -7 and $+8$ mμ away from the principal band in the case of the heteroannular dienes, -10 and $+12$ mμ apart for the homoannular dienes, and -13 and $+15$ mμ apart in the trienes. These secondary bands may appear only as inflections on the absorption curve. However, in some compounds, this can be considered as an indication of impurity. Dienes that are enol acetates prepared from α,β-unsaturated ketones do not exhibit these secondary absorption bands.



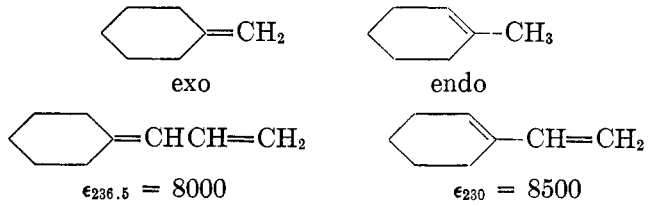


(R = H, CH_3CO)

The $\Delta^{3,5}$- and $\Delta^{4,6}$-dienes have the same substitution: namely, three alkyl residues and one exocyclic double bond; however, the $\Delta^{4,6}$ compounds absorb 4 mμ toward longer wave lengths and have higher extinction coefficients. Though the compounds in the $\Delta^{4,6}$ group have a 3-hydroxy or 3-acetoxy substituent (see page 58), the bathochromic shift cannot be wholly attributed to electron interaction of the allylic alcohol, since both 2,4-pentadiene and 2,4-pentadien-1-ol absorb at 223 mμ (47, 164a). The α-hydroxy group, however, may account for the higher extinction coefficient for these compounds.

Calculation of the principal absorption band of steroid polyenes

A method of calculating the principal absorption band of the heteroannular dienes was devised by Woodward (465) and was extended by Fieser and Fieser (129) to include the homoannular dienes, trienes, and some of the tetraenes. In this method it is assumed that the base absorption value for a hypothetical heteroannular diene is 214 mμ and for a homoannular diene, 253 mμ. Each alkyl substituent or ring residue is considered to contribute a bathochromic shift of 5 mμ. It was observed (465) that in the conjugated diene systems, a double bond exocyclic to a six-membered ring causes a bathochromic shift of approximately 5 mμ due to the strain in the molecule. This is illustrated below (45, 121).



Where an exocyclic bond is common to two rings, the displacement is 10 mμ. Each double bond that extends the conjugation of the diene produces a bathochromic shift of 30 mμ. Where a steroid triene is composed of a heteroannular and a homoannular system as in 2,4,6-cholestatriene, the base value for the homoannular diene is used. The principal absorption band of heteroannular polyenes can be calculated (124) by equation 1 and that of homoannular polyenes by equation 2.

$$\lambda_{max.}\ (\text{in m}\mu) = 214 + 5m + 30(n - 2) + 5e \qquad (1)$$

$$\lambda_{max.}\ (\text{in m}\mu) = 253 + 5m + 30(n - 2) + 5e \qquad (2)$$

In both equations, m is the number of alkyl groups or residues, n is the number of conjugated double bonds, and e is the number of exocyclic double bonds.

The calculated values for the steroid polyenes are given in the last columns of tables 4 to 6. Considering that all alkyl or ring residues and exocyclic double bonds are assumed to be equivalent, irrespective of their position in the steroid nucleus, it would seem that the observed and calculated values are in good agreement, that is, within 4 mμ with the exception of a few compounds. Notable exception to the non-equivalence of the exocyclic double bond is observed in those double bonds involving the cyclopentano ring. The $\Delta^{6,8(14)}$- and $\Delta^{8,14}$-

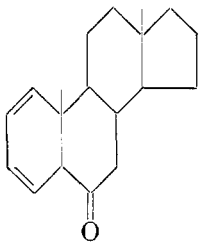
dienes absorb at 253 and 248 mμ, respectively, which values are 9 and 4 mμ higher than calculated, thus indicating that an exocyclic double bond involving the cyclopentano ring is under greater strain and causes a bathochromic shift of 9–14 mμ instead of 5 mμ. The $\Delta^{7,14}$-dienes absorb at either 242 or 248 mμ, $\epsilon_{max.}$ = 10,000–15,000, a fact difficult to explain. However, in recent publications (24a, 134a) the value ϵ_{242} = 10,000 appears to be the correct one. This value seems to be a contradiction of the above statement about the greater strain of an exocyclic double bond involving the cyclopentano rings. However, $\Delta^{7,14}$-dienes have a cisoid chromophore system (24a, 134a), which system in steroids and triterpenes usually absorbs at a lower extinction coefficient than the corresponding transoid chromophore grouping. It has been stated (48a) that structural changes that cause relatively small loss in planarity of the resonating system will result in little change in wave-length location, but the intensity of absorption will be lowered. However, if the loss in planarity is large, the characteristic absorption band itself will be displaced toward shorter wave lengths. The absorption of the $\Delta^{7,14}$-dienes at a lower wave length appears to be due to a steric interference of resonance. The observed absorption, 238 mμ for 3α-acetoxy-16,20-pregnadien-11-one (375), is at variance with the calculated value of 224 mμ; this also indicates the more highly strained nature of a double bond involving ring D. The absorption of the cross-conjugated $\Delta^{6,8(14),9(11)}$-triene cannot be calculated. The absorption bands at ϵ_{243} = 12,000 and ϵ_{285} = 9100 indicate the presence of the two dienic components $\Delta^{6,8(14)}$ and $\Delta^{8(14),9(11)}$; however, interaction between the two systems occurs, since the observed bands are approximately 10 mμ lower than those calculated for the individual dienes.

IV. ULTRAVIOLET ABSORPTION OF STEROIDS CONTAINING A DOUBLE BOND CONJUGATED WITH A CARBONYL GROUP

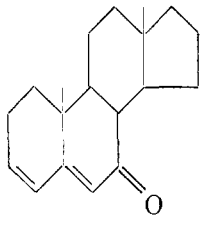
The conjugation of a double bond with a carbonyl group produces an intense chromophore system whose principal band lies between 230 and 270 mμ and which has a much weaker band at 300–330 mμ. The latter is attributed to the displacement of the normal carbonyl absorption. Each successive double bond that extends the conjugation shifts the absorption bands further toward longer wave lengths. Neglecting factors that have bathochromic effects, the absorption bands for the various conjugated ketones fall into three well-defined areas.

KETONES	$\lambda_{max.}$
	mμ
α,β-Unsaturated ketones Enediones Cross-conjugated dienones	230–270
Dienones Cross-conjugated trienones	279–315
Trienones	348–388

As in the dienes, if additional olefinic bonds form a homoannular diene component of a dienone or trienone, a greater bathochromic displacement occurs and with a lower extinction coefficient than if a heteroannular dienone or trienone is formed. The homoannular dienones absorb near 315 mμ and the heteroannular at 280–285 mμ. However, if the additional double bond leads to the formation of a cross-conjugated system, the bathochromic shift for that bond is com-



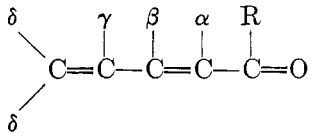
315 mμ (7600)



279 mμ (26,200)

paratively small. This effect is expected, since the molecule is not linearly conjugated. The $\Delta^{1,4}$-dien-3-ones have effectively the absorption of the conjugated ketone Δ^{4}-en-3-one, and the Δ^{1} double bond in $\Delta^{1,4,6}$-trien-3-one causes a bathochromic shift of only 14 mμ with respect to the $\Delta^{4,6}$-3-one component. In each of the above examples the cross-conjugated ketone has a lower extinction coefficient.

Alkyl substituents or ring residues on the ethylene chromophore have a bathochromic effect but not with the same regularity as in the conjugated dienes. Woodward (464) observed that the average displacement due to an alkyl or ring residue was 11 mμ for α,β-unsaturated ketones. Concurrently, it was observed (119a) that the alkyl contribution varied from 5 to 19.5 mμ. However, an alkyl group on a beta carbon atom produces a greater displacement by 5.5 mμ



than one on an alpha carbon atom. The generalization that an auxochrome at the end of a conjugated system produces a greater bathochromic shift than if at the middle was also observed (46) for halogen, thioether, and alkoxyl groups. The alkylation effect in the dienones is similar to that of the simple α,β-unsaturated ketones in that substitution in the γ- and δ-positions contributes a greater bathochromic effect than substitution in the α- or β-position (120a). In Fieser and Fieser's method (129) of calculating the principal maxima of the dienones, it was assumed that substitution of alkyl groups in the γ- and δ-positions produces a bathochromic shift of 18 mμ. Since it is unreasonable to expect that the alkylation effect in the more highly unsaturated ketones, such as the trienones, would increase at the same rate, the bathochromic shift is arbitrarily leveled off at 18 mμ.

Woodward (464) tabulated the absorption of a number of α,β-unsaturated ketones, including steroids, and found that they fall into three groups when classified according to the number of alkyl substituents. The bathochromic displacement of exocyclic double bonds was also taken into consideration.

α,β-UNSATURATED KETONES	$\lambda_{max.}$
	$m\mu$
Monosubstituted (α or β)	225 ± 5
Disubstituted ($\alpha\beta$ or $\beta\beta$) no exocyclic double bond	235 ± 5
Disubstituted ($\alpha\beta$ or $\beta\beta$) one exocyclic double bond	240 ± 5
Trisubstituted ($\alpha\beta\beta$) no exocyclic double bond	247 ± 5
Trisubstituted ($\alpha\beta\beta$) one exocyclic double bond	252 ± 5

It was subsequently observed (142a) that conjugated cyclopentenones were an exception, in that they absorb approximately 11 mμ lower than the corresponding cyclohexenones with the same degree of alkylation. A few cyclopentenones were synthesized (137a) and the following summary was made:

CYCLOPENTENONES	$\lambda_{max.}$
	$m\mu$
Monosubstituted (β)	214 ± 5
Disubstituted (α,β)	224 ± 5
Trisubstituted (α,β,β)	236 ± 5

French (137b) has suggested that in the substituted cyclopentenones the conjugated atoms are no longer coplanar, with the result that maximum resonance is somewhat restricted and a shift to lower wave lengths occurs. The two possible conjugated cyclopentenones in the steroids Δ^{14}-en-16-one and Δ^{15}-en-17-one have not been prepared to date except in compounds where either ring A or ring B or both are benzenoid. The compound 3-hydroxy-1,3,5,14-estratetraen-16-one has a strong absorption band at 227 mμ, which is attributed (439) to the β,β-disubstituted conjugated ketone. In general, the spectra of the ring B or ring AB benzenoid compounds containing an α,β-unsaturated ketone in ring D are too complex to establish definitely the contribution of the conjugated ketone.

Tables 7–10 summarize the ultraviolet absorption of the various unsaturated ketones. Though the range is wide for the absorption values in table 7, it is found that where there are many compounds in a class the vast majority of the values are near that of the average. In the Δ^4-en-3-one group about 10 per cent of the compounds are outside the 240–242 mμ range and for these there is no apparent structural reason. Approximately 70 per cent of the compounds have an $\epsilon_{max.}$ between 15,000 and 18,000. A few compounds containing an isolated oxido group have an $\epsilon_{max.}$ of 11,000–14,000. In the Δ^1-en-3-one group the presence of a C_{17}-hydroxy ester or a C_{17}-carboxylic acid and its ester has a hypochromic effect on the extinction coefficient, and the compounds absorb at 7000–8000. A few unsaturated acids, aldehydes, and nitriles are also included in tables 7 and 9.

TABLE 7

Ultraviolet absorption of α,β-unsaturated steroid ketones

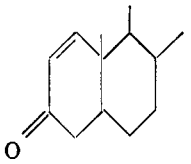
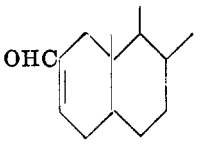
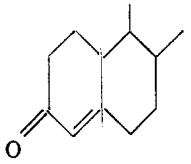
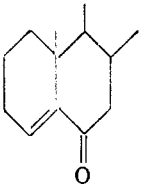
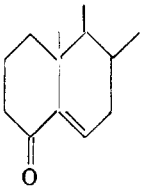
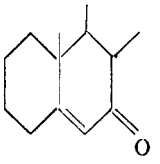
COMPOUND	AVERAGE		RANGE		$\lambda_{max.}$ CALCULATED
	$\lambda_{max.}$	$\epsilon_{max.}$	$\lambda_{max.}$	$\epsilon_{max.}$	
	mμ		mμ		mμ
 Δ^1-3-one	230	10,700	229–232	10,000–12,600	227
 Δ^2-2-formyl	235 300	12,600 70			227
 Δ^4-3-one	241 306	16,600 94	239–244 295–313	10,500–22,700 70–146	244
 Δ^4-6-one	244 310	6,300 100	243–244 300–320	6,300–6,400 85–120	242
 Δ^5-4-one	241	5,200	240–241	3,200–7,200	242
 Δ^5-7-one	239	12,000	238–240	8,900–15,100	244

TABLE 7—*Continued*

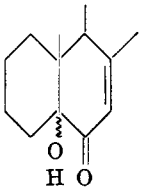
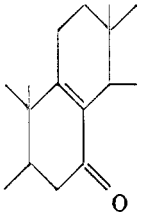
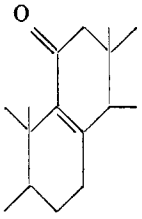
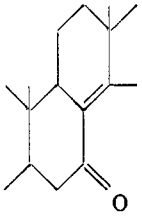
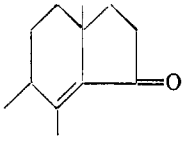
COMPOUND	AVERAGE		RANGE		$\lambda_{max.}$ CALCULATED
	$\lambda_{max.}$	$\epsilon_{max.}$	$\lambda_{max.}$	$\epsilon_{max.}$	
	mμ		mμ		mμ
 Δ^{7}-6-one	252 329	13,400 130	252–253 323–333	13,100–13,600 100–160	244
 $\Delta^{8(9)}$-7-one	253	11,200	252–254	8,300–13,200	249
 $\Delta^{8(9)}$-11-one	254	9,100	252–255	8,700–9,600	249
 $\Delta^{8(14)}$-7-one	262	9,500	260–263	7,800–10,800	259
 $\Delta^{8(14)}$-15-one	259	13,000	259	12,700–13,300	259

TABLE 7—*Continued*

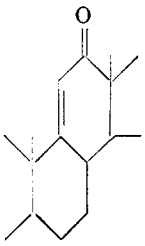
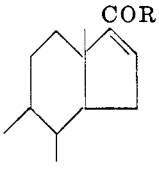
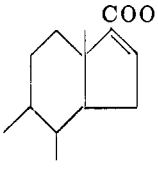
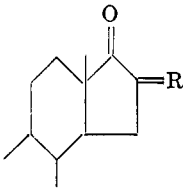
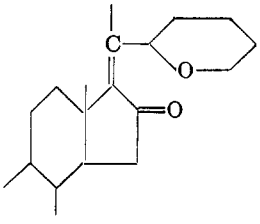
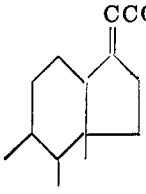
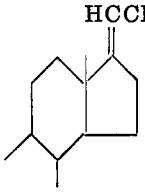
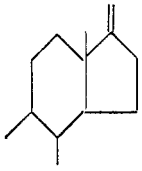
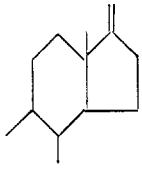
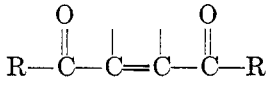
COMPOUND	AVERAGE		RANGE		$\lambda_{max.}$ CALCULATED
	$\lambda_{max.}$	$\epsilon_{max.}$	$\lambda_{max.}$	$\epsilon_{max.}$	
	$m\mu$		$m\mu$		$m\mu$
 Δ^{9}-12-one	240 318	11,200 85	238–243 311–322	8,300–15,800 71–120	244
 Δ^{16}-20-one	240 314	10,500 95	239–242 310–318	8,000–16,000 64–126	237
 Δ^{16}-17-COOH (R = H, CH_3)	228	12,600	225–230	12,600	
 Δ^{16}-methylene-17-one	R = CH_2.... R = $C(CH_3)_2$	228 250 338	8,000 14,800 100		230 254
 Δ^{17}-16-one		236	14,800		244

TABLE 7—*Concluded*

COMPOUND	AVERAGE		RANGE		$\lambda_{max.}$ CALCULATED
	$\lambda_{max.}$	$\epsilon_{max.}$	$\lambda_{max.}$	$\epsilon_{max.}$	
	mμ		mμ		mμ
 Δ^{17}-21-one	242 310	20,000 120			244
 Δ^{17}-21-al	244	26,900	244	26,300–27,500	244
 Δ^{17}-21-COOH	222	15,300	222–224	12,600–16,600	
 Δ^{17}-21-nitrile	224	11,600	223–225	10,500–13,800	

In general, the acids and nitriles absorb 10–20 mμ lower than the corresponding conjugated ketones, while the aldehydes absorb at nearly the same position.

The conjugated ethylenic diketones behave like the α,β-unsaturated ketones

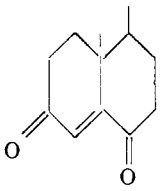
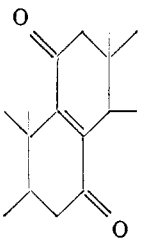
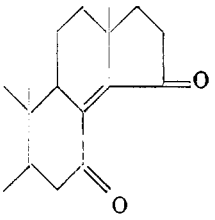
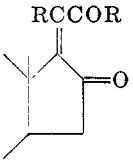


with the exception that the second carbonyl group produces a variable bathochromic shift but of smaller magnitude than an ethylenic bond in the same

position. It appears (129) that the enediones resonate between the two ketone groups and absorb 10–20 mμ higher than the more active chromophore system

TABLE 8

Ultraviolet absorption of steroid enediones

COMPOUND	AVERAGE		RANGE		$\lambda_{max.}$ CALCULATED
	$\lambda_{max.}$	$\epsilon_{max.}$	$\lambda_{max.}$	$\epsilon_{max.}$	
	mμ		mμ		mμ
 Δ^4-3,6-dione	253	11,200	252–254	10,800–11,400	244
 $\Delta^{8(9)}$-7,11-dione	270	7,400	268–272	6,300–8,700	249
 $\Delta^{8(14)}$-7,15-dione	255	5,000			259
 Δ^{17}-16,22-dione	246	13,500			254

of the alternate α,β-unsaturated ketones. However, $\Delta^{8(14)}$-ene-7,15-diones are an exception, in that they absorb 4 mμ lower and with approximately half the intensity. This may be attributed to a loss in coplanarity of the conjugated atoms.

TABLE 9

Ultraviolet absorption of steroid dienones

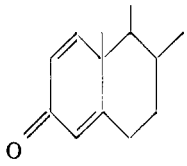
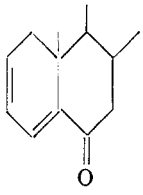
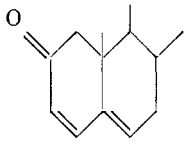
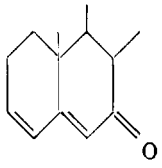
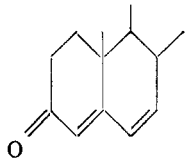
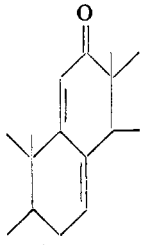
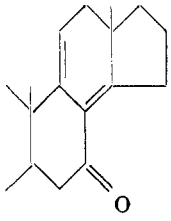
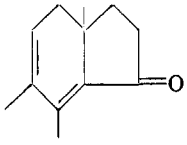
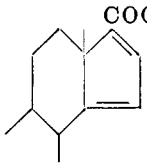
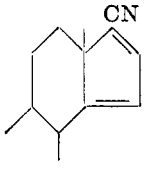
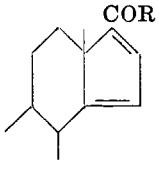
COMPOUND	AVERAGE		RANGE		$\lambda_{max.}$ CALCULATED
	$\lambda_{max.}$	$\epsilon_{max.}$	$\lambda_{max.}$	$\epsilon_{max.}$	
	$m\mu$		$m\mu$		$m\mu$
 $\Delta^{1,4}$-3-one	244	15,000	243–245	10,000–18,600	244
 $\Delta^{2,4}$-6-one	315	7,000	314–317	6,300–7,600	316
 $\Delta^{3,5}$-2-one	290	12,600			286
 $\Delta^{3,5}$-7-one	279	26,400	277–280	24,400–28,000	280
 $\Delta^{4,6}$-3-one	284	28,000	281–284	25,000–30,000	280
 $\Delta^{7,9}$-12-one	239 292	3,700 13,100	238–240 290–293	3,700–3,800 12,900–13,500	303

TABLE 9—*Concluded*

COMPOUND	AVERAGE		RANGE		$\lambda_{max.}$ CALCULATED
	$\lambda_{max.}$	$\epsilon_{max.}$	$\lambda_{max.}$	$\epsilon_{max.}$	
	$m\mu$		$m\mu$		$m\mu$
 $\Delta^{8(14),9}$-7-one (?)	223 298	15,600 5,000	298–300	4,800–5,300	
 $\Delta^{8(14),9}$-15-one (?)	307	10,000			356
 $\Delta^{14,16}$-17-COOH	295	12,000	292–298	10,500–15,800	
 $\Delta^{14,16}$-17-nitrile	286	13,200	286	11,200–14,800	
 $\Delta^{14,16}$-20-one	307	17,000			334

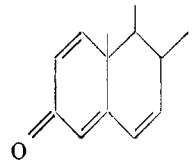
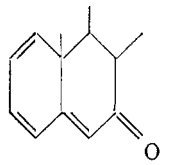
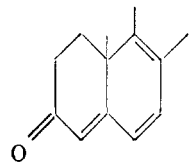
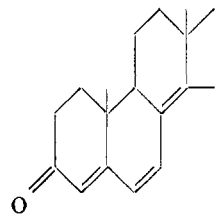
The formation of a pyridazine (ϵ_{260} = 2000) by the reaction of the enedione with hydrazine is a useful reaction in establishing the structure of this conjugated system.

All the trienones that contain a homoannular diene component, including the cross-conjugated $\Delta^{1,4,6}$-trien-3-one, have three absorption bands in contrast to

the heteroannular trienones, which have but one. It was shown (48a) that in conditions of steric inhibition of resonance, bands will appear that are characteristic of the partial chromophores and which increase in intensity as the intensity of the main band decreases. This is the case in the $\Delta^{1,3,5}$-trien-7-one

TABLE 10

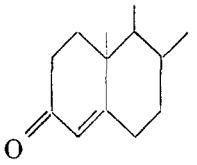
Ultraviolet absorption of steroid trienones

COMPOUND	AVERAGE		RANGE		$\lambda_{max.}$ CALCULATED
	$\lambda_{max.}$	$\epsilon_{max.}$	$\lambda_{max.}$	$\epsilon_{max.}$	
	$m\mu$		$m\mu$		$m\mu$
 $\Delta^{1,4,6}$-3-one	223	13,500	222–224	10,700–15,500	
	256	11,900	256–258	9,300–13,500	
	298	15,300	296–300	12,300–18,600	280
 $\Delta^{1,3,5}$-7-one	230	18,600			
	278	3,720			
	348	11,000			348
 $\Delta^{4,6,8(9)}$-3-one	244	17,800			
	284	2,190			
	388	12,300			384
 $\Delta^{4,6,8(14)}$-3-one	348	26,500			356

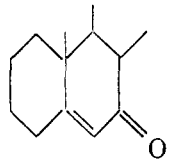
and $\Delta^{4,6,8(9)}$-trien-3-one, where the band at the shortest wave length is the most intense.

Conjugated ketones that have the double bond at the $C_{4,5}$-position resemble the dienes in that they absorb at a longer wave length and with a higher intensity

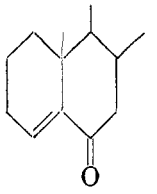
than when the bond is at the $C_{5,6}$-position. In each comparison, the systems contain the same number of alkyl substituents and exocyclic double bonds.



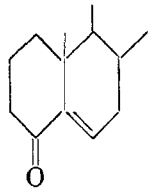
ϵ_{241} = 16,600



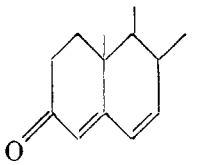
ϵ_{239} = 12,000



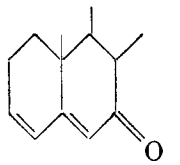
ϵ_{244} = 6300



ϵ_{241} = 5200



ϵ_{284} = 28,000



ϵ_{279} = 26,400

The unusually low extinction coefficient for the Δ^4-en-6-ones and Δ^5-en-4-ones can be attributed to steric inhibition of resonance.

A. Varichromic effects of covalently unsaturated atoms and groups α and β to the double bond of conjugated ketones

In the α,β-unsaturated ketones, and to a lesser degree in dienones, a number of isolated chromophores are found that exert a hypsochromic shift, as illustrated in table 11. From a synthetic viewpoint, this observation is of value in indicating the degree of success in introducing these isolated chromophores into the conjugated ketones. The conversion of cortisone (238 mμ) to compound F (241 mμ), and *vice versa*, is clearly indicated by ultraviolet absorption.

There are two examples of a Δ^4-en-3-one containing a C_{12}-ketone group which produces a 5-mμ hypsochromic shift in one case and none in the other. There are few dienones that contain isolated chromophores; however, those containing a C_{11}-ketone group absorb 2–4 mμ toward the lower wave length as compared to the non-substituted compound. Hyperconjugation of the $C_{14,15}$-oxido group with Δ^{16}-en-20-ones causes a bathochromic displacement of 7 mμ, while in the Δ^{16}-ene-17-acids the shift is 3–6 mμ.

Hydroxyl, acetoxy, and bromine substituents α and β to the double bond of unsaturated ketones have varichromic effects on the absorption of the principal band, as is shown in table 12. Bromine causes bathochromic shifts and hydroxyl and acetoxy groups produce hypsochromic shifts.

The displacements cannot be wholly attributed to electronic interaction, as can be seen by the difference in action of the 6α- and 6β-hydroxy and 6α- and

TABLE 11

Hypsochromic effects (in mμ) of isolated chromophores

COMPOUND	Δ^5	Δ^7	$\Delta^{8(14)}$	Δ^9	Δ^{11}	Δ^{14}	Δ^{15}	3-KETO	6-KETO	11-KETO	12-KETO	17-KETO
Δ^1-ene-3-keto									−2	−4		0
Δ^4-ene-3-keto		−3		−1	−3	−3	−1			−3		−1
Δ^9-ene-12-keto								0				−2
Δ^{16}-ene-20-keto	0	−1	−10	−2				0		−5	−11	

TABLE 12

Effect of covalently unsaturated groups adjacent to α,β-conjugated ketone groups

COMPOUND	GROUP POSITION	VARICHROMIC SHIFT
		mμ
Δ^4-3-one	6α-Hydroxy	Little or no effect
$\lambda_{max.}$ = 241 mμ	6α-Acetate	0 to −6
	6β-Hydroxy	−3 to −6
	6β-Acetate	−3 to −6
	7β-Hydroxy	Little or no effect
	7β-Acetate	−3
	2-Bromo	+3
	2-Iodo	+2
	2,2-Dibromo-6β-acetate	+9
	6α-Chloro	−2
	6β-Chloro	Little or no effect
	6α-Bromo	Little or no effect
	6β-Bromo	+8
Δ^4-6-one	3β-Hydroxy	−5
$\lambda_{max.}$ = 244 mμ	3β-Acetate	−8
Δ^5-7-one	3β-Hydroxy	Little or no effect
$\lambda_{max.}$ = 240 mμ	3β-Acetate	−5
	3β,4β-Dihydroxy	−5
	3β,4β-Diacetate	−9
$\Delta^{8(9)}$-7-one	11α-Hydroxy	Little or no effect
$\lambda_{max.}$ = 253 mμ	11α-Acetate	Little or no effect
$\Delta^{9(11)}$-12-one	7α-Hydroxy	Little or no effect
$\lambda_{max.}$ = 240 mμ	7α-Acetate	−3
Δ^{16}-11,20-dione	15-Acetate	−2
$\lambda_{max.}^{ether}$ = 231 mμ	15-Bromo	+4
	15-Iodo	+12
$\Delta^{1,4}$-3-one	6β-Bromo	+5
$\lambda_{max.}$ = 244 mμ		

6β-bromo compounds of Δ^4-en-3-one. A steric factor must also be considered. As is anticipated, the hydroxyl group β to the double bond is without effect, since it is removed from the immediate area of the α,β-unsaturated ketone; however,

the marked shift of the acetates is to be noted. In all groups, the extent of the shift is sometimes influenced by the substituents on the C_{17} carbon atom.

B. Calculation of the principal absorption band of conjugated ketones

In a method similar to that applied to conjugated olefins, Fieser and Fieser (129) calculated the principal absorption band of the α,β-unsaturated ketones, dienones, and trienones. With a minor modification, table 13 outlines the scheme and the assumed values for each factor that contributes to the absorption of conjugated ketones.

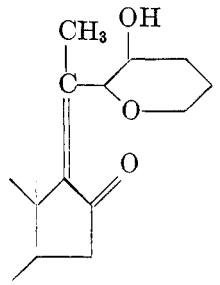
With few exceptions, the agreement between the observed and the calculated is good, as is illustrated in the last column in tables 7 to 10. The substitution of an auxochrome for a hydrogen atom on the double bond of conjugated ketones usually produces bathochromic displacements and will be discussed in Section V

TABLE 13

Calculation of absorption maxima of α,β-unsaturated ketones, dienones, and trienones

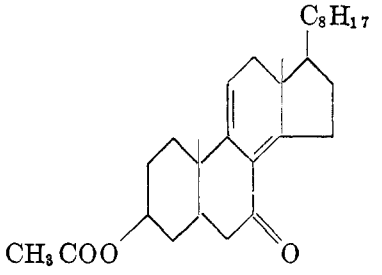
Parent system	215 mμ
Increments for alkyl substituents: α	10 mμ
β	12 mμ
γ	18 mμ
δ	18 mμ
Increment for each exocyclic >C=	5 mμ
Increment for each —C=C— extending conjugation	30 mμ
Increment for the presence of a homoannular diene component	38 mμ
$\lambda_{max.}^{alc.}$	Total

There is a large deviation between the observed, 252 mμ, and the calculated value, 244 mμ, for the Δ^7-en-6-one compounds. These compounds have a 5-hydroxy substituent which may have a bathochromic effect through possible hydrogen bonding. The large difference between the observed, 236 mμ, and the calculated value, 244 mμ, of the Δ^{17}-en-16-one compound may be due to steric hindrance because of the large group at the C_{20}-position.

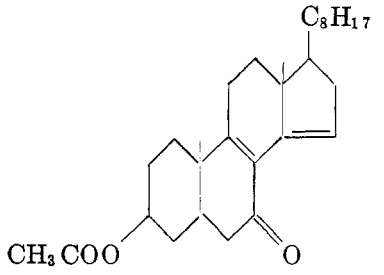


There are a few anomalies in the dienone group. The conjugated ketone $\Delta^{7,9}$-dien-12-one exhibits two relatively strong absorption bands, of which the band

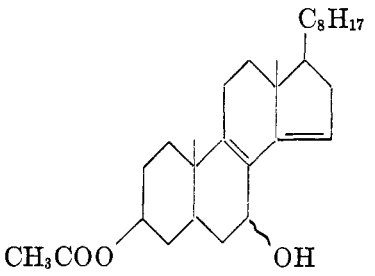
at 240 mμ is probably that of the Δ^{9}-en-12-one component. The band at 293 mμ is 10 mμ lower than the calculated value for the dienone. The structural assignment of the double bonds in the $\Delta^{8(14),9}$-dien-7-one (ϵ_{298} = 5000) compounds has been questioned. Woodward (footnote in reference 404) suggested the alternate structure $\Delta^{8(14),15}$-dien-7-one, since it is also consistent with the chemical evidence and the calculated absorption maximum of 295 mμ. However, the observed extinction coefficient is too low for a heteroannular dienone. Wintersteiner and Moore (458) prepared a dienone for which two structures, I and II, were formulated. Structure I was preferred on the basis of ultraviolet absorption, ϵ_{297} = 4800, although II also complied with the chemical evidence. The com-



I



II



III

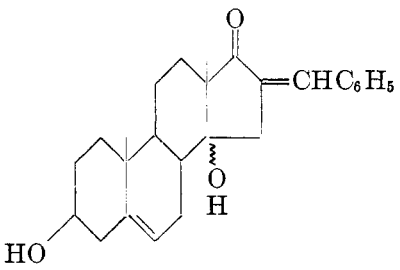
pound also had a strong end absorption below 240 mμ, which was subsequently shown (315a) to be a strong band, ϵ_{223} = 15,600. Reduction of the dienone by lithium aluminum hydride (315a) yielded an amorphous product which had a strong absorption at 248 mμ comparable to that of a $\Delta^{8,14}$-diene or structure III. If the proposed structure I were correct, the reduced product should absorb at approximately 283 mμ, the absorption of a $\Delta^{8(14),9}$-diene, since reductions by lithium aluminum hydride normally do not induce rearrangement of dienes. On the basis of the meager evidence presented, structure II appears to be the correct one. However, the absorption of 248 mμ does not rule out the possibility of a $\Delta^{8(14),15}$-diene. The system acts, partially, as a linearly conjugated diene; however, there is steric interference of resonance.

The structure and homogeneity of $\Delta^{8(14),9}$-dien-15-one is in doubt (129).

The chromophore system in $\Delta^{14,16}$-dien-20-one is probably not coplanar and thus would account for the wide discrepancy between the calculated value,

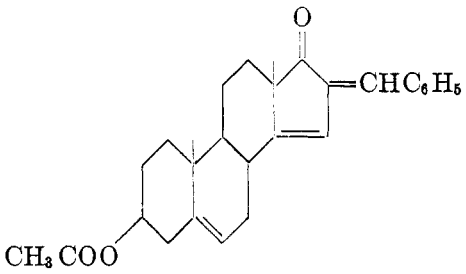
334 mμ, and the observed value, 307 mμ. In this group, the C_{17}-carboxy esters absorb 12 mμ lower and the C_{17}-nitrile compounds 21 mμ lower, the extinction coefficient in each being about 12,000.

It is interesting to note that compound V (370a) appears to act as a linearly conjugated chromophore system. However, the band at 334 mμ is due to a highly



IV

$\epsilon_{221} = 8{,}300$
$\epsilon_{290} = 24{,}500$



V

$\epsilon_{234} = 12{,}900$
$\epsilon_{258} = 8{,}300$
$\epsilon_{334} = 23{,}200$

strained system caused by the introduction of the double bond at C_{14} by the dehydration of IV.

V. EFFECT OF AUXOCHROMES ON THE ABSORPTION OF CONJUGATED DIENES AND KETONES

Auxochromes are groups which when substituted for hydrogen atoms in conjugated systems cause bathochromic and hyperchromic shifts. This discussion will be limited to coördinatively unsaturated groups containing unshared electron-pairs, such as —OR, —SR, and halogens. Their effect is apparently due to the interaction of the unshared electron-pairs with the unsaturation or π-electrons of the adjacent double bond. These effects are minimized if the free electron-pairs become shared, as is shown by the sulfoxide in table 14, where one of the free electron-pairs is now shared, causing a bathochromic displacement of only 23 mμ as compared to 33 mμ for the thioenol ether. A sulfone should have little or no effect.

In an excellent series of papers (45a, 46, 47) the effect of auxochromes on aliphatic and aromatic conjugated systems was analyzed. Special emphasis was placed on a correlation of the degree of bathochromic displacement of the auxochrome with the position of the substituent element in the Periodic Table. The generalizations observed for aliphatic systems apply to the steroid conjugated systems and are summarized as follows:

1. Chromophores attached to an ethylenic linkage which may be either isolated or form part of a conjugated system generally increase both $\lambda_{max.}$ and $\epsilon_{max.}$

2. The bathochromic effects depend primarily on the nature of the element vicinal to the ethylenic bond varying in the order O < S, Cl < Br, and C <

TABLE 14

Ultraviolet absorption of enol derivatives of conjugated steroid ketones

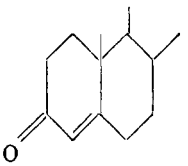
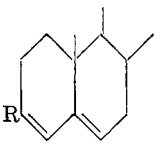
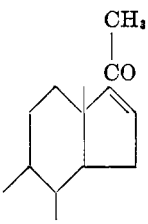
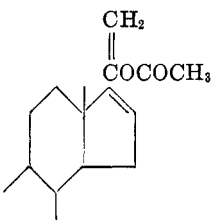
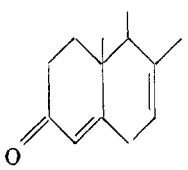
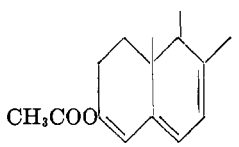
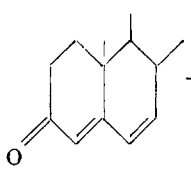
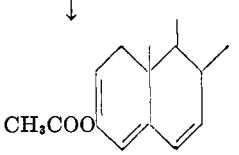
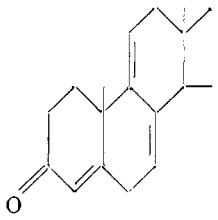
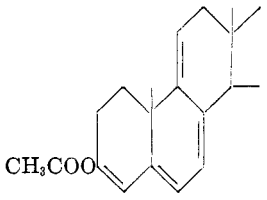
COMPOUND	ENOL DERIVATIVE	$\lambda_{max.}$	$\epsilon_{max.}$	VARICHROMIC SHIFT IN ABSORPTION OF CONJUGATED POLYENE
		$m\mu$		$m\mu$
				
Δ^4-3-one	$\Delta^{3,5}$			
ϵ_{241} = 16,600	R = CH_3COO—	235	17,000	
	R = C_2H_5O—	241	22,600	+6
	R = CH_2S—	268	22,600	+33
	R = $CH_2S(=O)$—	258	21,400	+23
	R = Cl	238	23,200	+3
	R = Br	238	22,700	+3
				
Δ^{16}-20-one	$\Delta^{16,20}$	239	15,100	−1
ϵ_{240} = 10,500				
				
$\Delta^{4,7}$-3-one	$\Delta^{3,5,7}$	301	19,300	0
ϵ_{239} = 15,100		315	21,300	
		331	17,700	
	Two forms isolated			
$\Delta^{4,6}$-3-one				
ϵ_{284} = 28,800	$\Delta^{2,4,6}$	303	14,600	−3

TABLE 14—*Concluded*

COMPOUND	ENOL DERIVATIVE	$\lambda_{max.}$	$\epsilon_{max.}$	VARICHROMIC SHIFT IN ABSORPTION OF CONJUGATED POLYENE
		$m\mu$		$m\mu$
				
$\Delta^{4,7,9}$-3-one	$\Delta^{3,5,7,9}$	338	16,400	
ϵ_{242} = 32,000		355	19,700	
		374	14,600	

N > O > Cl. The shift is greater on ascending the first two rows of the Periodic System and reaches a maximum with nitrogen in the first group.

3. The effect of any one substituent also depends on the nature of the conjugated ethylenic system to which it is attached, increasing in the following order:

$$X{-}C{=}C < X{-}C{=}C{-}C{=}C < X{-}C{=}C{-}\overset{\overset{O}{\|}}{C}{-}O < X{-}C{=}C{-}C{=}O$$

4. Substituents in conjugated ketonic systems produce larger bathochromic shifts when they are located at the end of the system than when they are cross-conjugated.

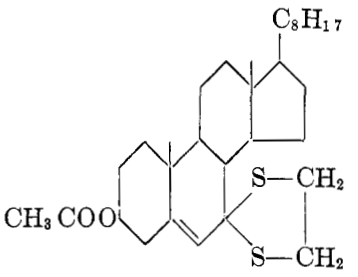
$$X{-}C{=}C{-}C{=}O > \begin{matrix} & X & \\ & | & \\ C{=}C{-}C{=}O & & \end{matrix}$$

5. The effects of two or more substituents are roughly additive.

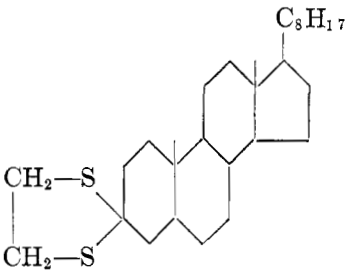
A. Enol esters of conjugated ketones

The conversion of conjugated ketones to substituted polyenes (enol esters or ethers) is of importance as an additional means of characterizing these compounds. In the steroid field the reaction has been applied mainly to the Δ^4-en-3-one compounds. Table 14 summarizes the known enol derivatives. It is evident that the degree of bathochromic displacement varies with the different auxochromes, in support of previous observations. The $\Delta^{3,5}$-diene and the $\Delta^{2,4,6}$-trienes do not exhibit the two secondary absorption bands normally associated with conjugated polyenes.

It is interesting to note that ethylene mercaptals containing a double bond β to the quaternary carbon of the spirane ring, as in 7-ketocholesteryl acetate ethylene mercaptal (VI), absorb at 222 mμ, $\epsilon_{max.}$ = 6400. If the ethylenic bond is absent, as in 3-ketocholestane ethylene mercaptal (VII), the absorption is



VI



VII

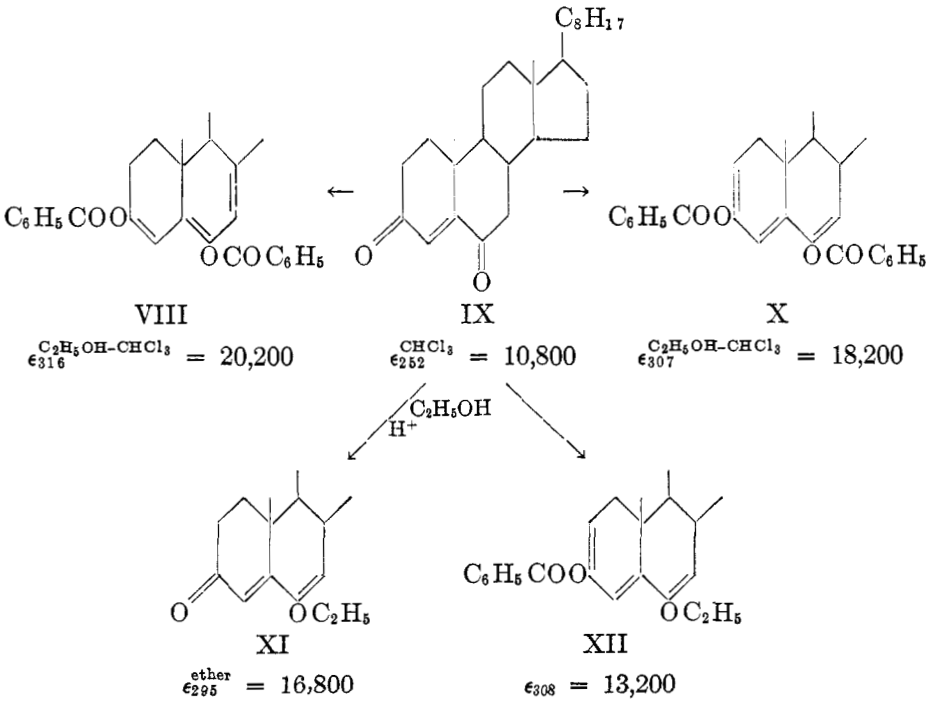
rather weak, 240 mμ, $\epsilon_{max.}$ = 333. The oxygen analogs, the ethylene ketals, have no characteristic bands in the ultraviolet.

B. Enol esters of enediones

The conjugated enediones are similar to the α,β-unsaturated ketones in their enolic behavior, except that there are two enolizable carbonyl groups which can yield conjugated trienes or dienones if partially esterified. Of the three known steroids in this group two have been isolated in the free enolic state: 5-cholestene-3,4-dione (diosterol) and 5-cholestene-3,7-dione.

(1) 4-Cholestene-3,6-dione (IX)

The dibenzoylation (345) of IX yielded two compounds depending on the method of preparation. Both dibenzoates, VIII and X, exhibited an additional strong peak at 230 mμ, $\epsilon_{max.}$ = 48,400 and 37,600, respectively, which is charac-



VIII $\epsilon_{316}^{C_2H_5OH\text{-}CHCl_3}$ = 20,200

IX $\epsilon_{252}^{CHCl_3}$ = 10,800

X $\epsilon_{307}^{C_2H_5OH\text{-}CHCl_3}$ = 18,200

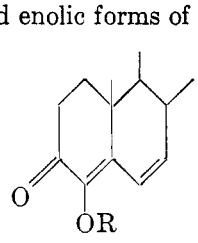
XI ϵ_{295}^{ether} = 16,800

XII ϵ_{308} = 13,200

teristic of the benzoyl moiety. The absorption bands of the resulting trienes (VIII, X, and XII) agree closely with those containing no substituents; however, the secondary absorption bands associated with these trienes are missing for the benzoates. The difference in the bathochromic effect of coördinatively unsaturated groups containing unshared electron-pairs when substituted on an ethylenic bond of a conjugated ketone as compared with a conjugated polyene is illustrated by compounds XI and XII. The C_6-ethoxy group in XI exerts approximately a 17-mμ shift toward longer wave lengths with respect to the parent $\Delta^{4,6}$-dien-3-one compound, while comparatively no effect on the principal band of triene XII is observed. The extinction coefficient in each example has been lowered appreciably.

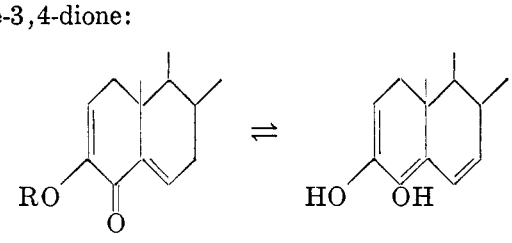
(2) 5-Cholestene-3,4-dione

Fieser (130) elucidated the structure of diosterols, the name given to the two isolated enolic forms of 5-cholestene-3,4-dione:



Diosterol I

R = H; $\epsilon_{313.5}$ = 4680
R = C_6H_5CO; ϵ_{232} = 15,500
ϵ_{287} = 25,700



XIII XIV

Diosterol II

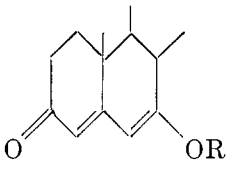
R = H; ϵ_{265} = 5130, ϵ_{300} = 5370
R = CH_3CO; ϵ_{245} = 14,800
R = C_6H_5CO; ϵ_{234} = 20,000

To explain the second absorption band of almost equal intensity at 300 mμ for Diosterol II, it was suggested that in solution there is an equilibrium mixture of XIII and XIV. The absorption band of the trienediol XIV is near that of a $\Delta^{2,4,6}$-triene (306 mμ) if the possible bathochromic contribution of the enolic hydroxyls is ignored. However, the possibility that this second band is a resonance hybrid cannot be ruled out, since only enol esters of XIII have been isolated.

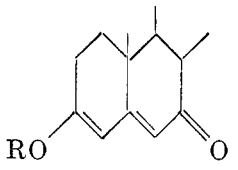
The bathochromic effect of a hydroxyl group in the α-position of an α,β-conjugated ketone will be discussed in greater detail in the following section on α-diketones. The hydroxyl group exerts a 29.5-mμ shift in Diosterol I with respect to the non-substituted $\Delta^{4,6}$-dien-3-one. If the possible effect of the C_5-ethylene group is neglected, a shift of 35 mμ occurs for the hydroxyl group in Diosterol II with respect to the calculated value of a non-substituted conjugated ketone. The conversion of the enols to their esters results in a marked hypsochromic shift to an absorption near that of the non-substituted conjugated ketone. The enol benzoate of Diosterol I absorbs 3 mμ higher than the non-substituted $\Delta^{4,6}$-dien-3-one compounds. Though the bathochromic shift of the enol esters of Diosterol II is difficult to estimate, since there is no example of the parent cross-conjugated system, in any event the shift would be quite small.

(3) 5-Cholestene-3,7-dione

The ultraviolet absorption spectra indicated (20, 146) that in alcoholic solution the compound existed mainly in the enolic form. Two possible structures were proposed:



XV



XVI

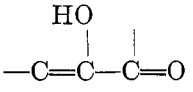
R = H; ϵ_{320} = 24,300, $\epsilon_{392.5}^{\text{alkaline } C_2H_5OH}$ = 62,200
R = CH_3CO; $\epsilon_{282.5}$ = 22,500
R = CH_3; ϵ_{308} = 27,600

Structure XVI is preferred (146) on the basis of rotational measurements and other considerations. In the following section on enol acetates of α-diketones it is observed that an acetate group on the α-carbon of the ethylene moiety of an α,β-unsaturated ketone exerts a bathochromic effect of approximately 6 mμ with respect to the parent conjugated ketone. Assuming that the bathochromic influence of an acetate group at the end of a conjugated ketone is approximately the same, then the absorption should be at 291 mμ for XV, since the parent ketone, $\Delta^{4,6}$-dien-3-one, absorbs at 285 mμ, and the absorption should be at 283 mμ for XVI, since $\Delta^{3,5}$-dien-7-one absorbs at 277 mμ. Thus the absorption data also indicate that structure XVI is correct.

It is interesting to note the large bathochromic displacement, 31 mμ, caused by the C_3-methoxy group, which illustrates the greater bathochromic effect of a coördinatively unsaturated group containing unshared electron-pairs at the end of a conjugated system than when placed in a cross-conjugated position as in XI, where the alkoxy group contributes a shift of 17 mμ.

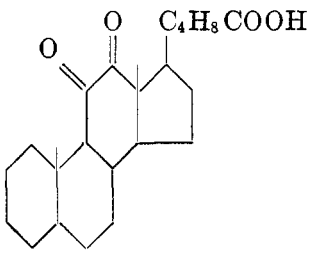
C. α-Diketones and their enols

In contrast to isolated carbonyl groups which have a rather weak absorption in the range of 280–300 mμ, many steroid α-diketones exhibit an intense absorption in the neighborhood of 280 mμ which is associated with the enolic structure



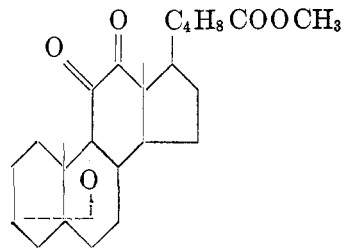
and in one example an additional peak, ϵ_{296} = 79, was reported which is due to the carbonyl group. Two steroid α-diketones have been isolated purely in the keto form, one of which cannot possibly enolize. Both exhibit two very weak carbonyl absorption bands.

A 20-keto-21-aldehyde (137) exhibits a weak absorption band at ϵ_{440} = 20 similar to that of methylglyoxal, which also absorbs at this wave length with approximately the same intensity.



11,12-Diketocholanic acid

$\epsilon_{226}^{\text{hexane}} = \sim 130$, $\epsilon_{279} = 87$, $\epsilon_{347} = 47$



3,9-Oxido-11,12-diketocholanic acid methyl ester

$\epsilon_{295} = 104$, $\epsilon_{376} = 39$

The enols of α-diketones are presented in table 15. The average bathochromic shift of a hydroxy group in the α-position of an α,β-conjugated ketone (enolic form of α-diketones) is 39 mμ and for the enol acetates 6 mμ, with an extinction coefficient substantially lower than that of the non-substituted unsaturated ketone. Where a condition of cross-conjugation exists, as in Diosterol I and in 4-hydroxy-Δ^4-ene-3,6-dione, the bathochromic shift is lower, 29.5 and 22 mμ, respectively. Whether the lower extinction coefficient of the enols is due to enol–keto tautomerism or to the electronic interaction of the hydroxy group with the chromophore system is difficult to say. In all likelihood the hypochromic effect is due to a combination of both factors, with greater emphasis placed on the latter. The factors that favor the latter explanation are that the enol acetates absorb with only a slightly higher extinction coefficient than the free enols and that no carbonyl absorption band above 300 mμ has been reported. In effect a condition of cross-conjugation exists where the enols and their acetates are in conjugation with the ethylenic bond to which they are attached and, as in other cross-conjugated systems, the $\epsilon_{max.}$ is lower than that of the more active chromophoric system.

The large bathochromic effect of the enols is due to ionization and not to chelation, as previously postulated. This fact was brought out in a study (42) of various alkylated 1,3-cyclohexanediones. Since the absorption band, under these circumstances, is influenced by the degree of dissociation of the weakly acidic enol, a shift to longer wave lengths was expected and found upon increasing the dilution of the material in polar solvents. No observed shift of the absorption band on greater dilution has been observed in the steroid enolic α-diketones, a result which indicates that the acidity of these enols is of a much lower order.

D. β-Diketones and their enol esters

The compound 3α,12α-diacetoxypregnane-16,20-dione (258) is an example of a steroid β-diketone. Its enol acetate absorbs at 249 mμ, $\epsilon_{max.} = 11{,}200$.

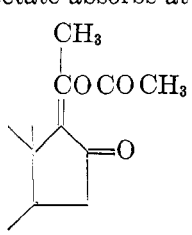


TABLE 15

Ultraviolet absorption of enols of α-diketones

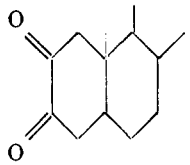
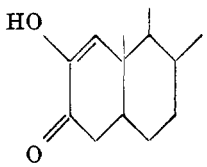
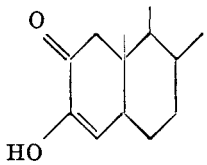
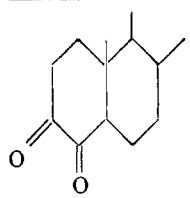
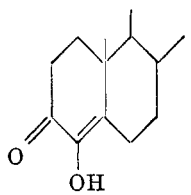
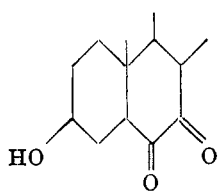
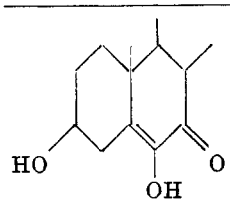
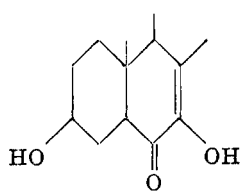
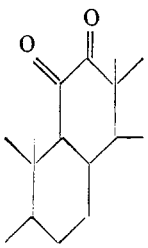
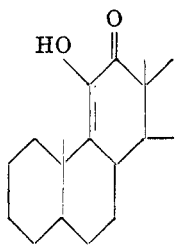
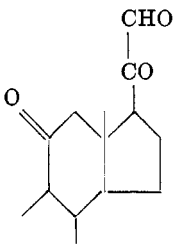
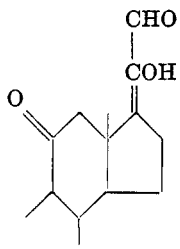
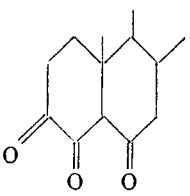
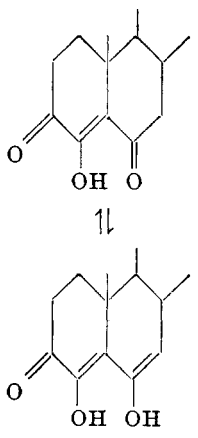
COMPOUND	ENOL FORM	$\lambda_{max.}$	$\epsilon_{max.}$	BATHOCHROMIC SHIFT IN ABSORPTION OF PARENT CONJUGATED KETONE
		mμ		*mμ*
 2,3-diketo		270	8,500	+40
	2-acetate	237	8,900	+7
		272	5,000	~+42
	3-acetate	238	7,400	~+8
 3,4-diketo (diketo form also isolated)	 4-acetate	280 ($CHCl_3$)	11,500	+39
		248 ($CHCl_3$)	14,500	+8
 6,7-diketo	 or 	275	10,700	~+35

TABLE 15—*Concluded*

COMPOUND	ENOL FORM	$\lambda_{max.}$	$\epsilon_{max.}$	BATHOCHROMIC SHIFT IN ABSORPTION OF PARENT CONJUGATED KETONE
		mμ		mμ
		281	~7,000	+41
11,12-diketo (diketo form also isolated)	11-acetate	244	~9,500	+4
		283	~12,000	+39
20-keto-21-al (dicarbonyl form also isolated)	20-acetate	246 (ether)	14,300	+2
		275 (ether) 335	5,000 8,000	+22 +25
3,4,6-triketo				

E. Effect of halogen atoms

It has been observed (45a, 46, 100, 292a) that the bromine atom on the ethylenic linkage of α,β-unsaturated ketones causes large bathochromic shifts

and this is accompanied by a lower extinction coefficient when compared to the parent non-substituted ketone. Attention was focused (100) on this point by the fact that many steroid conjugated ketones containing a bromine atom on the double bond did not exhibit this spectroscopic change. Thus it is evident that the structural assignments must be in error.

If the bathochromic effects of the $C_{2,2}$-dibromo and $C_{6\beta}$-bromo atoms, which were observed in the section on isolated ketones, are taken into account, the average bathochromic shift for a bromine atom on the α-position of a double

TABLE 16

Bathochromic effect of bromine substitution on the double bond of conjugated steroid ketones

COMPOUND	HALOGEN POSITION		$\Delta\lambda$ BATHOCHROMIC SHIFT
			$m\mu$
Δ^1-3-one	2-Bromo	$\epsilon_{256} = 7,600$	+26
$\epsilon_{230} = 10,700$	2,4-Dibromo	$\epsilon_{261} = 6,600$	+31
Δ^4-3-one	4-Bromo	$\sim\epsilon_{270} = 13,000$	$\sim$+29
$\epsilon_{241} = 16,600$	2,2,4-Tribromo	$\epsilon_{277} = 13,150$	+36
	2,2,4,6-Tetrabromo	$\epsilon_{287} = 13,000$	+46
Δ^5-7-one	3,4,6-Tribromo	$\epsilon_{268} = 10,000$	+29
$\epsilon_{239} = 12,000$			
$\Delta^{1,4}$-3-one	2-Bromo	$\epsilon_{255} = 12,400$	+11
$\epsilon_{244} = 15,000$	2,4,6-Tribromo	$\epsilon_{274} = 10,600$	+30
$\Delta^{3,5}$-7-one	6-Bromo	$\sim\epsilon_{288} = 20,000$	+9
$\epsilon_{279} = 26,400$	4,6-Dibromo	$\epsilon_{303} = 11,200$	+24
$\Delta^{4,6}$-3-one	2,4-Dibromo	$\epsilon_{293} = 14,600$	+9
$\epsilon_{284} = 28,800$	4,6-Dibromo	$\epsilon_{296} = 19,400$	+12
	4,6,7-Tribromo	$\epsilon_{313} = 17,400$	+29
$\Delta^{1,4,6}$-3-one	2,4-Dibromo		
$\epsilon_{223} = 13,500$		$\epsilon_{228} = 14,000$	+5
$\epsilon_{256} = 11,900$		$\epsilon_{279} = 10,000$	+23
$\epsilon_{298} = 11,100$		$\epsilon_{324} = 12,100$	+26

bond of a steroid conjugated ketone is found to be 26 mμ. Nussbaum and coauthors (292a) found the average shift to be 23 mμ for a bromine on the α-position of the double bond and 30 mμ for the β-position.

The bromo compounds of α,β-unsaturated ketones that did not exhibit this shift were not included in table 16. If the structures of the bromo derivatives of dienones and trienones are assumed to be correct, then the average bathochromic shift for a bromine atom on the double bond of these compounds is 12 mμ.

VI. ULTRAVIOLET ABSORPTION OF DERIVATIVES OF STEROID KETONES

Oximes, semicarbazones, and 2,4-dinitrophenylhydrazones are the derivatives often used to characterize steroid ketones (48, 101, 120). Of the three, the dinitrophenylhydrazones are preferred because of their ease of preparation, their crystallizability, and their high melting points. The ultraviolet absorption of these derivatives offers specific information, in that additional evidence is given with respect to the extent of conjugation of ethylene bonds with the carbonyl group. The average absorption values for the steroid derivatives are given in table 17.

TABLE 17

Ultraviolet absorption of derivatives of the carbonyl group of steroids

POSITION	OXIMES		SEMICARBAZONES		2,4-DINITROPHENYLHYDRAZONE	
	λ	$\epsilon_{max.}$	λ	$\epsilon_{max.}$	λ	$\epsilon_{max.}$
	mμ		mμ		mμ	
3-one			228	12,900	245, 367	10,700, 24,400
6-one			228	12,900		
17-one, 20-one					~245, 370	—, 25,900
20,21-α-diketone					349, 395, 450	31,200, 22,000, 21,000
Δ^1-3-one			266	25,800	257, 383	16,900, 28,600
Δ^4-3-one	240	21,600	270	30,300	259, 392	20,200, 31,200
Δ^4-6-one			255	8,500	257, 377	12,300, 24,900
Δ^5-7-one	238	14,200				
Δ^{16}-20-one			267	23,800	384	26,800
$\Delta^{1,4}$-3-one			298	23,400	254, 301, 401	17,000, 7,600, 34,500
$\Delta^{2,4}$-6-one					257, 320, 408	11,700, 7,830, 25,100
$\Delta^{4,6}$-3-one			303	44,200	269, 309, 401	18,400, 14,500, 37,500
$\Delta^{1,4,6}$-3-one			~309	~32,000		
$\Delta^{4,6,8(14)}$-3-one					427	41,000

A. Oximes

Oximes of isolated ketones have no characteristic absorption from 200 to 400 mμ; however, the carbonyl band is absent, as is expected of all derivatives of ketones. The oximes of α,β-unsaturated ketones absorb at nearly the same point as the parent ketone and the extinction coefficient is 3000–6000 higher. It is thus evident that the —C(=NOH)— group is of the same order of activity as —C=O when conjugated with a double bond. Though there are an insufficient number of examples (120), it appears that the location of the oxime band is relatively independent of the degree of alkyl substitution on the ethylenic bond.

B. Semicarbazones

As in the aliphatic conjugated ketones, the ultraviolet absorption spectra of the semicarbazones of steroids clearly indicate the extent of conjugation (120). The semicarbazone of an isolated ketone absorbs at 228 mμ and for each double

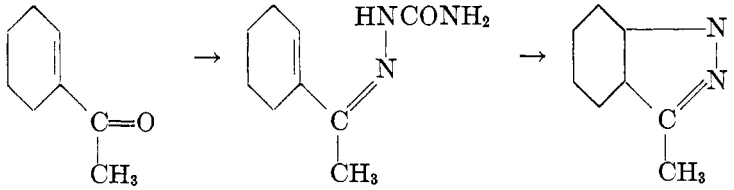
bond in conjugation there is a bathochromic shift of 30–40 mμ, accompanied by an increase in the intensity of absorption which is in line with the bathochromic effect of an ethylenic bond. However, if comparison is made of the absorption of the parent conjugated ketone with that of its derivative, it is found that the semicarbazone moiety contributes a variable bathochromic shift of 26–36 mμ for an α,β-unsaturated ketone and 19 mμ for a linearly conjugated dienone. Since in each class of chromophoric systems the semicarbazones absorb in a narrow range, it appears that the alkyl groups and exocyclic bonds are without influence. The range is 267–270 mμ for the α,β-unsaturated ketones with the exception of Δ⁴-en-6-one, which will be discussed in a following paragraph.

Since it was shown (48, 120) that the conjugating power of $-\overset{|}{C}=N-$ and $-\overset{|}{C}=\overset{|}{C}-$ groups is of the same order, the absorption of semicarbazones seemed unusually high. The possibility of enolization,

$$-\overset{|}{C}=\overset{|}{C}-\overset{|}{C}=N-N=\overset{OH}{\overset{|}{C}}-NH_2$$

which extends the conjugated system by an additional double bond and would account for the large bathochromic and hyperchromic changes, was ruled out by the fact that the corresponding *N*-methylsemicarbazone, in which enolization cannot occur, absorbed at a slightly higher wave length, the added displacement being due to the methyl group. Thus it is evident that the bathochromic effect is due to the —NH— group and the partially transmitted conjugation with the carbonyl group of the semicarbazone moiety.

The absorption of the semicarbazone of Δ⁴-en-6-one is an exception among the α,β-unsaturated ketones, in that the location of the band has been displaced only 11 mμ with respect to that of the parent ketone and the extinction coefficient is approximately one-third that normally observed for semicarbazones. This anomalous absorption is probably due to steric hindrance. It was observed (48a) in certain compounds where steric interference occurs, that the $\lambda_{max.}$ is unaffected and the $\epsilon_{max.}$ is appreciably lowered. The same effect is observed for the derivatives of the carbonyl function, where both the $\lambda_{max.}$ and $\epsilon_{max.}$ are now lowered. This condition applies to the Δ⁴-en-6-ones and Δ⁵-en-4-ones, both of which exhibit a rather low extinction coefficient as compared to the other conjugated ketones. Though no derivative of the carbonyl moiety of Δ⁵-en-4-ones has been reported, the ultraviolet absorption characteristics should be similar to those of the Δ⁴-en-6-ones.



ϵ_{233} = 12,500 ϵ_{260} = 24,000 ϵ_{240} = 9600

It is interesting to note that semicarbazones of pulegone, mesityl oxide, and 1-acetyl-1-cyclohexene prepared (86a) under stringent conditions can close the ring to form substituted pyrazolines (see page 86).

It is of interest to note that the semicarbazone of the cross-conjugated $\Delta^{1,4}$-dien-3-one absorbs at 298 mμ, a value similar to that of a linearly conjugated dienone system; however, the extinction coefficient is near that of an α,β-unsaturated ketone derivative. Since the Δ^4-en-3-one and $\Delta^{1,4}$-dien-3-one compounds absorb at nearly the same band, 241–244 mμ, the semicarbazones offer a means of differentiation between these two chromophoric systems. The additional double bond in cross-conjugation in the above example causes a bathochromic shift of 30 mμ. However, in the semicarbazone of $\Delta^{1,4,6}$-trien-3-one the Δ^1 double bond contributes only a 6-mμ shift toward the longer wave length.

C. 2,4-Dinitrophenylhydrazones

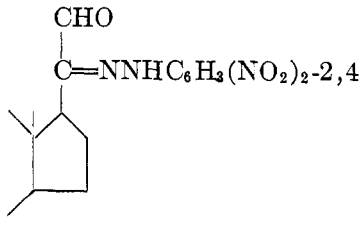
The principal ultraviolet absorption band of dinitrophenylhydrazones ranges from 370 mμ for the saturated ketone derivatives to 410 mμ for the conjugated and cross-conjugated dienone derivatives. Chloroform is the preferred solvent for the steroid dinitrophenylhydrazones.

Braude and Jones (48) observed that for the 2,4-dinitrophenylhydrazone of non-conjugated carbonyl compounds, where the primary amino group of the hydrazine moiety is replaced by the —C=N— group, no appreciable change in absorption occurs from that of 2,4-dinitrophenylhydrazine if the bathochromic effect of alkyl groups is considered. Thus, the conjugating power of the —C=N— group is considerably smaller when attached to a conjugated system through an —NH— group than when directly in conjugation. The —NH— group thus has a smaller transmitting capacity for conjugation than an ethylenic bond, a fact also established for semicarbazones.

The chromophoric system is extended by an additional double bond in the 2,4-dinitrophenylhydrazones of α,β-unsaturated ketones and, because of the smaller chromolatory capacity of the —NH— group, the bathochromic shift is smaller than usually observed for an ethylenic bond. The shift is approximately 20 mμ and even less when extended to a dienone derivative. However, in extending the conjugation of $\Delta^{4,6}$-dien-3-one to $\Delta^{4,6,8(14)}$-trien-3-one, the double-bond increment is 27 mμ.

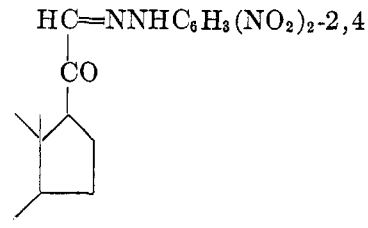
In a series of compounds containing a C_{20}-(2,4-dinitrophenylhydrazone) and a C_{21}-hydroxyl group it was observed (136) that the latter group exerts a hypsochromic shift of 3–7 mμ and the C_{21}-acetate a shift of 11 mμ if comparison is made with the absorption, 370 mμ, of a C_{20}-(2,4-dinitrophenylhydrazone) containing a methyl group in the C_{21}-position. The hypsochromic effect of an acetate group on the α-carbon of the chromophoric system is also observed in a C_2-acetate-C_3-(2,4-dinitrophenylhydrazone), where a shift of 7 mμ occurs.

A similar condition exists in the 2,4-dinitrophenylhydrazones of compounds containing a ketone group at C_{20} with an aldehyde group at C_{21}, i.e., in α-dicarbonyls (136).



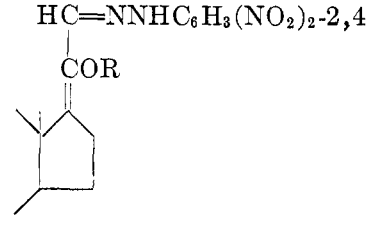
XVII

$\epsilon_{370} = 20,500$
$\epsilon_{401} = 22,200$



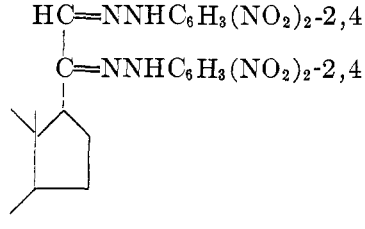
XVIII

$\epsilon_{351} = 24,400$



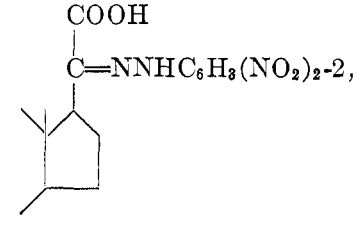
XIX

R = H	R = CH_3CO
$\epsilon_{268} = 13,000$	$\epsilon_{262} = 14,100$
$\epsilon_{305} = 9,960$	$\epsilon_{289} = 8,600$
$\epsilon_{379} = 26,400$	$\epsilon_{373} = 30,900$



XX

$\epsilon_{349} = 31,200$
$\epsilon_{395} = 22,000$
$\epsilon_{450} = 21,000$



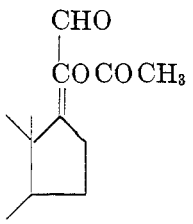
XXI

$\epsilon_{364} = 24,900$

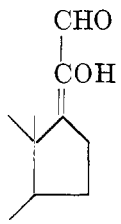
With methanol as the solvent, XVII exhibited a single peak at 365 mμ characteristic of the 2,4-dinitrophenylhydrazone of the non-conjugated ketone and XVIII exhibited one at 358 mμ. The dimethoxy derivative of the C_{21}-carbonyl function of XVII has an absorption, 366 mμ, like that of compounds having a C_{21}-hydroxyl group, and the diacetoxy derivative has an absorption, 357.5 mμ, like that of a C_{21}-monoacetate.

The absorption bands of XX are characteristic of the 2,4-dinitrophenylhydrazone of an α-diketone, where partial conjugation occurs between the two dinitrophenylhydrazone systems, resulting in a marked shift in the spectrum toward the red (48).

The absorption of XXI is similar to that of pyruvic acid. The enol, XIX, is interesting, in that the hydroxyl group has little or no effect on the principal band. The absorption of the 2,4-dinitrophenylhydrazone of Δ^{17}-en-21-al would be at about 380 mμ. Normally the hydroxyl group on the ethylene bond of an α,β-unsaturated ketone exerts a bathochromic shift of 40 mμ. The acetate of the enol XIX exerts a hypsochromic effect of 5.5 mμ with respect to the enol. In the parent aldehydes the difference is 36 mμ. Since the —NH— group in 2,4-dinitrophenylhydrazones has a smaller transmitting capacity for conjugation, it is to be



$\epsilon_{246}^{\text{ether}} = 14,300$



$\epsilon_{282}^{\text{methanol}} = 12,500$

expected that changes in the carbonyl part of the molecule would not have a strong effect on the absorption of the chromophoric system.

When R = H in XIX a band appears at 305 mμ and when R = CH_3CO a band appears at 289 mμ; these bands are absent in the spectra of the 2,4-dinitrophenylhydrazones of α,β-unsaturated ketones.

Unlike oximes and semicarbazones, alkyl substituents on the ethylenic bond of a 2,4-dinitrophenylhydrazone of an α,β-unsaturated ketone exert a bathochromic effect (48). This is observed in the difference in absorption of the 2,4-dinitrophenylhydrazones of Δ^1-en-3-one and Δ^4-en-3-one as given in table 17.

The presence of a C_{11}-keto group causes a hypsochromic shift of 5 mμ in the absorption of a 2,4-dinitrophenylhydrazone of Δ^4-en-3-one, and a C_6-(α-methoxy) group, while it has no effect on the parent ketone, causes a bathochromic shift of 13 mμ in the principal band of the 2,4-dinitrophenylhydrazone, with a minor band appearing at 309 mμ.

The 2,4-dinitrophenylhydrazone of Δ^4-en-6-one absorbs at a lower $\lambda_{max.}$ and $\epsilon_{max.}$ than is expected for this system, the reason being similar to that already discussed for the semicarbazones.

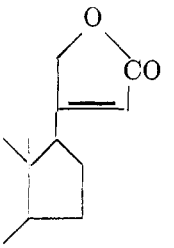
In addition to the principal band, the 2,4-dinitrophenylhydrazones of non-conjugated and of α,β-unsaturated ketones have minor bands at 245 and 257 mμ, respectively. The dienones have a third band at 300–320 mμ, which can be used to differentiate them from the aforementioned systems. It is interesting to note that the principal bands of the 2,4-dinitrophenylhydrazones of $\Delta^{1,4}$-dien-3-one and $\Delta^{4,6}$-dien-3-one are at the same point, 401 mμ, though the parent compounds absorb 40 mμ apart. Thus, as in the semicarbazones, the $\Delta^{1,4}$-dien-3-one system acts as if it were linearly conjugated.

Though there is a large difference, 31 mμ, in absorption between $\Delta^{2,4}$-dien-6-one, $\epsilon_{315} = 7600$, and $\Delta^{4,6}$-diene-3-keto, $\epsilon_{284} = 29,000$, it is found that the difference in the absorption of the respective 2,4-dinitrophenylhydrazones is only 7

mμ. However, the large difference in extinction coefficient is still maintained. In general, the oxime, semicarbazone, and 2,4-dinitrophenylhydrazone moieties contribute a more or less constant increment to the extinction coefficient of the overall system. Thus the differences in extinction coefficient that exist between two parent ketone members in any particular class should carry over to their derivatives.

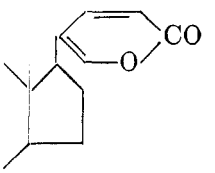
VII. ULTRAVIOLET ABSORPTION OF UNSATURATED STEROID LACTONES

The strong ultraviolet absorption of many steroid cardiac glycosides is associated with a conjugated unsaturated cyclic lactone at the C_{17}-position. Two lactones, cyclobutenolide and cyclopentenolide, have been found, as indicated by structures XXII and XXIII, respectively.



XXII

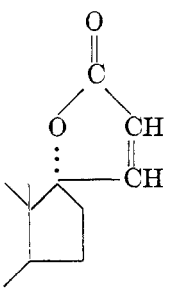
$\epsilon_{217} = 15{,}400$



XXIII

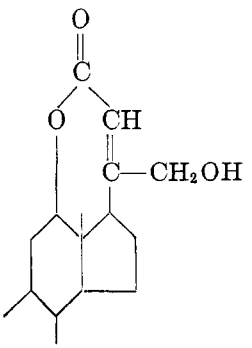
$\epsilon_{300} = 5450$

The cyclobutenolides exhibit a weak carbonyl absorption which appears as an inflection between 260 and 290 mμ. If an aldehyde group is present at C_{10} a definite band appears at 303–308 mμ with an extinction coefficient of approximately 40. The bathochromic effect of alkyl groups also applies to unsaturated lactones, since substitution of a methyl group on the α-position of the double bond shifts the band to 227 mμ. Lactones which involve the $C_{17,17}$- and $C_{12,17}$-positions (see XXIV and XXV, respectively) appear to be sterically hindered, since the extinction coefficient is appreciably lowered and the band is shifted slightly toward the lower wave lengths.



XXIV

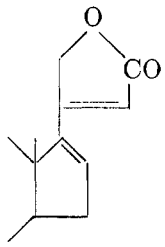
$\epsilon_{215} = 8300$



XXV

$\epsilon_{221} = 7150$

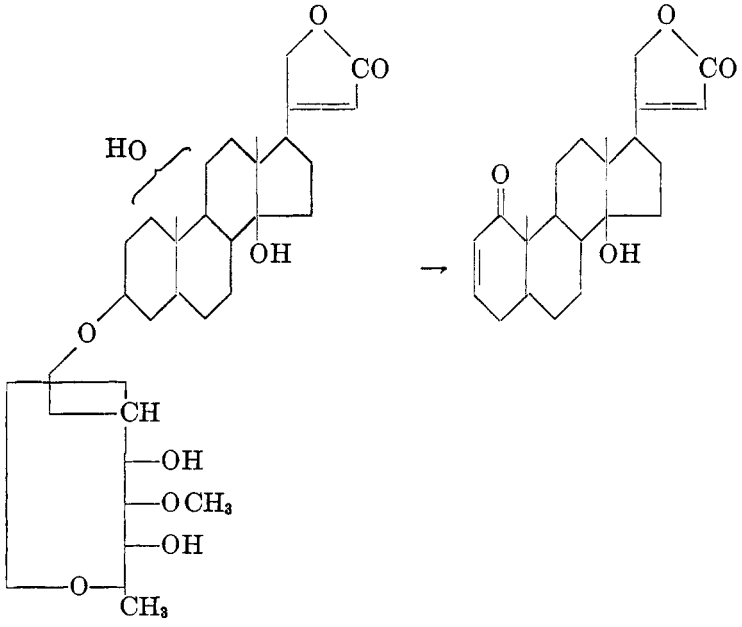
Many cyclobutenolides have a weak band at 270–275 mμ which is due to the presence of XXVI as an impurity. The conjugation of an additional double bond at C_{16} shifts the principal band to 271 mμ with a slightly higher extinction co-



XXVI

ϵ_{271} = 17,800

efficient. A second band appears at approximately 220 mμ, $\epsilon_{max.}$ = 5000, which, because of its frequent occurrence, is unlikely to be due to the 16-dihydro-17-cyclobutenolide as an impurity. A third double bond in conjugation at C_{14} shifts the absorption further toward the red, producing a broad band at 335 mμ with a still higher extinction coefficient accompanied by a band at 221 mμ of lower intensity. Many compounds isolated from degradation studies of cardiac glycosides have not been tabulated in the index of compounds, because names were not given to them nor were their structures fully elucidated. However, they are of no significance, since the chromophore system in all examples was that of



XXVII

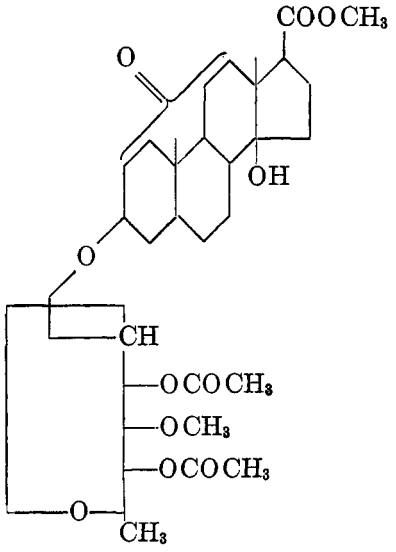
ϵ_{217} = 19,000

XXVIII (?)

ϵ_{217} = 25,100

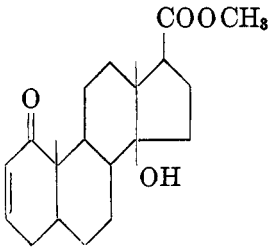
ϵ_{230} = 29

either a cyclobutenolide or a cyclopentenolide. However, one series of compounds is of interest. In the proof of structure of acovenoside A (XXVII), compound XXVIII was isolated as an oxidative degradation product (416). To account for the unusually high extinction coefficient at 217 mμ and the displaced carbonyl absorption band at 330 mμ, formula XXVIII was proposed, which contains the structure of an α,β-unsaturated ketone. Further stepwise degradation studies led to the isolation of three compounds (XXIX, XXX, and XXXI), of which XXX was isolated in rather small amounts and is of interest since a Δ^2-en-1-one has never been reported before. Since its structure is still in doubt, it was not reported in the section on α,β-unsaturated ketones. If the absorption values of XXVII and XXX are added together, the summation is nearly equal to the



XXIX

$\epsilon_{270-300(\text{inflect.})} = 8$



XXX (?)

$\epsilon_{225} = 8100$

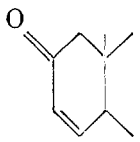
$\epsilon_{333} = 81$

$C_{32}H_{48}O_{11}$

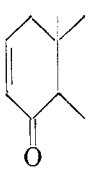
XXXI

$\epsilon_{290} = 37$ (structural analog of XXIX)

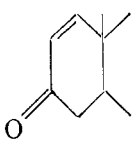
ultraviolet absorption of XXVIII. The presence of the following conjugated ketones, of which only XXXIV is known, was not excluded.



XXXII



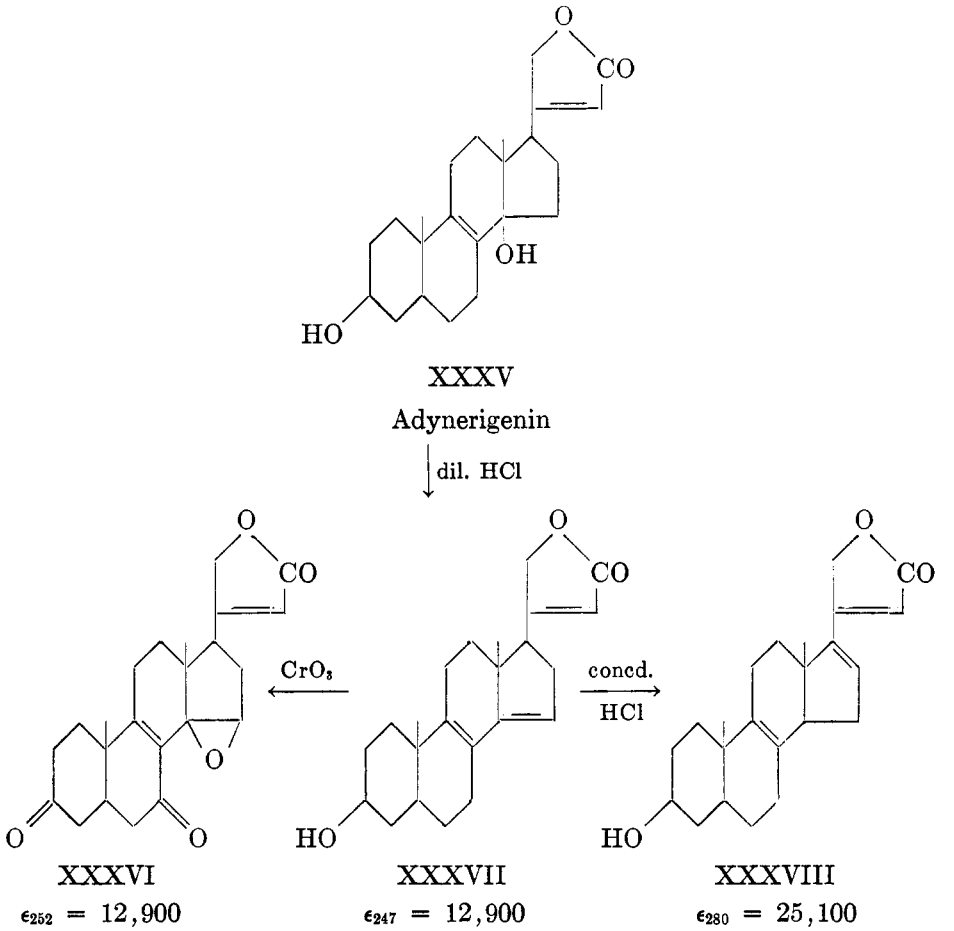
XXXIII



XXXIV

$\epsilon_{230} = 10,700$

The anhydro forms of adynerigenin are another example of two isolated chromophore systems in a molecule in which each acts independently of the other with respect to ultraviolet absorption. Structures XXXVI, XXXVII, and XXXVIII are as proposed by Fieser and Fieser (129), in that they fit the spectroscopic evidence, whereas those of Tschesche do not. Since the spectrum was not taken below 240 mμ, the cyclobutenolide band was missed. The value ϵ_{280} = 25,100 for XXVIII is higher than normally expected for this chromophore system, and the reported extinction coefficient for XXXVII is low for a $\Delta^{8,14}$-diene.



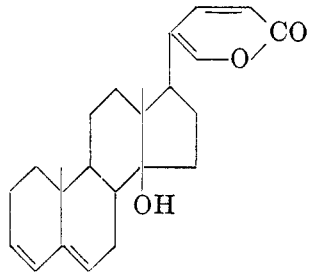
XXXV
Adynerigenin

XXXVI
ϵ_{252} = 12,900

XXXVII
ϵ_{247} = 12,900

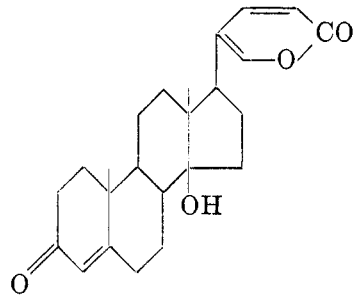
XXXVIII
ϵ_{280} = 25,100

The cyclopentenolides have a broad absorption band at approximately 300 mμ, $\epsilon_{max.}$ = 5500. There is indication of a second band below 220 mμ with an extinction coefficient above 10,000. If a second isolated chromophore system is present, as in scillaridin A and scillarenone, the absorption of the compound is a summation of the absorptions of the individual systems.



Scillaridin A

ϵ_{230} = 17,000 (broad)
$\epsilon_{244(\text{inflect.})}$ = ~ 10,000
ϵ_{300} = 5010 (broad)



Scillarenone

ϵ_{240} = 17,800 (broad)
ϵ_{300} = 5,500 (broad)

The presence of a $\Delta^{14,16}$-diene system in cross-conjugation with the C_{17}-cyclopentenolide exerts no bathochromic shift. However, the extinction coefficient at 300 mμ is approximately 16,000 and a shallow decline occurs from 340–380 mμ, ϵ = 1600–790.

Data on the ultraviolet absorption of the various unsaturated cyclic lactones are summarized in table 18.

VIII. ULTRAVIOLET ABSORPTION OF STEROIDS CONTAINING BENZENOID RINGS

The fine spectral structure normally associated with the benzene moiety is absent in steroids containing a benzenoid system. Ring A benzenoid compounds exhibit two bands of absorption in the ultraviolet, one of high intensity near 210 mμ and a second of low intensity near 260 mμ. In the more highly alkylated ring B benzenoid compounds, these bands are displaced to 224 and 269 mμ and a third weak band appears at 278 mμ. Auxochromic substituents on the benzene rings exert both a bathochromic and a hyperchromic effect. The presence of a C_3-hydroxy or -methoxy group shifts the weak band at 260 mμ to 280 mμ with a sevenfold increase in intensity, while an acetate group to a large extent negates this effect. The bathochromic shift is attributed to electronic interaction. A large number of compounds in this class have an inflection at approximately 220 mμ.

The ultraviolet absorption spectra can differentiate the three possible systems in which a double bond is conjugated with a ring A benzenoid compound, as illustrated by compounds 1, 2, and 3 in table 19. Generally in chromophoric systems where a phenyl group is in conjugation with another chromophore three broad regions of absorption can be discerned (47). A high-intensity band occurs at 200–215 mμ, which is probably an intensified and slightly displaced ethylenic absorption; a second strong band about a third as intense as that of the first at 230–260 mμ, due to the new conjugated system; and a low-intensity benzenoid absorption at 270–280 mμ. For the steroids the limits should be approximately 10–20 mμ higher because of the bathochromic effect of the C_3-hydroxyl group

TABLE 18

Ultraviolet absorption of unsaturated steroid lactones

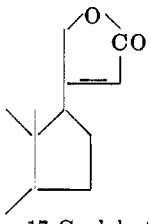
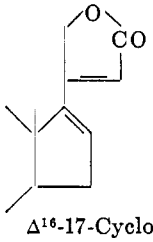
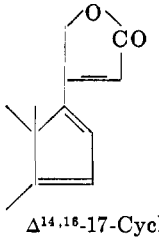
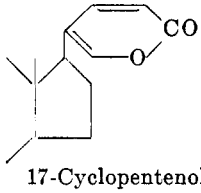
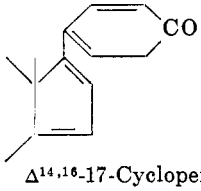
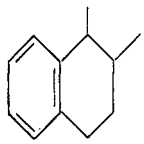
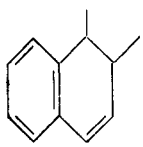
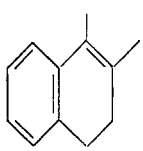
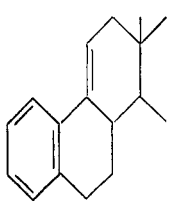
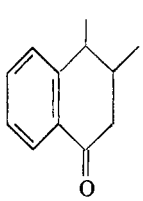
COMPOUND	AVERAGE		RANGE	
	$\lambda_{max.}$	$\epsilon_{max.}$	$\lambda_{max.}$	$\epsilon_{max.}$
	mμ		*mμ*	
 17-Cyclobutenolide	217	15,400	215–218	10,000–20,000
 Δ^{16}-17-Cyclobutenolide	271	17,800	270–273	16,200–22,450
 $\Delta^{14,16}$-17-Cyclobutenolide	335	20,100	332–337.5	17,800–22,400
 17-Cyclopentenolide	300	5,450	293–308	4,000–7,100
 $\Delta^{14,16}$-17-Cyclopentenolide	300	16,600		

TABLE 19

Ultraviolet absorption of steroids containing benzenoid rings

NO.	COMPOUND	SUBSTITUENT	AVERAGE		RANGE	
			$\lambda_{max.}$	$\epsilon_{max.}$	$\lambda_{max.}$	$\epsilon_{max.}$
		Ring A				
			mμ		mμ	
1...		3-OH, 3-OCH_3	280	2,270	278–282	1,900–2,600
		3-$OOCCH_3$	268	775	268	700–850
		1-CH_3,3-OH; 1-CH_3,4-OH; or 1-OH,4-CH_3	283	2,140	282–285	1,800–2,400
		1-CH_3,3-$OOCCH_3$; 1-CH_3,4-$OOCCH_3$; or 1-$OOCCH_3$,4-CH_3	268	340	267–268	310–390
2...		3-OH	222	30,200	220–224	28,800–30,900
			262	9,100	262–263	8,500–10,000
			271(i)*	6,900	270–272(i)	6,300–7,500
			304	2,800	302–306	2,500–2,950
		3-$OOCCH_3$	226	31,600		
			264	11,200	264	10,200–12,300
		3-$OOCC_6H_5$	230	30,900		
			262	10,700		
		1-CH_3,3-OH	228	28,000	228	25,000–30,900
			267	7,900	266–268	7,900–7,940
			275(i)	6,300		
			305	1,750	304–306	1,600–1,910
		1-CH_3,3-$OOCCH_3$	223	26,900	222–224	26,300–27,500
			265	8,600	264–266	8,510–8,710
3...		3-OH	274	15,800	273–275	14,500–17,000
			336	130	335–336	31–230
		3-OCH_3	275	17,300	273–275	15,900–18,500
4...		3-OH	264	18,000		
			300	3,000		
		3-OCH_3	264	19,450	264	18,000–20,900
			299	3,050	299	3,000–3,100
5...		3-OH	256	8,000		
			326	3,000		
		3-$OOCCH_3$	~250	~9,000		
			~300	~1,900		

* (i) signifies an inflection.

TABLE 19—*Continued*

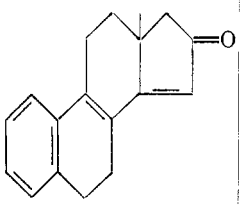
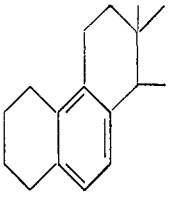
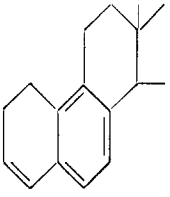
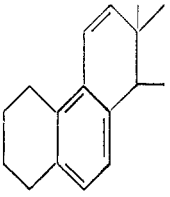
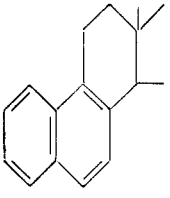
NO.	COMPOUND	SUBSTITUENT	AVERAGE		RANGE	
			$\lambda_{max.}$	$\epsilon_{max.}$	$\lambda_{max.}$	$\epsilon_{max.}$
		Ring A—*Continued*				
			mμ		*mμ*	
6...		3-OCH_3.....	257.5	10,700		
			280(i)	5,000		
			360	27,500		
		Ring B				
7...		None.....	224	10,000		
			269	420	268–270	345–550
			278	250	277–278	240–250
8...		None.....	~224	~22,500	~224	~20,000–25,000
			~231	~22,000	~230–231	~17,000–27,000
			268	6,300	268	4,600–7,900
			~308	~350	~308	~300–400
			~314	~140	~314	~80–200
			~323	~175	~323	~100–250
		3-OCH_3.....	270	18,350	270	16,200–20,500
9...		None.....	270	11,500		
		Ring AB				
10..		None.....	230.5	93,300		
			282	5,380	282	5,010–5,760
			321	740	321–321.5	560–910
					230	39,800
					267–270	4,500–7,100
		3-OH.....			278–282	4,900–7,400
					289–294	3,500–5,500
					325–332	2,400–3,800
					338–345	3,000–4,800

TABLE 19—*Continued*

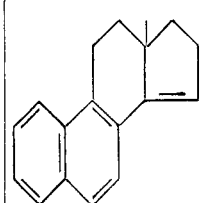
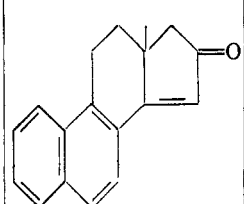
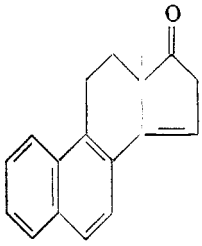
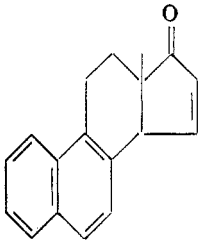
NO.	COMPOUND	SUBSTITUENT	AVERAGE		RANGE	
			$\lambda_{max.}$	$\epsilon_{max.}$	$\lambda_{max.}$	$\epsilon_{max.}$
		Ring AB—*Continued*				
			mμ		mμ	
		3-OCH_3			229–232	64,600
					265–269	5,100–5,900
					275–278	5,600–6,600
					315–323	1,900–2,000
					333–336	2,300–2,700
		6-OCH_3			225	28,800
					240–243	38,900–42,700
					300–303	6,200–6,500
		1-CH_3,3-OH			~235–236	~63,000–79,000
					~272–273	~5,600–7,100
					~284–285	~6,300–6,900
					~295–297	~4,500–5,600
					~329–330	~1,900–2,000
					~344	~2,500
		1-CH_3,3-$OOCCH_3$			~234–236	~79,000–100,000
					~278	~7,100–8,900
					~316	~1,800–2,200
					~330	~2,500
11		None			251–255	45,700–49,000
					262	41,700
					281–285	12,300–13,500
					292–295	14,500–16,600
					303–305	11,500–13,500
					253–254	45,700–46,800
					262–263	44,700–45,700
					281	13,800
		3-OCH_3			292–294	15,900–18,600
					303–305	14,800–17,800
					333	2,190
					350	1,740
		6-OCH_3	260	44,700		
			302	8,700		
			330	4,200		
			347	2,950		
12		None			219–220	20,900–21,900
					231–239	12,000–16,200
					245–247	11,500–13,500
					255–260(i)	16,600–18,600
					266–268	30,900–36,300
					275–277	36,300–42,700
					315–318	25,700–29,500
					360(i)	4,100–4,900
					226	19,500–21,900
					260–264(i)	20,000–22,400
		3-OH 3-OCH_3			268–275(i)	27,500–28,200
					281–283	28,800–31,600
					333–342	24,500–27,500

TABLE 19—*Concluded*

NO.	COMPOUND	SUBSTITUENT	AVERAGE		RANGE	
			$\lambda_{max.}$	$\epsilon_{max.}$	$\lambda_{max.}$	$\epsilon_{max.}$
		Ring AB—*Concluded*				
			mμ			
13..						
			219	29,500		
			243	20,000		
		15-$COOC_2H_5$.....	247	20,000		
			264	26,900		
			310	17,800		
		3-OCH_3,	223	30,200		
		15-$COOC_2H_5$.....	265	25,100		
			323	18,200		
			213	24,500		
		6-OCH_3,	224	25,100		
		15-$COOC_2H_5$.....	269	24,000		
			311	12,900		
			354	5,900		
14..						
			230	77,600		
		None.....	270	6,800		
			321	660		
		15-COOH.....	228	89,100		
			273	7,800		
			235	77,600		
		3-OCH_3,15-COOH..	318	2,900		
			334	2,700		
			235	57,500		
		3-OCH_3,15-$COOCH_3$	275	5,400		
			318	2,100		
			333	2,100		
			215	39,800		
		6-OCH_3,15-COOH..	243	43,700		
			296	5,900		
			327	3,200		
			242	41,700		
		6-OCH_3,15-$COOCH_3$	296	5,900		
			325	2,600		

and the more highly alkylated benzenoid ring. It is of interest to note that in these compounds no hypsochromic shift occurs upon acetylation of the hydroxyl group. Compounds of types 3, 4, and 9 (see table 19) have a high-intensity band near 210 mμ. A methoxy group on the double bond of compound No. 8 exerts a strong hyperchromic shift on the band at 270 mμ.

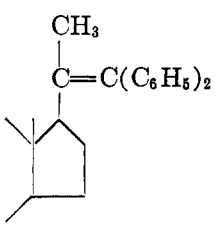
Owing to the complexity of the ultraviolet absorption of steroids containing a naphthalenoid system in rings A and B, in which an additional chromophore is in conjugation, it is extremely difficult to interpret the spectra. An additional factor which contributes to the confusion is the presence of auxochromic groups

on the naphthalene ring, which effect considerable change in the spectra of the parent compound through electronic interaction. However, by relating the spectra to simpler ring systems containing the identical conjugated chromophores, evidence for the structure of the more complex compounds can be obtained. The method was used to advantage by Wilds (436) in establishing the structure of a number of synthetic compounds containing a cyclopentanophenanthrene ring system in which α,β-unsaturated ketones are conjugated with a benzenoid or naphthalenoid ring. Inasmuch as many of the compounds in this class cannot be truly classified as steroids, only a few representative examples are listed in table 19.

IX. ULTRAVIOLET ABSORPTION OF CONJUGATED SYSTEMS CONTAINING A PHENYL CHROMOPHORE

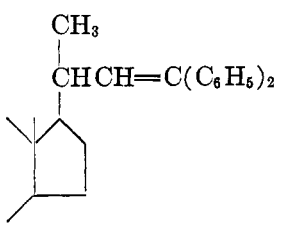
The isolated phenyl group has, besides minor bands, two principal bands, one of high intensity near 200 mμ, probably due to displaced ethylenic absorption, and a low-intensity band near 260 mμ, which is similar in position but much less intense than the maxima of aliphatic conjugated trienes. In the degradation of the C_{17} side chain of steroids, a number of compounds were made in which a phenyl group is conjugated with a carbonyl group or with double bonds; these are summarized in table 20. These compounds absorb between 20 and 30 mμ higher than the comparable conjugated diene or unsaturated ketone with approximately the same intensity. The phenyl group is therefore approximately equivalent to 1.5 ethylenic bonds (47, 436). The conjugated phenyl ketones and phenylethylenes have an additional band in the neighborhood of 200–210 mμ.

The low extinction coefficient of two compounds in the diphenylethylene group can be attributed to steric inhibition of resonance. Though the double bond of XXXIX has an additional alkyl substituent, it absorbs 5 mμ lower and with a much lower $\epsilon_{max.}$ than XL. In the other example, where both a C_{12}-hydroxy or -acetoxy substituent and the C_{20} side chain of XXXIX are sterically in the α-position, the extinction coefficient is approximately half that of the compound in which the C_{12}-hydroxyl group is in the β-position; however, in each example the $\lambda_{max.}$ is at 250 mμ.



XXXIX

ϵ_{245} = 11,800

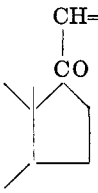
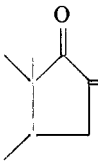
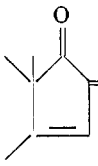
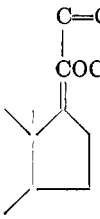
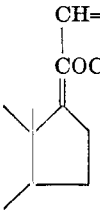


XL

ϵ_{250} = 17,200

TABLE 20

Ultraviolet absorption of conjugated systems containing the phenyl chromophore

COMPOUND	AVERAGE		RANGE	
	$\lambda_{max.}$	$\epsilon_{max.}$	$\lambda_{max.}$	$\epsilon_{max.}$
	mμ		*mμ*	
$(C_6H_5)_2CH-$	259	680	255–262	630–780
C_6H_5CO-	243	12,700	243	12,500–12,800
	280	1,000	280	980–1,030
	294	23,200	294	22,500–24,000
	221	8,300		
	290	24,500		
	234	12,700	234	12,600–12,900
	257	8,500	256–258	8,300–8,900
	334	23,100	334–335	22,600–23,400
$(C_6H_5)_2C{=}CHCH{=}CHCO-$	242	13,100	242	12,300–13,900
	338	30,400	338	29,000–31,800
$(C_6H_5)_2C{=}C-$	250	18,900	245–252	10,200–20,000
$(C_6H_5)_2C{=}CHC{=}C-$	310	17,800		
	294	~33,000		
	304	~33,500		
	320	~22,750		
	245	17,400	245	16,200–18,500
	335	48,900	335	47,600–51,000

X. TABLES OF DATA ON THE ULTRAVIOLET ABSORPTION OF STEROID COMPOUNDS

Tables 21 to 32 include nearly all steroids prepared or isolated through 1951 which exhibit an ultraviolet absorption spectrum. The data for compounds prior to 1940 were obtained from Dannenberg's dissertation (83).

The compounds are to a large extent arranged in order of increasing carbon content. The data given can usually be found in the first reference listed if more than one is given.

TABLE 21

Ultraviolet absorption of chromophoric esters of hydroxy steroids

COMPOUND	$\lambda_{max.}$	$\epsilon_{max.}$	SOLVENT*	REFERENCES
	$m\mu$			
3β-Acetoxy-17α-benzoxyandrostane	230, 270	12,300, 170	A	(77)
5-Androstene-3β,17α-diol				
17-benzoate	229, 272, 280	14,300, 1,000, 900	A	(77)
3-acetate 17-benzoate	230, 273, 280	14,000, 980, 850	A	(77)
3,17-dibenzoate	230, 274, 280	28,600, 1,840, 1,485	A	(77)
3β,17β-Dibenzoxy-7β-hydroxy-5-androstene	230, 272, 280	28,800, 1,700, 1,400	A	(77)
3β,7α,17β-Tribenzoxy-5-androstene	230, 274, 280	43,600, 2,690, 2,160	A	(77)
Cholesterol				
3-benzoate	230, 273, 280	15,300, 970, 760	AC	(34, 140)
3-benzoate 7α-bromo	229	24,400	E	(379)
3-thioacetate	233	4,630	AC	(34)
3-thiobenzoate	239, 270	11,500, 8,350	AC	(34)
3-(2,4-dinitrophenyl thioether)	228, 270, 340	10,660, 5,940, 12,630	AC	(77)
7β-(4′-acetaminoanilino) 3-benzoate	229, 275–280	18,110, 21,050	A	(379)
7β-anilino	255, 304–306	17,600, 3,220	A	(379)
3-acetate 7β-anilino	255, 302–305	17,350, 2,840	A	(379)
7β-anilino 3-benzoate	231, 255, 304	18,000, 18,600, 3,200	A	(379)
7β-anilino 3-(3,5-dinitrobenzoate)	249, 255, 304	26,400, 27,000, 4,130	A	(379)
3-benzoate 7β-piperidino	229	14,300	A	(379)
7β-(3′-pyridinoamino)	260, 323	21,800, 3,720	A	(379)
3-benzoate 7β-(3′-pyridinoamino)	230, 259, 322	18,200, 22,900, 3,850	A	(379)
3-benzoate 7β-(4′-carbethoxypiperazino)	230	17,100	A	(379)
7α-Hydroxycholesterol				
7-benzoate	230, 272	12,750, 740	A	(462, 461)
3,7-dibenzoate	230, 272	24,300, 1,590	A	(462)
7β-Hydroxycholesterol				
7-benzoate	231, 272	12,500, 705	A	(463)
3,7-dibenzoate	229, 270, 280	28,600, 1,630, 1,410	A	(77, 463)
5-Cholestene-3β-methanol				
benzoate	228, 272, 280	13,400, 890, 730	A	(415)
3,5-dinitrobenzoate	No selective maximum†		AC	(415)
5,8-Peroxido-6-cholesten-3β-ol benzoate	230, 274, 280	13,500, 950, 760	A	(77)
7-Cholesten-3β-ol benzoate	228, 272, 280	11,560, 1,140, 1,040	A	(77)
Ethyl 12-trimethylammonium-iodide-cholanate	220‡	12,600	A	(77)

* A = ethanol; AC = sample dissolved in a minimum of chloroform and diluted with ethanol; E = ethyl ether.
† The compound has a strong end absorption, which at 228 mμ is approximately 22,800.
‡ The band at 220 mμ is due to the iodide moiety.

TABLE 22

*Ultraviolet absorption of steroids containing isolated double bonds**

COMPOUND	$\lambda_{max.}$	$\epsilon_{max.}$	ϵ_{210}	ϵ_{215}	ϵ_{220}	ϵ_{228}	REFERENCE
	$m\mu$						
Disubstituted olefinic bonds:							
Δ^2							
2-Cholestene	203	600	200	—	—		(41)
Δ^6							
6-Cholestene-3β,5α-diol	204	1300	600	100	—		(41)
3-acetate	204	1700	900	350	200		(41)
Δ^{11}							
11-Cholestene-3α,24-diol	203	2500	800	200	—		(41)
3α-Hydroxy-11-cholenic acid	205	2400	1000	350	150		(41)
Trisubstituted olefinic bonds:							
Δ^4							
4-Cholestene	203	4000	3000	1500	850		(41)
Δ^5							
5-Cholene-3β,24-diol	203	3000	1800	850	550		(41)
5-Cholestene	204	3700	2700	1400	700		(41)
Cholesterol	203	3400	1600	700	400		(41)
3-acetate	203	2800	1500	800	550		(41)
3-chloride	205	4700	3500	1400	400		(41)
3-bromide	210	—	5600	5100	3500		(41)
β-Sitosterol	203	2800	1600	750	350		(41)
24(28)-Dihydrofucosterol	204	2800	1800	550	400		(41)
Dehydroepiandrosterone	204	3300	1700	650	300		(41)
Pregnenolone	204	3300	1800	600	300		(41)
7α-Hydroxycholesterol	205	3300	1600	500	300		(41)
7α-methoxy	206	4100	3000	1200	500		(41)
7β-Hydroxycholesterol	205	3700	2400	600	200		(41)

TABLE 22—*Concluded*

COMPOUND	$\lambda_{max.}$	$\epsilon_{max.}$	ϵ_{210}	ϵ_{215}	ϵ_{220}	ϵ_{223}	REFERENCE
	mμ						
Δ^7							
7-Ergostene	207	4200	4000	2900	1500		(41)
7-Ergosten-3β-ol	207	4500	4300	3000	1500		(41)
3-acetate	208	4900	4700	3500	1800		(41)
Δ^9							
Methyl 9-cholenate	206	3400	2900	1400	500		(41)
9-Cholen-24-ol	206	3700	2400	1500	500		(41)
Δ^{14}							
Dihydroxycholanic acid	205	3600	2600	1000	300		(41)
methyl ester	205	3500	2500	900	200		(41)
14-Ergosten-3β-ol	204	4100	2400	800	100		(41)
3-acetate	204	4100	2800	1000	300		(41)
Tetrasubstituted olefinic bonds:							
$\Delta^{8(9)}$							
8-Cholestene	207	4600	4400	3900	3400	2800	(41)
8-Cholesten-3β-ol	207	4700	4500	4000	3500	2900	(41)
8-Cholesten-3-one	207	4700	4400	4000	3500	2800	(41)
$\Delta^{8(14)}$							
3β-Acetoxy-8-pregnen-20-one	205	10500	—	6700	—	—	(252)
8-Ergostene	208	10400	10100	8400	5700	3500	(41)
8-Ergosten-3β-ol	208	9800	9500	8100	6000	3400	(41)
3-acetate	209	10600	10500	9200	7000	4400	(41)
8-Ergosten-3-one	208	9700	9500	7500	5300	3000	(41)
8-Cholesten-3β-ol	208	10000	9900	8300	6000	3600	(41)
3-acetate	208	10000	9800	8600	6700	4500	(41)
3β-Acetoxy-22-iso-8-allospirostene	203	7700	—	4050	—	—	(252)
Apocholic acid	208	7000	6500	4700	3100		(41)
methyl ester	208	9000	8600	6300	3900		(41)
$\Delta^{9(10)}$							
Westphalen's diol	205	9300	7700	4700	1900		(41)
diacetate	206	10000	8400	5100	2000		(41)
Westphalen's diketone	205	7800	6300	5000	4000		(41)
Isolated dienes:							
Stigmasterol ($\Delta^{5,22}$)	204	3800	1800	600	200		(41)
Fucosterol ($\Delta^{5,24(28)}$)	203	4300	2200	1000	600		(41)
Zymosterol ($\Delta^{8(9),24}$)	205	6700	5600	4800	4000		(41)
Zymostadienone ($\Delta^{8(9),24}$)	205	6800	6000	4800	3700		(41)
7,22-Ergostadiene	205	5400	4900	3500	1700		(41)
7,22-Ergostadien-3β-ol	205	5700	4800	3300	1700		(41)
3-acetate	206	6100	5400	3900	2000		(41)
5,17-Pregnadiene-3β,21-diol	205	6000	4800	1600	300		(41)

* The extinction coefficients at 210, 215, 220, and 223 mμ indicate the slope of the absorption curve and are not specific bands.

TABLE 23

Ultraviolet absorption of steroids containing isolated ketone groups

COMPOUND	$\lambda_{max.}$	$\epsilon_{max.}$	SOLVENT*	REFERENCES
Monoketones				
	mμ			
3-Keto:				
17α-Hexahydrobenzoxyandrostan-3-one	281	31	A	(438)
17β-Hydroxyalloandrostan-3-one	281	28	A	(77)
3-(2,4-dinitrophenylhydrazone) 17-hexahydrobenzoate	367	25,800	C	(77)
4-bromo-17-hexahydrobenzoate 2-iodo	258	910		(340)
17-Hydroxy-19-nor-5(10)-androsten-3-one	272-294(i)†	51	A	(40)
3-Ketoetioallocholanic acid				
2-iodo methyl ester	256	980	A	(340)
3-(2,4-dinitrophenylhydrazone)	243, 366	9,800, 17,400	C	(77)
3-Cholestanone	~286	~16		(231)
2-iodo	258	810	A	(340)
3-(2,4-dinitrophenylhydrazone)	367	25,700	C	(77)
3-(α-methyl 2,4-dinitrophenylhydrazone)	245, 387	10,700, 17,800	C	(77)
5α,6β-dichloro 3-(2,4-dinitrophenylhydrazone)	366	25,400	C	(29)
3-ethylene mercaptol	240	333	A	(140)

TABLE 23—*Continued*

COMPOUND	$\lambda_{max.}$	$\epsilon_{max.}$	SOLVENT*	REFERENCES
Monoketones—*Continued*				
	mμ			
3-keto:—Continued				
2-Hydroxycholestan-3-one				
2-methyl sulfonate	226	9,300	A	(77)
2-acetate 3-(2,4-dinitrophenylhydrazone)	247, 360	11,600, 24,500	C	(77)
5α-Hydroxycholestan-3-one				
3-(2,4-dinitrophenylhydrazone) 6β-chloro	366	27,200	C	(29)
3-Sitostanone				
3-(2,4-dinitrophenylhydrazone)	255, 281, 291, 368	18,000, 14,000, 10,000, 25,500	C	(48)
6-keto:				
3,5-Cyclocholestan-6-one	~280	~25		(373,231)
3-Acetoxycholestan-6-one	280	40		(21)
5-bromo	308	125		(21)
7β-bromo	310	160		(21)
5,7β-dibromo	340	160		(21)
5′,7β-dibromo	305	125		(21)
5α-Hydroxycholestan-6-one				
6-semicarbazone	228	13,000	A	(319)
2-Cholesten-6-one	285–300	50		(43)
5α-Hydroxy-2-cholesten-6-one				
6-semicarbazone	226	12,100	A	(319)
7-keto:				
3β,11α,20β-Trihydroxyallopregnan-7-one	No selective maximum			(412)
3β,20β-Diacetoxy-9α,11α-oxidoallopregnan-7-one	No selective maximum			(412)
7-Cholestanone	292	40	A	(461)
3β-Acetoxycholestan-7-one	287	40	A	(21)
6α-bromo	282	40	A	(21,129)
6β-bromo	313	160	A	(21,129)
5,6β-dibromo	314	160	A	(212,129)
3β-Acetoxy-8,9-oxido-22-ergosten-7-one	No selective maximum above 230 mμ			(405)
3β-Acetoxy-8,14 oxidoergostan-7-one	No selective maximum above 230 mμ			(404)
3β-Acetoxy-8,14-oxido-22-ergosten-7-one	No selective maximum above 230 mμ			(405)
11-keto:				
Methyl 3α-acetoxy-11-ketocholanate	No selective maximum above 220 mμ		A	(241)
3β-Acetoxyergostan-11-one	290	50	A	(175)
3β-Acetoxy-22-ergosten-11-one	280–290	107	A	(175)
12-keto:				
12-Ketocholanic acid	~288	~70	A	(256)
methyl ester	No selective maximum			(5)
Kammogenin	286	30	A	(256)
3β-Hydroxy-5-solaniden-12-one	~282	~80	A	(377)
15-keto:				
3β-Acetoxy-8,14-oxidoergostan-15-one	No selective maximum above 230 mμ			(404)
16-keto:				
3α,12α-Dihydroxyetiocholan-16-one	No selective maximum from 225 to 350 mμ			(258)
3β,20β-Diacetoxyallopregnan-16-one	2?7	35	A	(188)
17-keto:				
Androsterone	294	48	A	(77)
3-acetate	293	45	A	(77)
3-acetate 17-(2,4-dinitrophenylhydrazone)	366	25,680	C	(77)
Epiandrosterone				
3-acetate	294	48	A	(77)
3-acetate 17-(2,4-dinitrophenylhydrazone)	372	110,000‡	C	(186)
3-acetate 16-sulfonic acid	300	98	A	(77)
9,11-Oxidoepiandrosterone	225§	1,260	A	(318)
3β-Hydroxyetiocholan-17-one				
17-(2,4-dinitrophenylhydrazone)	370	112,000‡	C	(186)
	400		AA	(186)
Dehydroepiandrosterone	292	45	A	(77)
3-benzoate	229, 273, 280	14,300, 990, 790	AC	(34)
3-acid succinate	230, 290	871, 66	A	.77)
3-chlorocarbonate	290	60	A	(77)
17-(2,4-dinitrophenylhydrazone)	370	105,000‡	C	(186)
	395		AA	(186)
3-mercaptan	No selective maximum from 220 to 310 mμ		AC	(34)
3-thioacetate	233	4,670	AC	(34)
3-ethyl thioether	295	54	A	(77)
3-thiobenzoate	239, 270	12,100, 9,150	AC	(34)
3-(2,4-dinitrophenyl)thioether	268(i), 339	6,300, 13,500	A	(77)
3-ethyl sulfone	293	53	A	(77)
3-disulfide	246	559	A	(77)
3β-Acetoxy-5,14-androstadien-17-one	285	50	A	(77)
3β-Acetate-13-iso-5,14-androstadien-17-one	~275	~230	A	(39)

TABLE 23—*Continued*

COMPOUND	$\lambda_{max.}$	$\epsilon_{max.}$	SOLVENT*	REFERENCES
Monoketones—*Continued*				
	mμ			
20-keto:				
3β-Hydroxyallopregnan-20-one	284	50		(306)
3-acetate 20-(2,4-dinitrophenylhydrazone)	370	21,400	C	(77)
3β-Hydroxy-5-pregnen-20-one	285	50	A	(77)
3-acetate	285	40	A	(77)
20-(2,4-dinitrophenylhydrazone)	245, 372	14,700, 30,400	C	(77)
3-mercaptan	280	65	A	(77)
3-thioacetate	234	4,620	A	(77)
3-acetate 20-enol acetate	No selective maximum from 215 to 300 mμ		A	(77)
3β-Hydroxy-7-allopregnen-20-one	282	60	A	(97)
3-acetate	284	50	A	(97)
3β-Acetoxy-9-allopregnen-20-one	280	78	A	(94)
3β-Acetoxy-16-(β-benzoxyethylmercapto)-5-pregnen-20-one	230	15,100	A	(335)
3β-Acetoxy-16-(γ-methyl-5-acetoxyvalerate)-7-allopregnen-20-one	276	42	A	(97)
3β-Acetoxy-17α-hydroxy-5-pregnen-20-one	295	~50	A	(187)
3β-Acetoxy-17β-hydroxy-5-pregnen-20-one	294	~60	A	(187)
3β-Acetoxy-17-iso-14,15β-oxidoallopregnan-20-one	284	69		(306)
3β-Acetoxy-16,17-oxidoallopregnan-20-one	299	40		(306)
3β-Acetoxy-21-phenoxy-5-pregnen-20-one	272¶	1,780		(178)
21-Acetoxy-3α,12α-dihydroxypregnan-20-one	285	76	A	(77)
3β,21-Diacetoxy-16,17-oxidoallopregnan-20-one	290	45		(307)
3α-Acetoxy-21-diazopregnan-20-one	240–290(p)†, 380	10,000, 32		(356)
3β-Acetoxy-16,17-methylene-5-pregnen-20-one	~275	~60	A	(373)
3β-Acetoxy-21-diazo-16,17-pyrazole-5-pregnen-20-one	275, 330(i)†	10,400, 310	A	(77)
Diketones				
3,11-diketo:				
Methyl 3,11-diketocholanate	No selective maximum		A	(241)
12α-bromo 3-(2,4-dinitrophenylhydrazone)	367	25,000	C	(264)
4,12α-dibromo 3-(2,4-dinitrophenylhydrazone)	364	24,500	C	(264)
Methyl 12α-bromo-3,11-diketo-4-methoxycholanate 3-semicarbazone	230	13,600	M	(264)
3-(2,4-dinitrophenylhydrazone)	370	26,500	C	(264)
3,12-diketo:				
3,12-Diketocholanic acid	~288	~70	A	(256)
3,12-Solanidanedione	282	70	A	(377)
3,17-diketo:				
3,17-Androstanedione	290	61	A	(77)
2-iodo	256	710	A	(340)
3,20-diketo:				
21-Acetoxy-14-pregnene-3,20-dione	229§	1,580	A	(276)
6,17-diketo:				
2-Androstene-6,17-dione	285–300	110	A	(43)
7,11-diketo:				
Methyl 3α-acetoxy-7,11-diketocholanate	290	100	A	(175)
3β-Acetoxy-22-ergostene-7,11-dione	290	100	A	(175)
11,20-diketo:				
3α,21-Dihydroxypregnane-11,20-dione				
20-(2,4-dinitrophenylhydrazone)	367	22,700	C	(136)
	371	24,400	B	(136)
12α-bromo 20-(2,4-dinitrophenylhydrazone)	366	23,100	C	(136)
	369	24,000	B	(136)
3-acetate 12α-bromo 20-(2,4-dinitrophenylhydrazone)	363	23,100	C	(136)
	366	24,500	B	(136)
21-acetate 12α-bromo 20-(2,4-dinitrophenylhydrazone)	359	24,200	C	(136)
	363	24,600	B	(136)
3,21-diacetate 20-(2,4-dinitrophenylhydrazone)	360	24,000	C	(136)
	364	24,400	B	(136)
3,21-diacetate 12α-bromo 20-(2,4-dinitrophenylhydrazone)	359	24,600	C	(136)
	362	24,000	B	(136)
3,21-diacetate 12α,21-dibromo 20-(2,4-dinitrophenylhydrazone)	362	22,400	C	(136)
3α-Acetoxy-12α-bromo-11,20-diketo-21-pregnanoic acid 20-(2,4-dinitrophenylhydrazone)	364	24,900	C	(136)
	376	25,500	B	(136)
20-(2,4-dinitrophenylhydrazone) methyl ester	364	26,600	C	(136)
	367	27,000	B	(136)

TABLE 23—*Concluded*

COMPOUND	$\lambda_{max.}$	$\epsilon_{max.}$	SOLVENT*	REFERENCES
		Diketones—*Continued*		
	mμ			
16,22-diketo:				
Dihydrokryptogenin	283	70	A	(256)
Kryptogenin	285	65	A	(255, 256)
		Triketones		
3,11,20-triketo:				
21-Acetoxy-12α-bromopregnane-3,11,20-trione 20-(2,4-dinitrophenylhydrazone)	359	24,100	C	(136)
	362	24,700	B	(136)
2,21-Diacetoxy-17α-hydroxypregnane-3,11,20-trione	No selective maximum from 220 to 330 mμ			(267)
3-(2,4-dinitrophenylhydrazone)	365	25,600	C	(267)
4,21-Diacetoxy-17α-hydroxypregnane-3,11,20-trione 3-(2,4-dinitrophenylhydrazone)	358	22,000	C	(267)

* A = ethanol; AA = alkaline ethanol, usually 0.1 *N*; AC = sample dissolved in a minimum of chloroform and diluted with ethanol; B = acetone; C = chloroform; M = methanol.
† (i) signifies an inflection; (p) signifies a plateau.
‡ The extinction coefficient is too high.
§ A high-absorbing impurity is present.
¶ The band is due to the benzoyl group.

TABLE 24

Ultraviolet absorption of steroids containing isolated aldehyde groups

COMPOUNDS	$\lambda_{max.}$	$\epsilon_{max.}$	SOLVENT*	REFERENCE
	mμ			
10-aldehyde:				
Dianhydrodihydrostrophanthidin	303	126	A	(115)
Monoanhydrodihydrostrophanthidin	303	25	A	(115)
21-Aldehyde:				
3,20-Dihydroxy-21-dimethylacetal-5-pregnene	No selective maximum		A	(382)

* A = ethanol.

TABLE 25

Ultraviolet absorption of conjugated olefins

COMPOUND	$\lambda_{max.}$	$\epsilon_{max.}$	SOLVENT[a]	REFERENCES
		Dienes		
	mμ			
$\Delta^{2,4}$				
2,4-Cholestadiene	267, 275	6,300, 6,300		(396, 83)
α-Cholesterylene(bis-$\Delta^{2,4}$)	~266, 275, ~287	~30,000, ~39,000, ~27,000		(294)
$\Delta^{3,5}$				
3-Methylene-4-cholestene	233, 239	16,230, 17,260	CH	(288)
$\Delta^{3,5}$(b)				
Testosterone				
3-enol acetate 17-acetate	239	15,500	C	(83, 428)
3-enol acetate 17-propionate	235	18,900	A	(77)
3-(β-benzoxyethyl)thioenol ether 17-benzoate	230, 268	37,200, 16,600	A	(339)
3-benzylthioenol ether	268	24,000	A	(333)
3-benzylthioenol ether 17-benzoate	228, 268	28,800, 20,900	A	(339)
3-pyridinium chloride 17-propoxy	330	10,000	C	(286)
3,5-Androstadien-17-one	220(i), 234, 243(p)[c]	—, 18,000, —	E	(53, 83)
3-chloro	238	23,200	E	(83)
3-bromo	238	22,700	E	(83)

TABLE 25—*Continued*

COMPOUND	$\lambda_{max.}$	$\epsilon_{max.}$	SOLVENT[a]	REFERENCES
		Dienes—*Continued*		
	$m\mu$			
$\Delta^{3,5}$(b)—*Continued*				
4-Androstene-3,17-dione				
3-enol ethyl ether	241, 280–300	19,700, 64	A	(77)
3-(β-hydroxyethyl)thioenol ether	268	25,700	A	(339)
3-(β-hydroxyethyl)hemithioketal[d]	238	20,000	A	(339)
3-benzylthioenol ether	268	24,600	A	(333, 339)
3-benzylsulfoxidoenol ether	258	22,400	A	(333)
Methyl 19-acetoxymethyl-3,5,14-etiocholatrienate	232	26,300[e]	A	(234)
3,5,20-Pregnatriene	228, 235, 243	—, 25,100[e], —	A	(150)
20β-Hydroxy-4-pregnen-3-one				
3-benzylthioenol ether	268	25,700	A	(333)
17α,20β-Dihydroxy-4-pregnen-3-one				
3-benzylthioenol ether	268	25,100	A	(333)
3,5-Pregnadien-20-one	228, 234	18,600, 20,000	A	(333)
20-semicarbazone	232	30,900	A	(333)
Progesterone				
3-enol acetate	235	17,500	A	(77, 83)
3,20-dienol diacetate ($\Delta^{3,5,20}$)	~235	~19,500	A	(282)
3-benzylthioenol ether	268	22,900	A	(333)
3-benzylsulfoxidoenol ether	258	20,900	A	(333)
16α-Hydroxyprogesterone				
3-benzylthioenol ether 16-thiobenzyl	268	23,400	A	(333)
20-semicarbazone	268	23,400	A	(333)
17α-Hydroxyprogesterone				
3-benzylthioenol ether	268	24,000	A	(333)
21-Acetoxy-3,5-pregnadien-20-one	228, 234	10,200, 10,700[f]	A	(333)
Desoxycorticosterone acetate				
3-benzylthioenol ether	268	20,000	A	(333)
3-benzylsulfoxidoenol ether	258	20,900	A	(333)
16-Isopropylidene-3,5-androstadiene	235	19,100		(344)
21-Acetoxy-16,17-oxido-4-pregnene-3,20-dione				
3-enol ethyl ether	241	21,900	M	(219)
21-Acetoxy-17α-hydroxy-4-pregnene-3,11,20-trione				
3-enol ethyl ether	242	26,300	M	(219)
3,5-Cholestadiene	~229, 235, 244(i)[c]	~18,000, 19,700, ~13,600	IA	(144, 13, 403, 390)
4-Cholesten-3-one				
3-enol acetate	238	16,800	C	(83,428)
4,6-dibromo 3-enol acetate	245		A	(129)
3-ethylthioenol ether	272	26,000	E	(316)
3-benzylthioenol ether	268	20,500	A	(339, 333)
22-Iso-3,5-spirostadiene	228, 234	18,600, 20,000	A	(333)
22-Iso-4-spirosten-3-one				
3-benzylthioenol ether	268	20,400	A	(333)
3-Methyl-3,5-cholestadiene	231,239	21,500, 22,700	CH	(288)
$\Delta^{4,6}$				
4,6-Androstadiene-3β,17β-diol	232, 240, 248	21,900, 23,400, 19,500	A	(290)
3β-Hydroxy-4,6-androstadien-17-one	232, 238	21,700, 23,600	A	(77)
3β-Hydroxy-4,6-pregnadien-20-one	232, 240, 248	37,200, 39,900, 26,300[e]	A	(97)
4,6-Choladienic acid	235	17,200		(83)
3β-Acetoxy-4,6-norcholestadiene	232, 239, 248	6,180, 6,950, 4,370[f]	A	(4)
4,6-Cholestadiene	238	24,000	E	(109, 144, 82)
4,6-Cholestadien-3β-ol				
3-acetate	232, 239, 248	17,800, 20,100, 12,700	A	(4, 38, 297, 388, 400)
3-benzoate	239, 280	38,200, 1,100	A	(33, 400)
3-thiobenzoate	245, 272	29,800, 13,700	AC	(35)
4,6-Cholestadienyl-7-ether (bis-$\Delta^{4,6}$)	243, 249(i)[c]	54,000, 48,000	E	(463)
22-Iso-4,6-spirostadien-3β-ol	232, 240, 248	24,000, 25,700, 16,600	A	(343, 332)
3-acetate	232, 238, 248	21,900, 24,000, 15,100	A	(343, 332)
3-benzoate	240	42,700	A	(343)
3-(*p*-nitrobenzoate)	250	29,500	A	(343)
3β-Acetoxy-4,6,22-ergostatriene	~232, 240, ~247	~24,600, ~27,000, ~18,000	E	(147)

TABLE 25—*Continued*

COMPOUND	$\lambda_{max.}$	$\epsilon_{max.}$	SOLVENT[a]	REFERENCES
	Dienes—*Continued*			
	mμ			
$\Delta^{5,7}$				
5,7-Androstadiene-3β,17β-diol	271, 282, 293	11,200, 11,750, 6,800	A	(6, 290, 83, 58, 87)
3,17-diacetate	271, 281, 292	10,800, 11,300, 6,400	A	(6)
3-acetate 17-benzoate	229, 271, 281, 293	14,850, 12,450, 12,700, 7,000	A	(6)
17-benzoate	229, 271, 281, 293	12,300, 10,800, 11,150, 5,600	A	(6)
3,17-dibenzoate	229, 271, 281, 293	25,900, 14,000, 14,200, 7,250	A	(6)
3β-Hydroxy-5,7-androstadien-17-one	271, 282, 293	10,410, 10,900, 6,250	A	(6)
3-acetate	271, 281, 293	11,300, 11,850, 6,700	A	(6)
3-benzoate	229, 271, 281, 293	13,500, 12,600, 12,800, 7,000	A	(6)
3β-Hydroxy-5,7-pregnadien-20-one	272, 282, 294	19,100, 20,400, 12,300[e]	A	(97)
3-acetate	272, 282, 294	11,600, 12,200, 7,100	A	(8, 6, 97)
3-benzoate	229, 272, 282, 294	13,000, 12,350, 12,700, 7,225	A	(6, 97)
3β,21-Dihydroxy-5,7-pregnadien-20-one	272, 282, 294	11,400, 11,950, 7,180	A	(6)
21-acetate	272, 282, 294	12,030, 12,800, 7,650	A	(9)
3,21-diacetate	272, 282, 294	10,400, 11,100, 6,450	A	(6)
3,21-dibenzoate	229, 272, 282, 294	31,800, 13,400, 13,850, 7,460	A	(6)
3β-Hydroxy-5,7-choladienic acid	271, 281, 294	10,200, 10,500, 6,300		(148, 83)
5,7-Norcholestadien-3β-ol	~270, 281, ~290	~5,000, 6,210, ~3,100[f]	A	(4)
3-acetate	~270, 281, ~290	~4,000, 4,200, ~2,000[f]	A	(4)
3-benzoate	~230, ~270, 281, ~290	~15,900, ~6,310, 8,450, ~4,000[f]	A	(4)
5,7-Cholestadiene	~273, 280, ~295(i)[c]	—, 11,100, —		(83, 88)
3-chloro	263, 273, 283, 295	9,250, 12,070, 12,600, 7,700	AC	(37)
3-bromo	235, 274, 285, 297	3,050, 12,710, 13,550, 8,040	AC	(37)
7-Dehydrocholesterol	272, 282, 293	11,250, 11,900, 6,650	A	(33, 84, 194, 414, 415)
3-acetate	271, 282, 293	11 500, 12,160, 6,820	A	(415, 33)
3-methyl ether	272, 282, 294	9,900, 10,600, 5,950	A	(36)
3-benzoate	230, 272, 282, 294	14,200, 13,360, 13,510, 7,290	A	(33)
3-(*p*-nitrobenzoate)	271, 282	22,940, 19,600	A	(33, 194)
3-(3,5-dinitrobenzoate)	271, 282, 293	16,650, 14,940, 8,750	A	(33)
3-mercaptan	273, 283, 295	12,800, 13,550, 7,800	AC	(35)
3-thioacetate	232(i), 265(i)[c], 274, 284, 296	5,490, 9,000, 12,800, 13,800, 7,950	AC	(35)
3-thiobenzoate	239, 274, 284, 295	13,000, 21,400, 20,750, 12,400	AC	(35)
3-disulfide	273, 284, 296	24,460, 26,460, 15,510	AC	(414)
3-rhodanide	274, 285, 297	12,090, 13,410, 8,050	A	(414)
3-bromo	275, 285, 297	13,000, 13,500, 9,000	CH	(38)
22-Iso-5,7-spirostadien-3β-ol	270, 282, 292	14,500, 15,100, 9,120	A	(343)
3-acetate	270, 280, 292	15,500, 15,900, 9,780	A	(343)
3-benzoate	228, 270, 282, 292	14,800, 13,800, 13,800, 7,760	A	(343)
3-(*p*-nitrobenzoate)	270, 282	31,600, 27,600	A	(343)
3-(2,4-dinitrobenzoate)	260, 270, 280, 292	15,100, 15,100, 13,500, 8,130	A	(343)
5,7-Cholestadiene-3β-methanol	271, 282, 293	11,260, 11,970, 6,850	A	(415)
3-acetate	271, 282, 293	11,720, 12,400, 7,050	A	(415)
3-benzoate	228, 271, 282, 293	14,180, 12,320, 12,760, 7,090	A	(415)
3-(3,5-dinitrobenzoate)	260, 270, 282, 293	15,080, 14,310, 13,140, 7,810	AC	(415)
Methyl 5,7-cholestadiene-3-carboxylate	271, 282, 293	11,670, 12,250, 6,930	A	(415)
5,7,22-Ergostatriene	271, ~281, ~297			(88)
Ergosterol	271, 282, 293	11,450, 11,990, 6,880	A	(415, 194)
3-acetate	271, 282, 293	11,970, 12,450, 7,000	A	(415, 271)
3-benzoate	225, 260, 271, 280, 293			(450)
3-cinnamate	280			(450)
3-diphenylacetate	260, 270, 280			(450)
3-(4-nitrobenzoate)	261, 270, 281, 293(i)[c]	20,100, 20,000, 16,000, 9,100	H	(194)

TABLE 25—*Continued*

COMPOUND	$\lambda_{max.}$	$\epsilon_{max.}$	SOLVENT[a]	REFERENCES
		Dienes—*Continued*		
	mμ			
$\Delta^{5,7}$—*Continued*				
Ergosterol—*Continued*				
3-(3-nitro-4-methylbenzoate)	~261, ~271, ~282, ~294	~11,000, ~12,000, ~11,900, ~7,800	H	(194)
3-(3,5-dinitrobenzoate)	~260, ~271, ~282, ~293	~12,100, ~12,100, ~12,000, ~7,500	H	(194)
	~253, ~258, ~271, ~282, ~294	~15,800, ~14,500, ~13,700, 12,100, 7,500	A	(194)
3-(3,5-dinitro-4-methylbenzoate)	~261, ~271, ~281, ~293	~10,500, ~12,500, ~12,800, ~9,000	H	(194)
22-Dihydroergosterol	270, 280			(83, 449)
7-Dehydrocampesterol	272, 282	—, 10,600		(348)
Lumisterol	270, 280	—, 8,500	A	(444, 445, 167)
3-acetate	270, 280	12,000, 11,500[g]		(83, 444, 445)
Epilumisterol	274, ~280, ~295	9,900, ~9,100, ~4,500[g]	A	(166, 83)
Pyrocalciferol	274, 294			(12)
Isopyrocalciferol	262, 280			(54)
7-Dehydrositosterol	270, 280	—, 11,700	E	(83, 467)
7-Dehydrostigmasterol	270, 280		E	(83, 248)
Dihydrotachysterol	242, 261		E	(129)
$\Delta^{5,7'}$				
7-Methylenecholesterol	236	20,000		(83, 17)
$\Delta^{6,8(9)}$				
Isodehydrocholesterol	275	5,300	E	(451, 83)
6,8-Coprostadien-3β-ol	275	4,700		(83, 23)
$\Delta^{6,8(14)}$				
6,8-Cholestadiene[h]	245		A	(110, 22)
6,8-Cholestadiene-3β,9-diol	248			(452)
3-acetate	245	28,700[e]	E	(83, 451)
3,5-Cyclo-6,8,22-ergostatriene[i]	261	26,800	A	(134a)
6,8,22-Ergostatrien-3β-ol	248		E	(446)
(ergosterol-B_2)	253	17,000	A	(25)
3-acetate	253	17,000	A	(25)
3-benzoate	234, 252	23,000, 21,500	A	(25)
3,5-Cyclo-22α-6,8-spirostadiene	256		A	(134a)
$\Delta^{7,9(11)}$				
7,9-Androstadiene-3β,17β-diol	236, 243, 250	12,100, 13,800, 9,000	A	(10)
3,17-diacetate	235, 242, 250	13,100, 14,900, 9,600	A	(10)
3,17-dibenzoate	232, 250(i)[c], 273, 280	36,200, 10,300, 4,150, 3,300	A	(10)
7,9-Allopregnadiene-3β,20β-diol	235, 242	12,300, 13,500	A	(336)
3,20-diacetate	236, 242	12,900, 13,800	A	(336)
3β-Hydroxy-7,9-allopregnadien-20-one	236, 242	12,000, 13,500	A	(97)
3-acetate	236, 242	10,000, 10,700[f]	A	(97)
3-acetate 16α,17α-oxido	234, 242	13,500, 14,800	A	(336)
Methyl 3α-acetoxy-7,9-choladienate	244	17,400	A	(175)
Methyl 7,9-lithocholadienate	245	15,900	A	(131)
3-acetate	245	15,900	A	(131)
7,9-Cholestadiene[h]	243		A	(110, 22)
7,9-Cholestadien-3β-ol	236, 243, 252	14,100, 16,100, 10,600	A	(10, 131)
3-acetate	236, 243, 251	15,400, 17,000, 11,400	A	(10, 125, 451)
3-benzoate	234, 250, 273, 281	26,600, 12,500, 1,100, 900	A	(10)
7,9-Coprostadien-3β-ol(coprostadienol D)	240			(23)
3β,6α-Diacetoxy-7,9-cholestadiene	242	19,500	A	(30)
7,9-Cholestadiene-3β,6β-diol	248	15,000	E	(453)
3,6-diacetate	245	18,300	A	(30)
22-Iso-7,9-spirostadien-3α-ol	236, 244	13,800, 14,800	A	(468)
22-Iso-7,9-spirostadien-3β-ol	236, 242	13,200, 14,500	A	(342)
3-acetate	236, 242	13,500, 14,800	A	(342)
7,9,22-Ergostatriene (ergostatriene-D)	235, 243, 252			(169, 22)
7,9,22-Ergostratrien-3β-ol (ergosterol-D)	236, 243, 251	14,200, 15,700, 10,600	A	(10, 22, 74)
3-acetate	236, 242	11,700, 13,200	A	(26, 175, 32)
3β-Acetoxy-7,9-ergostadiene	235, 242	13,400, 13,400	A	(26)
Ergosterol-F[h]	235, 242			(441, 22)
Ergostatrienone-D	235, 243, 252			(169, 22)
7,9-Ergostadiene-3,5-diol	240	13,800	E	(83, 441)

TABLE 25—*Continued*

COMPOUND	$\lambda_{max.}$	$\epsilon_{max.}$	SOLVENT[a]	REFERENCES
		Dienes—*Continued*		
	mμ			
$\Delta^{7,14}$				
3α,12β-Dihydroxy-7,14-cholad ienic acid	241–248			(74, 23)
3,12-diacetate methyl ester	242	12,000		(309)
7,14-Cholestadiene[h]	242, 250		A	(110, 22)
Cholesterol-B_3	248			(83, 381)
3-acetate	248	15,100	E	(83, 451)
Ergosterol-B_3	242	10,100	C	(83, 74, 22)
acetate	242	9,900	A	(24a)
$\Delta^{8(9),14}$				
8,14-Androstadiene-3β,17β-diol				
3,17-diacetate	247	16,100	A	(10)
3,17-dibenzoate	232, 280	34,400, 1,820	A	(10)
3α,12β-Dihydroxy-8,14-cholad ienic acid[h]	249		A	(74, 23)
3,12-diacetate methyl ester	244[j]	17,800		(309, 23)
8,14-Cholestadiene	245[j]		A	(110, 22)
8,14-Cholestadien-3β-ol (cholestadienol-D)	250	20,000	A	(1, 155)
3-acetate	245[j]	11,700[f]	E	(451)
8,14-Coprostadien-3β-ol	248			(456, 23)
3β-Acetoxy-8,14-ergostadiene	248	19,800	A	(24a)
Ergosterol-B_1 $\Delta^{(8,14,22)}$	250	19,400	A	(134a, 446)
3-acetate	249	18,100	A	(134a)
Ergosteryl-B_1 chloride	248	18,300	A	(134a)
$\Delta^{9(11),12(23)}$				
9,12-Dehydronorcholadiene	242	19,500	E	(57)
$\Delta^{16,20(21)}$				
3α-Acetoxy-16,20-pregnadien-11-one	238	15,000	A	(375)
3β-Acetoxy-16-allopregnen-20-one				
20-enol acetate	~239	~14,500	A	(282)
3β-Acetoxy-5,16-pregnadien-20-one				
20-enol acetate	~239	~15,800	A	(282)
3β-Acetoxy-21,21-dimethyl-5,16,20-pregnatriene	240	~8,900	H	(326)
$\Delta^{16,20(22)}$				
5,16,20-Furostatriene-5β,26-diol	226	13,200	A	(372, 256)
3,26-diacetate	226	14,500	A	(372)
$\Delta^{22,24(28)}$				
3β-Acetoxy-5,22,24-stigmastatriene	238	15,800	A	(122)
Miscellaneous:				
3,5-Cyclo-6-cholestene	~210	~3000		(327, 231)
		Trienes		
$\Delta^{2,4,6}$				
17-Propionyloxy-2,4,6-androstatriene[k]	304	12,600	D	(286)
2,4,6-Cholestatriene[l]	298(i)[c], 307	—, 15,200	CH	(388)
	306	15,700	E	(388, 286, 111)
	307		A	(388)
4-Cholestene-3,6-dione 3-benzoate 3-enol ethyl ether	308	13,200	A	(345)
3,6-dienol dibenzoate	230, 307	48,400, 18,200	AC	(345)
4,6-Cholestadien-3-one 3-enol acetate	302	12,600	A	(84)
22-Iso-2,4,6-spirostatriene	296, 306, 320	18,600, 21,400, 14,100[c]	A	(332)
4,6-Ergostadien-3-one 3-enol acetate	304	16,600	A	(166, 83)
$\Delta^{3,5,7}$				
3,5,7-Cholestatriene[m]	303, 315, 330	12,540, 15,700, 11,100	IA	(144, 111, 286, 388)
4-Cholestene-3,6-dione 3,6-dienol dibenzoate	230, 316	37,600, 20,200	AC	(345)
4,6-Cholestadien-3-one 3-enol acetate	305, 316, 330	—, 20,000, —	A	(84)
22-Iso-4,7-spirostadien-3-one 3-enol acetate	302, 314, 330	20,000, 23,400, 17,400	A	(468)
3,5,7,22-Ergostatetraene	302, 316, 332	~16,000, 19,000, ~14,000	A	(83, 166)
4,7,22-Ergostatrien-3-one 3-enol acetate	301, 317, 331	~18,500, 21,400, ~18,000	A	(166, 83)

TABLE 25—*Concluded*

COMPOUND	$\lambda_{max.}$	$\epsilon_{max.}$	SOLVENT[a]	REFERENCES
		Trienes—*Continued*		
	mμ			
$\Delta^{3,5,7}$—*Continued*				
Lumistatetraene	314			(167)
4,7,22-Lumistatrien-3-one 3-enol acetate	301(i), 315, 331(i)[c]	—, 19,100, —	A	(166, 83)
$\Delta^{4,6,8(14)}$				
$\Delta^{4,6,8,22}$-Ergostatetraene	283	33,000	A	(134a)
$\Delta^{5,7,9(11)}$				
5,7,9-Androstatriene-3β,17β-diol	312, 324, 339	11,230, 12,680, 7,950	A	(7)
3,17-diacetate	312, 324, 339	9,900, 10,300, 6,400	A	(7)
3,17-dibenzoate	229, 312, 324, 340	30,250, 11,300, 12,700, 8,100	A	(7)
3β-Hydroxy-5,7,9-androstatrien-17-one	311(i), 322, 339(i)[c]	9,650, 10,800, 6,800	A	(7)
3-acetate	312(i), 323, 339(i)	9,900, 11,100, 6,900	A	(7)
3-benzoate	227, 311, 323, 336	17,350, 11,600, 12,850, 8,100	A	(7)
3β-Hydroxy-5,7,9-pregnatrien-20-one	312(i), 323, 339(i)	10,200, 11,550, 7,400	AC	(7)
3-acetate	312, 324, 339	11,500, 12,800, 7,700	A	(7, 11, 97)
3-benzoate	228, 312, 324, 339	16,900, 11,450, 12,900, 8,000	A	(7)
3β,21-Dihydroxy-5,7,9-pregnatrien-20-one	311, 324, 339	9,300, 10,700, 6,660	A	(7)
3,21-diacetate	312, 325, 339(p)[c]	10,500, 11,900, 7,400	A	(7)
5,7,9-Cholestatrien-3β-ol	312, 325, 339	10,100, 12,800, 7,950	A	(7)
3-acetate	311, 325, 340	10,300, 11,900, 7,450	A	(7)
3-benzoate	228, 282, 310, 325, 340	13,700, 4,700, 9,500, 10,900, 7,000	AC	(77, 7)
22-Iso-5,7,9-spirostatrien-3β-ol	310, 324, 338	13,200, 14,500, 8,900	A	(342)
3-acetate	310, 324, 338	15,100, 17,000, 10,500[e]	A	(342)
5,7,9,22-Ergostatetraen-3β-ol (dehydroergosterol)	325, 340	11,100, —	A	(166, 167, 443)
3-acetate	311, 325, 341	10,500, 12,100, 7,500	A	(7)
Dehydrolumisterol	320	7,500[f]		(167)
3-acetate	315 318	11,700	E	(83, 443) (85)
$\Delta^{5,7,14}$				
5,7,14,22-Ergostatetraen-3β-ol (14-dehydroergosterol)	319	17,500	A	(25)
3-acetate	319	15,000	A	(25)
3-benzoate	319	16,000	A	(25)
$\Delta^{6,8(14),9(11)}$				
3β-Acetoxy-6,8,9-cholestatriene	~243, 285	~12,000, 9,100	E	(453, 452, 451)
		Tetraenes		
$\Delta^{3,5,7,9(11)}$				
22-Iso-4,7,9-spirostatrien-3-one 3-enol acetate	336, 354, 372	17,800, 21,900, 16,200	A	(468)
4,7,9,22-Ergostatetraen-3-one 3-enol acetate	339, 356, 375	~15,000, 17,400, ~13,000	A	(166)
$\Delta^{4,6,8(9),11}$				
4,6,8,11-Cholestatetraen-3β-ol	355	13,500	E	(453)
$\Delta^{3,5,3',5'}$				
17,17′-Dipropionyloxy-3,3′-bis-3,5-androstadiene	298, 313	37,000, 53,000	C	(63)
3,3′-Bis-3,5-cholestadiene	280, 293, 305, 321	38,900, 53,700, 63,100, 45,700	E	(401)
	298, 312, 323	47,900, 63,100, 46,800	C	(401, 63)

[a] A = ethanol; AC = sample dissolved in a minimum of chloroform and diluted with ethanol; C = chloroform; CH = cyclohexane; D = dioxane; E = ethyl ether; H = hexane; IA = isopropyl alcohol; M = methanol.
[b] The bands or inflections at 228 and 244 mμ do not appear when a C_3-acetate or C_3-halogen is present.
[c] (i) signifies an inflection; (p) signifies a plateau.
[d] The hemithioketal is at the C_{17}-position.
[e] The extinction coefficient is too high.
[f] The extinction coefficient is too low.
[g] The extinction coefficient at 280 mμ should be the highest.
[h] The chemical individuality is questioned (22).
[i] It has been shown (231) that a cyclopropane ring has chromophoric powers approaching that of an ethylenic bond but weaker, since the three-membered ring is under less strain than a double bond. Thus it was expected (134a) that a cyclopropane ring would have a bathochromic effect of approximately 15 mμ when in conjugation with a conjugated diene.
[j] The absorption band should appear at 248–250 mμ.
[k] A $\Delta^{3,5,7}$-triene was proposed by the authors.
[l] The compound was previously described (111) as a $\Delta^{3,5,7}$-triene.
[m] The compound was previously described (111, 286) as a $\Delta^{2,4,6}$-triene.

TABLE 26

Ultraviolet absorption of conjugated steroid ketones

COMPOUND	$\lambda_{max.}$	$\epsilon_{max.}$	SOLVENT[B]	REFERENCES
		Enones		
	mμ			
Δ¹-3-one:				
17β-Hydroxy-1-alloandrosten-3-one	230	10,000	A	(56)
17-hexahydrobenzoate	232	6,800	A	(102)
2-bromo 17-hexahydrobenzoate	255	7,600	A	(104)
	254	7,700	E	(438, 209)
2,4-dibromo 17-hexahydrobenzoate	261	6,600	A	(104)
1-Alloandrostene-3,17-dione	230	10,200	A	(90, 61)
2-bromo	256	6,990	A	(103)
3-Keto-1-etioallocholenic acid	231	7,950	A	(77)
methyl ester	232	6,170	A	(102)
2-bromo methyl ester	257	7,080	A	(102)
3-(2,4-dinitrophenylhydrazone) methyl ester	257, 383	17,300, 30,000	C	(77)
3-(α-methyl-2,4-dinitrophenyl-hydrazone) methyl ester	245, 393	20,800, 21,600	C	(77)
1-Allopregnene-3,20-dione	230	12,600	A	(347, 61)
17α-Hydroxy-1-allopregnene-3,20-dione	230	11,300	A	(338, 341)
21-Acetoxy-1-allopregnene-3,20-dione	229	12,000	A	(77)
21-Acetoxy-17α-hydroxy-1-allopregnene-3,20-dione	230	11,000	A	(341)
21-Acetoxy-17α-hydroxy-1-allopregnene-3,11,20-trione	227	10,000	A	(293, 227)
21-Acetoxy-17α-hydroxy-1-pregnene-3,11,20-trione	225	9,130	M	(267)
3-(2,4-dinitrophenylhydrazone	381	28,300	C	(267)
21-Diazo-1-pregnene-3,20-dione	233, 240	17,100, 17,900	A	(77)
3-Keto-1-bisnorallocholenic acid	240			(60)
Methyl 12α-acetoxy-3-keto-1-cholenate	231	7,200	A	(202)
2-bromo	256	8,800	M	(202)
Methyl 12α-bromo-3,11-diketo-1-cholenate	224	9,890	M	(265)
3-(2,4-dinitrophenylhydrazone)	381	29,200	C	(265)
1-Cholesten-3-one	231	9,770	A	(102, 61, 213)
2-bromo	256	8,500	A	(102)
3-(2,4-dinitrophenylhydrazone)	257, 384	16,400, 27,100	C	(101)
3-(α-methyl-2,4-dinitrophenyl-hydrazone	248, 393	18,000, 20,000	C	(101)
2-bromo 3-(α-methyl-2,4-dinitro-phenylhydrazone)	245, 392	15,300, 16,700	C	(101)
3-semicarbazone	266	25,800	C	(77)
1-Coprosten-3-one	230	10,200	A	(98, 204)
2-bromo	256	7,400	M	(98, 204)
3-semicarbazone	270	9,670	C	(204)
1-Cholestene-3,6-dione	228	8,150	IA	(116)
2-bromo	257	7,450	IA	(116)
Δ²-2-formyl:				
2-Formyl-2-cholestene	235, 300	12,600, 71	A	(303)
2'-oxime	233	20,000	A	(303)
Δ⁴-3-one:				
19-Nortestosterone	241, 308	17,000, 93	A	(40)
4,16-Androstadien-3-one	240	17,800		(313)
Testosterone	241	15,800	A	(83)
	241	15,400	M	(83)
	240		C	(83)
	236	15,200	D	(83)
	234	15,600	E	(83)
	230	15,100	H	(83)
17-propionate	241	16,900	A	(284)
17-methoxyacetate	241	16,800	A	(284)
17-ethoxyacetate	241	17,100	A	(284)
17-n-propoxyacetate	240	17,000	A	(284)
17-isopropoxyacetate	241	16,500	A	(284)
17-n-butoxyacetate	240	15,600	A	(284)
17-methoxypropionate	241	17,000	A	(284)
17-hexahydrobenzoate	241	13,200	A	(102)
17-undecylenate	240	16,000	A	(77)
17-phenylacetate	240	16,000	A	(77)
17-phenylmercaptoacetate	240	22,700	A	(284)
17-benzylmercaptoacetate	240	18,200	A	(284)
17-methylmercaptopropionate	240	16,900	A	(284)
17-(2'-methylmercapto)propionate	241	17,700	A	(284)
17-(2'-ethylmercapto)propionate	241	17,300	A	(284)
17-methylmercaptobutyrate	241	16,800	A	(284)
17-(2'-methylmercapto)butyrate	241	17,900	A	(284)

TABLE 26—*Continued*

COMPOUND	$\lambda_{max.}$	$\epsilon_{max.}$	SOLVENT[a]	REFERENCES
		Enones—*Continued*		
	mμ			
Δ⁴-3-one:—Continued				
Testosterone—*Continued*				
2-bromo 17-hexahydrobenzoate	245	12,000	A	(102)
	~240	~13,500	E	(209)
2,6α-dibromo 17-acetate	240	12,600	A	(100)
2,6β-dibromo 17-acetate	248	12,900	A	(100)
2-iodo 17-hexahydrobenzoate	242	17,400	A	(340)
17-sodium sulfonate	241	17,700	A	(191)
	249	20,300	W	(191)
Epitestosterone	238	17,400		(354)
17-Acetoxy-14-allo-17-epitestosterone	240	15,400		(174)
16-Hydroxytestosterone	241	16,700	M	(83, 67)
	250	16,400	W	(83, 67)
16,17-acetonide	234	17,400	E	(83, 67)
4-Androstene-3,17-dione	240, 295	17,170, 146	A	(77, 83, 62, 429)
2-bromo	244	11,800	A	(103)
4-bromo (?)[b]	248	14,400	E	(83)
6α-bromo	240	17,000	A	(100, 350)
6β-bromo	245	10,300		(100, 83, 350)
2,4-dibromo	297(?)	10,300		(350)
2,6-dibromo	240	15,500	A	(100)
	248			(350)
2-iodo	242	14,800	A	(340)
3-semicarbazone	265	35,000	C	(62, 429)
17-(β-hydroxyethyl)hemithioketal	238	20,000	A	(339)
17-(β-benzoxyethyl)thioenol ether	232	24,000	A	(339)
4,7-Androstadiene-3,17-dione	237	14,800	A	(9)
4,11-Androstadiene-3,17-dione	238	16,600	A	(280)
4,14-Androstadiene-3,17-dione	237	16,800	A	(77)
4-Androstene-3,11,17-trione	239	13,800	A	(375, 83, 320)
disemicarbazone[c]	233, 271	~48,000 ~55,000		(83, 320)
17α-Methyltestosterone 3-(2,4-dinitrophenylhydrazone)	395	178,000[d]	C	(186)
Methyl 3-keto-14-iso-17-iso-19-nor-4-etiocholenate	240	14,100	A	(399)
ethyl ester	239	19,860	A	(112)
Methyl 3-keto-4-etiocholenate				
2-bromo	244	11,000	A	(102)
6β-bromo	248	14,800	A	(77)
2-iodo	244	20,000	A	(340)
6α-Hydroxy-3-keto-4-etiocholenic acid	239	17,060	A	(172)
6β-Hydroxy-3-keto-4-etiocholenic acid	238	12,250	A	(172)
Methyl 12α-hydroxy-3-keto-4-etiocholenate	241	14,940	A	(329)
Ethyl 19-hydroxy-3-keto-4-etiocholenate	243	14,860	A	(112)
19-acetate	239	15,470	A	(112)
3,11-Diketo-4-etiocholenic acid	238	20,200		(261)
Ethyl 3-keto-8,19-oxido-4-etiocholenate	243	13,610	A	(114)
Ethyl 8-hydroxy-3-keto-17-iso-21-nor-4-pregnene-19-carboxy-19→8-lactone-20-carboxylate	244	13,130	A	(18)
19-Norprogesterone	240	22,900[d]	A	(281)
3,20-di(2,4-dinitrophenylhydrazone)	380	60,300	C	(281)
17α-Ethyltestosterone	243	14,300	C	(83)
17β-Hydroxy-4,20-pregnadien-3-one	242	16,000	C	(83, 203)
17α-Ethynyltestosterone	240, 310	16,400, 85	A	(77, 353, 203)
17α-Ethynyltestosterone-20,21-C^{14}	241		A	(328)
20-Hydroxy-19-nor-4-pregnen-3-one	240	22,400[d]	A	(281)
20β-Hydroxy-4-pregnen-3-one	242	20,400[d]	A	(333)
17α-Hydroxy-20,21-oxido-4-pregnen-3-one	240	12,600	A	(77)
16α,20α-Diacetoxy-4-pregnen-3-one	241	17,000		(189)
17α,20β-Dihydroxy-4-pregnen-3-one	240	19,500[d]	A	(333)
Progesterone	241	17,000	A	(77)
	234	17,300	E	(83)
2,6,17-tribromo	250	16,200	A	(99)
20-ethylene hemithioketal	242	20,400	A	(335)
3,20-di(2,4-dinitrophenylhydrazone)	383	53,000	C	(91)
14-Allo-17-isoprogesterone	242, 305	16,600, 100		(302, 83)
7-Dehydroprogesterone	238	14,600	A	(9, 97)
11-Dehydroprogesterone	238	21,900[d]	A	(279)
12α-Hydroxyprogesterone	242	10,500	A	(394)
12-acetate	240	13,800	A	(423)
16α-Hydroxyprogesterone				
16-methoxy	241	16,600	M	(139)
16α or β-(β-hydroxyethylmercapto)	240	20,400	A	(335)
16α or β-(β-benzoxyethylmercapto)	234	38,000	A	(335)
16α- or β-thiobenzyl	240	19,500	A	(333)
3-semicarbazone 16-thiobenzyl	268	47,900	A	(333)

TABLE 26—*Continued*

COMPOUND	$\lambda_{max.}$	$\epsilon_{max.}$	SOLVENT[a]	REFERENCES
		Enones—*Continued*		
	mμ			
Δ⁴-3-one:—Continued				
17α-Hydroxyprogesterone	242	16,500	A	(236, 237, 338, 341)
2-iodo	244	14,100	A	(338)
17β-Hydroxyprogesterone	241	15,800	A	(162)
21-Acetoxy-17,20-oxido-4-pregnen-3-one	240	11,200	A	(371)
20α,21-Diacetoxy-17α-hydroxy-4-pregnen-3-one	241	17,400	M	(219)
20β,21-Diacetoxy-4-pregnene-3,11-dione	238	15,370		(376)
11β,17α,20β,21-Tetrahydroxy-4-pregnen-3-one	240			(321)
20,21-diacetate	241	20,000	M	(219)
20β,21-Diacetoxy-17β-hydroxy-4-pregnen-3,11-dione	239	28,300[d]	A	(375)
Desoxycorticosterone	240	19,000[d]	A	(83, 407)
21-acetate	240	~17,400	A	(83, 407)
14-Allo-17-isodesoxycorticosterone acetate	241	17,000	A	(180)
17-Isodesoxycorticosterone acetate	244	15,200	A	(393)
21-Acetoxy-4,7-pregnadiene-3,20-dione	237	13,600	A	(9)
21-Acetoxy-4,9-pregnadiene-3,20-dione	240	~12,600	A	(395)
21-Acetoxy-4,11-pregnadiene-3,20-dione	240	17,000	A	(433)
6α-Hydroxydesoxycorticosterone	240	15,230	A	(172)
6,21-diacetate	238	15,910	A	(172)
6β-Hydroxydesoxycorticosterone	235	13,730	A	(172)
6,21-diacetate	236	15,950	A	(172)
Corticosterone	240	20,000[d]	A	(83, 322)
12β,21-Dihydroxy-4-pregnene-3,20-dione				
21-acetate	244	13,200	A	(138)
12,21-diacetate	244	14,100	A	(138)
21-Acetoxy-14-hydroxy-14-iso-4-pregnene-3,20-dione	240	16,600	A	(276)
17α-Hydroxydesoxycorticosterone	240	16,600	A	(323, 83)
21-acetate	241	17,400	A	(233, 337, 375)
11-Dehydrocorticosterone acetate	238	13,300		(376)
12α-bromo	238	16,400	M	(267)
12α-bromo 3-(2,4-dinitrophenylhydrazone)	387	31,200	C	(267)
21-Acetoxy-4-pregnene-3,12,20-trione	240	17,800	A	(433, 138)
17α-Hydroxycorticosterone	241	13,800	A	(322)
21-acetate	243	15,370	A	(426, 425)
17α,21-Dihydroxy-4-pregnene-3,11,20-trione	238	16,000	A	(267,262)
21-acetate	238	15,800	A	(375, 267, 337)
3-(2,4-dinitrophenylhydrazone) 21-acetate	387	30,500	C	(267)
21-Diethylmercaptol-4-pregnene-3,20-dione	242	15,900	A	(382)
21-Al-20-hydroxy-4-pregnen-3-one 21-dimethylacetal	~225–245, 305	~15,900, 100	A	(382)
20-acetate 21-dimethylacetal	242	14,500	A	(382)
17β-Hydroxy-17α-propargyl-4-androsten-3-one	240	15,800	A	(145)
16-Methylprogesterone	236	36,300[d]	A	(432)
16,17-Methyleneprogesterone	240	21,000	A	(373)
17-Methylprogesterone	242	17,800	A	(301)
17-Methylprogesterone-B	242	17,400	A	(179)
3-Keto-4-bisnorcholenic acid	240	21,000[d]	C	(83, 60)
Methyl 12α-hydroxy-3-keto-4-bisnorcholenate	241, ~300	14,000, ~100	A	(329)
17-(17²-Oxopropyl)-4-androsten-3-one	240, 296(p)[e]	20,000[d], 105	A	(310)
Methyl-12α-hydroxy-3-keto-4-norcholenate	242	16,320	A	(329)
17α-Hydroxy-3-keto-4-norcholenic acid lactone	238	15,800	A	(370)
3-Keto-4-cholenic acid	240	19,000	A	(142)
methyl ester	241	16,800	A	(142)
Methyl 12α-hydroxy-3-keto-4-cholenate	242	14,500	A	(329)
3-(2,4-dinitrophenylhydrazone)	259,390	18,300, 30,700	C	(77)
2,2,4,6-tetrabromo 12-acetate	285	14,500	A	(201)
Methyl 12β-acetoxy-3-keto-4-cholenate	240	10,700	A	(52)
Methyl 12α-bromo-3,11-diketo-4-cholenate	238	16,600	M	(263, 266)
3-(2,4-dinitrophenylhydrazone)	387	30,200	C	(263, 265)
3-oxime (*N*- or *O*-acetyl)	250	9,740	C	(263, 265)
3-phenylhydrazone	323	24,600	MC	(265)
3-semicarbazone	269	32,200	M	(264)

TABLE 26—*Continued*

COMPOUND	$\lambda_{max.}$	$\epsilon_{max.}$	SOLVENT[a]	REFERENCES
		Enones—*Continued*		
	mμ			
Δ⁴-3-one:—Continued				
3,12-Diketo-4-cholenic acid	236	15,800	A	(83, 378)
4-Cholesten-3-one	241,312	18,000, 100	A	(218, 154, 311)
	234	16,400	E	(83)
6α-chloro	239	19,000	A	(330, 29)
6β-chloro	241	15,100	A	(29,330)
2-bromo	243	14,100	A	(77)
4-bromo(?)[b]	250	15,200	E	(83)
6α-bromo	238	15,800	A	(28)
6β-bromo	244	13,700	E	(83)
2,6β-dibromo	250	12,000	A	(100)
4,6-dibromo(?)[f]	248	14,400	E	(83)
2,2,4-tribromo	277	13,150	A	(201)
4,6,6-tribromo(?)[b]	253	13,900	E	(83, 129)
2,2,4,6-tetrabromo	290	12,100	A	(201)
3-acetimino	270	26,100	E	(83)
3-(2,4-dinitrophenylhydrazone)	256, 281, 292, 393	21,500, 16,000, 11,500, 29,500	C	(48)
3-oxime	240	23,000	A	(218)
3-semicarbazone	271	26,000	C	(218, 83)
6-sulfonic acid	237	13,000		(83, 448)
22-Iso-4-spirosten-3-one				
6α-bromo	238	18,200	A	(332)
2,6β-dibromo	250	16,600	A	(468)
Pennogenone	~240	~16,000	A	(256)
4,7-Cholestadien-3-one	238	15,500	A	(9)
22-Iso-4,7-spirostadien-3-one	238	19,500[d]	A	(468)
6α-Hydroxy-4-cholesten-3-one				
6-acetate	242	14,500		(330)
4-bromo 6″α″-methoxy(?)[b]	237	11,000	E	(83, 68)
3-(2,4-dinitrophenylhydrazone) 6″α″-methoxy	309, 405	18,600, 37,100	C	(29, 24)
6β-Acetoxy-2,2-dibromo-4-cholesten-3-one	250	9,430	IA	(116)
7β-Hydroxy-4-cholesten-3-one	243, 311	15,500, 85	A	(146)
7-acetate	238, 312	16,100, 60	A	(146)
7-benzoate	235, 280, 314	27,700, 820, 70	A	(146)
4,22-Ergostadien-3-one	242	18,200	A	(27)
4,7,22-Ergostatrien-3-one	239	15,100	A	(9, 430, 166)
3-semicarbazone	267	36,830	C	(120, 430)
4,7,22-Lumistatrien-3-one	229(?)	17,000	A	(83, 166)
4,24(28)-Fucostadien-3-one	240, 310	17,000, 70	A	(218)
3-(2,4-dinitrophenylhyzdraone)	392	32,000	C	(218)
3-oxime	241	23,000	A	(218)
3-semicarbazone	272	27,000	C	(218)
4,22-Stigmastadien-3-one	241, 308	17,000, 75	A	(218)
3-(2,4-dinitrophenylhydrazone)	242, 265, 280, 293, 393	21,500, 23,000, 18,500, 17,000, 31,000	C	(48,218)
3-oxime	240	22,000	A	(218)
3-semicarbazone	271	29,000	C	(218)
4-β-Sitosten-3-one	241, 307	17,000, 75	A	(218, 78)
3-(2,4-dinitrophenylhydrazone)	259, 282, 292, 395	21,500, 16,000, 14,000, 31,500	C	(48, 218)
3-oxime	240	20,000	A	(218)
3-semicarbazone	272	25,000	C	(218)
Δ⁴-3-one (miscellaneous):				
17α-Methyl-4,17-D-homoandrostadien-3-one	240	18,200	A	(355)
D-Homotestosterone	243	16,600		(143)
17-benzoate	238	31,700	A	(181)
D-Homoisotestosterone	243	19,100		(143)
4-D-Homoandrosten-3,17-dione	244	23,400		(143)
Testolactone	238	17,000	A	(246)
Testolactam	240	22,900	A	(226)
3-Keto-4-oxazolidine	242	24,000	A	(181)
N-acetyl	242	24,000	A	(181)
Koster's ketone	239	15,300	A	(77)
Δ⁴-6-one:				
4-Androstene-6,17-dione	244, 300	6,300, 120	A	(351)
4-Cholesten-6-one	243	6,360	A	(319)
6-(2,4-dinitrophenylhydrazone)	257, 377	12,300, 24,900	C	(319)
6-semicarbazone	253	7,050	A	(319)
3β-Hydroxy-4-cholesten-6-one	239, 319	6,300, 85	A	(165, 83)
3-acetate	236, 320	6,300, 89	A	(165, 212, 83)
3-acetate 4-bromo(?)[b]	245, 335	8,000, 120	A	(211, 83)
7-bromo	238–243	15,900	A	(132)
3-acetate 6-semicarbazone	258	9,980	A	(319)

TABLE 26—*Continued*

COMPOUND	$\lambda_{max.}$	$\epsilon_{max.}$	SOLVENT[a]	REFERENCES
		Enones—*Continued*		
	mμ			
Δ^{5}-*4-one:*				
17β-Hydroxy-5-androsten-4-one	240	3,200[g]	C	(129)
5-Cholesten-4-one	241	7,200		(65)
Δ^{5}-*6-nor-7-carboxylic acid:*				
3β-Hydroxy-6-nor-5-cholestene-7-carboxylic acid ethyl ester	230	10,000	A	(466, 164)
3-acetate	228	7,900	A	(466, 164)
3-acetate ethyl ester	230	8,000	A	(466, 164)
Δ^{5}-*7-one:*				
3β-Acetoxy-5-androstene-7-one	234	11,200	A	(153)
3β,17β-Dihydroxy-5-androstene-7-one	240	15,100	A	(173, 83, 58)
3,17-diacetate	237	14,100	A	(173)
3-acetate 17-benzoate 7-ethylenemercaptol	228	20,800	A	(140)
3β-Acetoxy-5-androstene-7,17-dione	235	12,300		(44)
3β-Acetoxy-5-pregnene-7,17-dione	235, 290	18,200, 71		(232)
7-Keto-5-cholenic acid	239			(81)
3β-Hydroxy-7-keto-5-cholenic acid	238	8,900	A	(83, 148)
3,4,6-Tribromo-5-cholesten-7-one	~288	~10,000	A	(212)
3β-Hydroxy-5-cholesten-7-one				
3-acetate	235	12,050	A	(461)
	234	14,200	E	(83, 111)
3-ethylmercapto	234	15,500	E	(316)
3-ethylsulfonyl	229	12,000	E	(316)
3-acetate 7-ethylenemercaptol	222	6,430	A	(140)
3-benzoate 7-ethylenemercaptol	230	19,400	A	(140)
7-oxime	238	14,200	E	(83, 111)
3β,4β-Dihydroxy-5-cholesten-7-one	235	9,300	A	(247, 298)
3-acetate	235	11,000	A	(247)
3,4-diacetate	231	9,300	A	(247)
3,4-dibenzoate	232	37,100	A	(247)
Δ^{7}-*6-one:*				
7-Bromo-7-cholestene-3,6-dione(?)[b]	256	8,000	C	(83, 69)
5-Hydroxy-7-ergostene-3,6-dione	252, 333	13,500, 160	C	(50, 83)
3β-Acetoxy-5-hydroxy-7,22-ergostadien-6-one	252, 333	13,600, 155	C	(50, 83)
3-Acetoxy-5-hydroxy-7,22-lumistadien-6-one	252, 323	13,100, 105	C	(50, 83)
5-Hydroxy-7,22-lumistadiene-3,6-dione	253, 325	13,500, 100		(167)
$\Delta^{8(9)}$-*7-one:*				
3β,11α,20β-Trihydroxy-8-allopregnen-7-one	254	12,900	A	(412)
3β-Hydroxy-8-allopregnene-7,20-dione	252	12,600	A	(92)
3β,11α-Dihydroxy-8-allopregnene-7,20-dione				
3-acetate	252	13,200	A	(92)
3,11-diacetate	252	11,700	A	(92)
Methyl 3α-hydroxy-7-keto-8-cholenate				
3-acetate	254	11,000	A	(131, 127)
3-formate	255	7,100	A	(127)
3β-Acetoxy-8-zymosten-7-one	252	10,000	A	(1)
3β-Hydroxy-8-cholesten-7-one				
3-acetate	254	9,680	A	(77)
3-benzoate	252	6,300	A	(131)
3β-Acetoxy-14-hydroxy-8-cholestene-7,15-dione	254	10,400	A	(459)
3β-Acetoxy-8,22-ergostadien-7-one	253	12,600	A	(175, 405)
3β-Acetoxy-8,22-stigmastadien-7-one	252	8,300	A	(406)
$\Delta^{8(9)}$-*11-one:*				
Methyl 3α-acetoxy-11-keto-8-cholenate	254	8,700	A	(185)
Methyl 3β-acetoxy-11-keto-8-cholenate	255	8,900	A	(185, 402)
3β-Acetoxy-8,22-ergostadien-11-one	253	9,550	A	(175)
$\Delta^{8(14)}$-*7-one:*				
3β-Acetoxy-8-cholesten-7-one	263	9,500	A	(458)
3β-Acetoxy-8-ergosten-7-one	262	10,000	A	(404, 405)
5-Hydroxy-8-ergostene-3,7-dione	254	10,800	E	(83, 287)
3β-Acetoxy-8-stigmasten-7-one	260	7,800	A	(406)
$\Delta^{8(14)}$-*15-one:*				
3β-Acetoxy-8-cholesten-15-one	259	12,750	A	(459)
3β-Acetoxy-8-ergosten-15-one	259	13,300	A	(404)

TABLE 26—*Continued*

COMPOUND	$\lambda_{max.}$	$\epsilon_{max.}$	SOLVENT[a]	REFERENCES
		Enones—*Continued*		
	mμ			
$\Delta^{9(11)}$-12-one:				
3β-Acetoxy-9-androstene-12,17-dione	238	15,800	A	(318)
Methyl 3α-acetoxy-12-keto-9-etiocholenate	240	10,000	A	(242)
9-Pregnene-3,12,20-trione	239	10,000	A	(163)
Methyl 3α-acetoxy-12-keto-9-norcholenate	240	8,500	A	(243)
Methyl 12-keto-9-cholenate	235	11,800	H	(5, 19)
3α-Hydroxy-12-keto-9-cholenic acid	240	10,700	A	(134)
methyl ester	240	12,000		(251)
3-acetate	241	9,000	A	(392)
3-acetate methyl ester	241	11,500	A	(5)
Methyl 3α-carbethoxy-12-keto-8-lithocholenate	239	12,600	A	(133)
3,12-Diketo-9-cholenic acid	243	12,200	A	(374)
methyl ester	238	8,300	A	(241)
3α,7α-Dihydroxy-12-keto-9-cholenic acid	240	9,770	A	(134)
7-acetate methyl ester	238	10,000	A	(134)
3,7-diacetate methyl ester	237	11,500	A	(134, 175)
3β-Hydroxy-22-iso-9-allospirosten-12-one	240, 322	13,500, 71	A	(93, 422)
3-acetate	238, 322	14,800, 64	A	(93)
3-acetate 23-bromo	240, 311	11,500, 120	A	(285)
9-Dehydromanogenic acid	240	10,000	A	(422)
$\Delta^{12(23)}$-22-one:				
12-Dehydronorcholen-22-one	234	15,500	E	(57)
Δ^{16}-17-carboxylic acid:				
Methyl 3β-acetoxy-16-etiocholenate	225	12,600	A	(273)
3β-Hydroxy-5,16-etiocholadienic acid	230	12,600		(352)
Methyl 3β-acetoxy-14,15-oxido-16-alloetiocholenate	233	7,200		(366)
Methyl 3β-acetoxy-5α,6β-dihydroxy-14,15β-oxido-16-alloetiocholenate	236	6,600	A	(183)
Methyl 3β-acetoxy-16-methyl-5,16-etiocholadienate	233	12,600		(352)
Δ^{16}-20-one:				
3α-Acetoxy-16-allopregnen-20-one 20-semicarbazone	267	24,400	C	(317)
3α-Hydroxy-16-pregnen-20-one 20-semicarbazone	267	24,000	C	(77)
3β-Acetoxy-16-allopregnen-20-one	240, 310	10,200, 150	A	(105, 306)
3β-Acetoxy-14,15β-oxido-16-allopregnen-20-one	248, 327	11,200, 71		(306)
16-Pregnene-3,20-dione	239	9,800	A	(83, 260)
3β-Hydroxy-5,16-pregnadien-20-one	241	8,000	A	(256)
	234	9,300	E	(83, 66)
3-acetate	239	9,100	A	(139)
	234	9,600	E	(83, 66)
20-semicarbazone	267	24,000	C	(317)
3-acetate 20-semicarbazone	267	24,000	C	(317)
	266	22,900	A	(135)
3-acetate 20-(2,4-dinitrophenylhydrazone)	384	26,800	C	(230)
3β-Acetoxy-7,16-allopregnadien-20-one	238	12,900	A	(97)
3β-Acetoxy-8(14),16-allopregnadien-20-one	230	11,700	A	(252)
3β-Acetoxy-9,16-allopregnadien-20-one	238	11,700	A	(94)
2,3β-Dihydroxy-5,16-pregnadien-20-one	~240	~7,000	A	(256)
3α,12α-Diacetoxy-16-pregnen-20-one	238, 315	11,600, 105	A	(105)
3α-Hydroxy-16-pregnene-11,20-dione	235	7,400	M	(289)
3β-Acetoxy-16-allopregnene-11,20-dione	235	9,050	A	(76)
3β-Acetoxy-16-allopregnene-12,20-dione	227–230	8,510	A	(424)
16-Pregnene-3,11,20-trione	235	8,900	M	(289)
3β-21-Diacetoxy-16-allopregnen-20-one	~242, ~310	~11,200, ~64		(307, 363)

TABLE 26—*Continued*

COMPOUND	$\lambda_{max.}$	$\epsilon_{max.}$	SOLVENT[a]	REFERENCES
		Enones—*Continued*		
	mμ			
Δ^{16}-20-one:—Continued				
3α,21-Diacetoxy-16-pregnene-11,20-dione				
12α-bromo	235	8,700	M	(80)
	231	8,700	E	(80)
12α,15α-dibromo	237	11,000	M	(79)
	235	11,000	E	(79)
12α,15β-dibromo	235	9,800	E	(79)
12α,15,21-tribromo	251	8,700	E	(80)
12α,15,21-tribromo (epimer)	251	8,600	E	(79)
12α-bromo 15α-iodo	243	13,000	E	(79)
12α-Bromo-3α,15,21-triacetoxy-16-pregnene-11,20-dione	229	9,800	E	(79)
3α-Acetoxy-12α,15-dibromo-21,21-dihydroxy-16-pregnene-11,20-dione	241	10,500	E	(79)
3β,21-Diacetoxy-14,15β-oxido-16-allopregnen-20-one	248	7,100		(307)
3β,12-Diacetoxy-16-methyl-16-pregnen-20-one	248	10,000	A	(105)
3β-Hydroxy-16-methyl-5,16-pregnadien-20-one				
3-acetate	250	11,500	A	(373, 432)
3-semicarbazone	268	~15,800		(432)
$\Delta^{16'}$-17-one:				
3β-Acetoxy-5-androsten-17-one				
16-methylene	228	7,940	A	(220)
16-isopropylidene	250, 338	14,800, 100	A	(344)
16-isobutylidene	245	12,800	E	(83, 67)
16-benzylidene	223, 295	8,220, 24,000	A	(77)
$\Delta^{16'}$-22-one:				
Fesogenin	245	13,700	A	(256)
5-Dihydrofesogenin	~245	~14,000	A	(256)
Δ^{17}-16-one:				
3β,22-Dihydroxy-22(26)-oxido-5,17-cholestadien-16-one	236	14,800	A	(372)
hydrazine product	238,256	20,000, 19,500	A	(372)
3-acetate hydrazine product	238,256	21,900, 19,500	A	(372)
Δ^{17}-20-al, carboxylic acid, or cyano:				
3β-Hydroxy-5,17-pregnadien-20-al	244	26,300	A	(176)
3-acetate	244	27,500	A	(176)
Methyl 3β-acetoxy-17-allopregnene-20-carboxylate	224	16,600		(300)
3β-Hydroxy-5,17-pregnadiene-20-carboxylic acid	222	12,600	A	(177)
ethyl ester	222	16,600	A	(177)
3-acetate ethyl ester	222	25,100[d]	A	(177)
4,21-Diacetoxy-5-hydroxy-3-keto-17-pregnene-20-cyano	225	10,500	A	(161)
3β,21-Diacetoxy-5,17-pregnadiene-20-cyano	224	10,500	A	(161)
11β,21-Dihydroxy-3-keto-17-pregnene-20-cyano	223	13,800	M	(425)
Δ^{17}-21-one:				
3β-Acetoxy-17(17²-oxopropylidene)-5-androstene	242, 310	20,000, 120	A	(310)
$\Delta^{20(22)}$-22-carboxylic acid:				
Methyl 3β-hydroxy-20-norallocholenate	231	15,800		(367)
3-acetate	230	20,000		(367)
Methyl 3β-acetoxy-5,20-norcholadienate	230	~20,000		(367)
3α,12β,21-Trihydroxy-20-norcholenic acid	229	12,600		(305)
$\Delta^{20(22)}$-22-cyano:				
3β-Hydroxy-5,20-bisnorcholadiene-22-cyano				
"trans"	226	12,300	A	(171)
"cis"	223	16,600	A	(171)

TABLE 26—*Continued*

COMPOUND	$\lambda_{max.}$	$\epsilon_{max.}$	SOLVENT[a]	REFERENCES
Enediones				
	mμ			
Δ^{4}-3,6-dione:				
17β-Acetoxy-4-androstene-3,6-dione	252	11,400	C	(83, 64)
4-Androstene-3,6,17-trione	252	10,800	C	(83, 64)
3,6-Diketo-4-etiocholenic acid	248	13,060	A	(172)
4-Cholestene-3,6-dione	252	11,400	C	(83, 64)
4,7-dibromo(?)[b]	254	9,100	C	(83, 69)
4,7,7-tribromo(?)[b]	257	10,200	C	(83, 69)
4,22-Ergostadiene-3,6-dione	254		E	(83)
4-Stigmastene-3,6-dione	254		A	(83)
Δ^{5}-3,4-dione:				
5-Cholestene-3,4-dione (Diosterol, enol forms)				
Diosterol I (4-hydroxy-4,6-cholestadien-3-one)	313.5	4,680	A	(130)
4-enol benzoate	232, 287	15,500, 25,700	A	(130)
Diosterol II (3-hydroxy-2,5-cholestadien-4-one)	265, 300	5,130, 5,370	A	(130)
3-enol acetate	245	14,800	A	(130)
3-enol benzoate	234	20,000	A	(130)
Δ^{5}-3,7-dione:				
5-Cholestene-3,7-dione, enol, (3-hydroxy-3,5-cholestadien-7-one)	320	24,300	A	(146, 20)
	393	62,200	AA	(146, 20)
enol acetate	283	22,500	A	(146, 20)
enol methyl ether	308	27,600	A	(146, 20)
enol ethyl ether	~310	~12,600[g]	A	(20)
$\Delta^{8(9)}$-7,11-dione:				
3β-Acetoxy-8-allopregnene-7,11,20-trione	268	6,600	A	(92)
Methyl 3α-acetoxy-7,11-diketo-8-cholenate	272	8,100	A	(175, 131)
3β-Benzoxy-8-cholestene-7,11-dione	269	6,300	A	(127, 131)
3β-Acetoxy-8,22-ergostadiene-7,11-dione	266	9,360	IO	(76)
	270	8,700	A	(76, 175)
$\Delta^{8(14)}$-7,15-dione:				
3β-Acetoxy-8-ergostene-7,15-dione	255	5,000	A	(404)
7,15-pyridazine	262	1,800	A	(404)
Δ^{17}-16,22-dione:				
3β,26-Dihydroxy-5,17-cholestadiene-16,22-dione				
3,26-diacetate	246	13,500	A	(372)
16,22-pyridazine	258, 296	2,140, 470	A	(372)
3,26-diacetate 16,22-pyridazine	258, 294	2,000, 410	A	(372)
Dienones				
$\Delta^{1,4}$-3-one:				
17α-Hydroxy-1,4-androstadien-3-one	244	15,800	A	(438)
	236	~16,000	E	(210)
2-bromo 17-hexahydrobenzoate	255	11,500	A	(104)
17-acetate 6-bromo	248	20,900	A	(228)
17-acetate 3-semicarbazone	~298	~22,000	C	(210)
1,4-Androstadiene-3,17-dione	244	17,000	A	(100)
6-bromo	250	21,900	A	(228)
3-Keto-1,4-etiocholadienic acid	245	18,600	A	(77)
methyl ester	245	13,200	A	(102)
3-(2,4-dinitrophenylhydrazone) methyl ester	250, 301, 401	16,200, 7,600, 34,200	C	(77)
17α-Hydroxy-1,4-pregnadiene-3,20-dione	244	13,800	A	(338, 341)
21-Acetoxy-17α-hydroxy-1,4-pregnadiene-3,20-dione	244	18,200	A	(341)
Methyl 3-keto-1,4-choladienate	236	15,100		(205)
3-semicarbazone	298	24,200		(205)
Methyl 12α-acetoxy-3-keto-1,4-choladienate	243	14,000	M	(202)
Methyl 12α-bromo-3,11-diketo-1,4-choladienate	240	13,200		(266)

TABLE 26—*Continued*

COMPOUND	$\lambda_{max.}$	$\epsilon_{max.}$	SOLVENT[a]	REFERENCES
		Dienones—*Continued*		
	mμ			
$\Delta^{1,4}$-3-one:—Continued				
1,4-Cholestadien-3-one	245	14,500	M	(202, 437)
	236	15,800	E	(83, 204)
6-bromo	250	17,400		(331, 205)
4,6-dibromo(?)	254	14,500	A	(201)
2,4,6-tribromo	274	10,600	A	(201)
3-(2,4-dinitrophenylhydrazone)	258, 400	17,900, 34,700	C	(101)
3-semicarbazone	302	18,800	C	(83, 204)
6β-Hydroxy-1,4-cholestadien-3-one				
2-bromo	255	14,560	IA	(116)
6-acetate 2-bromo	253	12,880	IA	(116)
1,4-Cholestadiene-3,6-dione				
2-bromo	255	11,130	IA	(116)
$\Delta^{2,4}$-6-one:				
2,4-Cholestadien-6-one	314	7,620	A	(319, 345)
6-(2,4-dinitrophenylhydrazone)	257, 320, 408	11,660, 7,830, 25,120	C	(319)
3-Acetoxy-2,4-cholestadien-6-one	317	6,300	A	(83, 164)
7-Methoxy-2,4-7-cholestatrien-6-one(?)	315	15,800[d]	A	(83, 164)
$\Delta^{2(2')4}$-3-one:				
2-Hydroxymethylene-4-cholesten-3-one	250, 310	12,600, 6,300		(298a)
$\Delta^{2,5}$-4-one:				
3-Hydroxy-2,5-cholestadien-4-one (Diosterol II enol)	265, 300	5,130, 5,370	A	(130)
3-acetate	245	14,800	A	(130)
3-benzoate	234	20,000	A	(130)
$\Delta^{3,5}$-2-one:				
3,5-Cholestadien-2-one	290	12,600		(357)
$\Delta^{3,5}$-7-one:				
17-Hydroxy-3,5-androstadien-7-one	280	28,000	C	(83, 58)
17-acetate	280	27,800	C	(83, 58)
Methyl 7-keto-3,5-etiocholadienate	279	25,120	A	(325)
Methyl 12α-acetoxy-7-keto-3,5-etiocholadienate	278	26,900		(240)
3,5-Cholestadien-7-one	277	24,400	A	(146, 212)
2-bromo	280			(222)
6-bromo(?)[b]	288, 344	~20,000, ~159	A	(212)
4,6-dibromo(?)[b]	303	11,200	A	(212)
3-Hydroxy-3,5-cholestadien-7-one	320	24,300	A	(146, 20)
(Enol of 5-cholestene-3,7-dione)	393	62,200	AA	(146, 20)
3-enol acetate	283	22,500	A	(146, 20)
3-methoxy	308	27,600	A	(146, 20)
3-ethoxy	~310	~12,600	A	(20)
$\Delta^{4,6}$-3-one:				
17β-Hydroxy-4,6-androstadien-3-one	284	29,500	A	(100, 431)
17-acetate	284	33,900[d]	A	(100)
3-(α-methyl-2,4-dinitrophenylhydrazone) 17-hexahydrobenzoate	266, 309, 404	14,100, 12,700, 30,900	A	(77)
4,6-Androstadiene-3,17-dione	282	33,100[d]	A	(100)
	273	26,500	E	(83)
Methyl 3-keto-4,6-etiocholadienate	283	30,500	A	(77)
3-(2,4-dinitrophenylhydrazone)	270, 310, 402	17,700, 13,900, 39,600	C	(101)
3-(α-methyl-2,4-dinitrophenylhydrazone)	272, 308, 398	16,900, 15,600, 37,200	C	(77)
6-Dehydroprogesterone	282	~25,100	A	(431)
6-Dehydrodesoxycorticosterone acetate	283	33,900[d]	A	(431)
Methyl 12α-bromo-3,11-diketo-4,6-choladienate	281	25,900	M	(265)
3-(2,4-dinitrophenylhydrazone)	308, 398	13,200, 36,200	C	(265)
4,6-Cholestadien-3-one	284	26,300	A	(437, 314, 463)
	283		D	(83)
2,4-dibromo	293	14,590	IA	(116)
4,6-dibromo(?)[b]	296	19,400	C	(83, 212)
4,6,7-tribromo(?)[b]	313	17,400	C	(212, 83)
3-(2,4-dinitrophenylhydrazone)	309, 405	18,600, 37,100	C	(29, 77, 247)
3-(α-methyl-2,4-dinitrophenylhydrazone)	270, 310, 404	17,100, 14,100, 37,700	C	(77)
3-oxime	280	18,100	C	(83)
3-semicarbazone	300	43,700	D	(247, 463)
4-Hydroxy-4,6-cholestadien-3-one (Diosterol I enol)	314	4,680	A	(130)
4-benzoate	232, 287	15,500, 25,700	A	(130)
6-ethoxy	295	16,800	E	(83)

TABLE 26—*Continued*

COMPOUND	$\lambda_{max.}$	$\epsilon_{max.}$	SOLVENT[a]	REFERENCES
		Dienones—*Continued*		
	$m\mu$			
$\Delta^{4,6}$-*3-one:—Continued*				
22-Iso-4,6-spirostadien-3-one	284	30,200[d]	A	(332)
4,6-Ergostadien-3-one (isoergosterone)	284	26,400	A	(9)
	281, 335	33,100, —	A	(166)
3-(2,4-dinitrophenylhydrazone)	308, 400	16,700, 35,900	C	(29)
3-semicarbazone	304	46,700	A	(83, 166)
6-Ethoxy-4,6-ergostadien-3-one	297		A	(83)
$\Delta^{5,7(7')}$-*7'-carboxylic acid:*				
3β-Acetoxy-5-cholestenylidene-7-acetic acid	268	14,500		(83)
$\Delta^{7,9(11)}$-*12-one:*				
3α-Hydroxy-12-keto-7,9-choladienic acid	240, 293	3,700, 12,900	A	(134, 175)
methyl ester	238, 290	3,800, 13,500	A	(134)
$\Delta^{8(9),14}$-*7-one:*[h]				
3β-Acetoxy-8,14-cholestadien-7-one	223, 298	15,630, 4,800	A	(77)
7-(2,4-dinitrophenylhydrazone)	261, 393	18,760, 23,681	C	(77)
$\Delta^{8(14),9(11)}$-*7-one:*				
3β-Acetoxy-8,9-ergostadien-7-one(?)	298[i]	5,010	A	(404)
3β-Acetoxy-8,9,22-ergostatrien-7-one(?)	300[i]	5,000	A	(405)
3β-Acetoxy-8,9,22-stigmastatrien-7-one(?)	299	5,300	A	(406)
$\Delta^{8(14),9(11)}$-*15-one:*				
3β-Acetoxy-8,9-ergostadien-15-one(?)[j]	307[k]	10,000		(404, 129)
$\Delta^{14,16}$-*17-carboxylic acid or nitrile:*				
Methyl 3β-acetoxy-14,16-alloetiocholadienate	292	15,800	A	(366)
Methyl 3β-acetoxy-14,16-etiocholadienate	295	11,000	A	(365)
Methyl 3β-acetoxy-5,14,16-etiocholatrienate	295	11,700		(183)
Methyl 3β-acetoxy-5,6α-oxido-14,16-alloetiocholadienate	295	11,000		(183)
Methyl 3β-acetoxy-5α,6β-dihydroxy-14,16-etiocholadienate	298	10,500		(183)
3β-Acetoxy-14,16-alloetiocholadienic acid nitrile	286	13,500	A	(304)
3β-Acetoxy-14,16-etiocholadienic acid nitrile	286	14,800	A	(365)
3β-Acetoxy-5,14,16-etiocholatrienic acid nitrile	286	11,200	A	(302)
$\Delta^{14,16}$-*20-one:*				
3β-Acetoxy-14,16-allopregnadien-20-one	309	12,600		(304, 306)
3β-Hydroxy-5,14,16-pregnatrien-20-one	307	17,000		(302)
3β,21-Diacetoxy-14,16-allopregnadien-20-one	233, 310[l]	2,500, 15,800		(307)
12α-Bromo-3α,21-diacetoxy-14,16-pregnadiene-11,20-dione	305	9,000	E	(79)
		Trienones		
$\Delta^{1,4,6}$-*3-one:*				
17β-Acetoxy-1,4,6-androstatrien-3-one	222, 256, 298	15,500, 13,500, 18,600	A	(100, 228)
1,4,6-Androstatriene-3,17-dione	222, 256, 298	15,500, 13,500, 18,600	A	(100, 228)
Methyl 12α-acetoxy-3-keto-1,4,6-cholatrienate				
2,4-dibromo	228(i)[e], 238, 278, 322	13,420, 14,100, 9,270, 11,100	A	(201)
1,4,6-Cholestatrien-3-one	224, 258, 300	10,700, 9,300, 12,900	A	(100, 331)
2,4-dibromo	228, 280, 326,	14,800, 10,400, 12,800	A	(201)
3-semicarbazone	~309	32,000		(205)
22-Iso-1,4,6-spirostatrien-3-one	222, 256, 296	13,500, 12,300, 14,130	A	(468)
$\Delta^{1,3,5}$-*7-one:*				
1,3,5-Cholestatrien-7-one	230, 278, 348	18,600, 3,720, 11,000	A	(468, 222)

TABLE 26—*Concluded*

COMPOUND	$\lambda_{max.}$	$\epsilon_{max.}$	SOLVENT[a]	REFERENCES
		Trienones—*Continued*		
	mμ			
$\Delta^{4,6,8(9)}$-3-one:				
4,6,8-Cholestatrien-3-one				
4-bromo(?)[m]	267, 298	12,200, 10,200	E	(83, 100)
4,6-dibromo(?)[m]	267, 298	12,200, 9,300	E	(83, 100)
22-Iso-4,6,8-spirostatrien-3-one	244, 284, 388	17,780, 2,190, 12,300	A	(468)
$\Delta^{4,6,8(14)}$-3-one:				
4,6,8-Ergostatrien-3-one	348	26,500	A	(25)
3-(2,4-dinitrophenylhydrazone)	427	41,000	C	(25)

[a] A = ethanol; AA = alkaline ethanol, usually 0.1 *N*; C = chloroform; D = dioxane; E = ethyl ether; H = hexane; IA = isopropyl alcohol; IO = isoöctane; M = methanol; MC = sample dissolved in a minimum of chloroform and diluted with methanol; W = water.

[b] Since a bromine atom on the double bond should cause a large bathochromic shift, it is unlikely that the structural assignmen t is correct.

[c] The band at 233 mμ is due to the C_{17}-semicarbazone.

[d] The extinction coefficient is too high.

[e] (p) signifies a plateau; (i) signifies an inflection.

[f] The compound is a 2,6β-dibromo derivative (100).

[g] The extinction coefficient is too low.

[h] Two alternate structures were proposed for the compounds in this group (see text).

[i] There is indication of a band below 220–230 mμ.

[j] The structure and homogeneity of the dienone are in doubt (129).

[k] A high-absorbing impurity is present.

[l] The spectra indicates the presence of the starting material, Δ^{16}-en-20-one.

[m] The compound is believed to be a $\Delta^{1,4,6}$-trien-3-one with a bromine atom on one of the double bonds (100).

TABLE 27

Ultraviolet absorption of steroid α-diketones and their enols

COMPOUND	$\lambda_{max.}$	$\epsilon_{max.}$	SOLVENT*	REFERENCES
	mμ			
2,3-Diketones:				
2,3,17-Androstanetrione, enol (Δ^2-3-ol-2-one)	272	9,550	A	(107)
3-enol acetate	236, 296	13,500, 79	A	(107)
3-enol tosylate	228, 294	20,000, 89	A	(107)
2,3-Cholestanedione, enol form "A" (Δ^2-3-ol-2-one)	272	5,000	A	(83, 408, 357)
3-enol acetate	238	7,400	A	(83, 408, 357)
2,3-Cholestanedione, enol form "B" (Δ^1-2-ol-3-one)	270	8,500	A	(83, 408, 357)
	268	10,400	E	(83, 408)
2-enol acetate	237	8,900	A	(83, 408, 357)
2,3-Cholestanedione, enol form "A + B"	320	3,700	AA	(83, 408)
3,4-Diketones:				
3,4-Cholestanedione, enol (Δ^4-4-ol-3-one)	280	11,500	C	(83, 70)
4-enol acetate	248	14,500	C	(83, 70)
3,4,6-Cholestanetrione, enol (Δ^4-4-ol-3,6-dione + $\Delta^{4,6}$-4,6-diol-3-one)	275, 335	5,000, 8,000	E	(129, 83, 448)
6,7-Diketone:				
3β-Acetoxy-6,7-cholestanedione enol (Δ^5-6-ol-7-one or Δ^7-7-ol-6-one)	275	10,700	A	(165)
11,12-Diketones:				
11,12-Diketocholanic acid	~226, 279, 347	~130, 87, 47	H	(83, 19)
enol (Δ^9-11-ol-12-one)	281	8,700	A	(83, 19)
Methyl 3,9-epoxy-11,12-diketocholanate	295, 376	104, 39	A	(268)
3β-Hydroxy-22-isoallospirostane-11,12-dione				
enol (Δ^9-11-ol-12-one)	282	1,900†	A	(95)
3-acetate 11-enol acetate	244	11,200	A	(95)
3α-Hydroxy-11,12-diketocholanic acid				
3-acid succinate methyl ester	284	140	A	(460)
11,12-dihydrazone	301	238	A	(460)
enol (Δ^9-11-ol-12-one)	281	7,000	A	(460)
enol (Δ^9-11-ol-12-one) methyl ester	280	5,200	A	(460)
3α-acetate 11-enol acetate methyl ester	243	7,800	A	(460, 95)

TABLE 27—*Concluded*

COMPOUND	$\lambda_{max.}$	$\epsilon_{max.}$	SOLVENT*	REFERENCES
	mμ			
20-Keto-21-aldehydes:				
21-Al-3β-hydroxy-5-pregnen-20-one 21-dimethyl acetal	~305	~63	A	(382)
21-Al-3α-hydroxy-11,20-pregnanedione 3-acetate 12α-bromo	440	20	A	(137)
3-acetate 12α-bromo 20-(2,4-dinitrophenylhydrazone)	370, 401	20,500, 22,200	C	(136)
	373, 380–392	22,200, 22,000	B	(136)
	365	24,700	M	(136)
12α-bromo-21,21-dimethoxy 20-(2,4-dinitrophenylhydrazone)	366	25,300	C	(136)
	365	25,600	B	(136)
3,21,21-triacetate 12α-bromo 20-(2,4-dinitrophenylhydrazone)	358	24,500	C	(136)
	359	24,400	B	(136)
3-Acetate 12α-bromo 21-(2,4-dinitrophenylhydrazone)	351	24,400	C	(136)
	360	24,800	B	(136)
	358	24,300	M	(136)
3-acetate 12α,17α-dibromo 21-(2,4-dinitrophenylhydrazone)	354	24,600	C	(136)
	378	26,700	B	(136)
	380	25,700	M	(136)
3-acetate 12α-bromo 20,21-bis-(2,4-dinitrophenylhydrazone)	349, 395, 450	31,200, 22,000, 21,000	C	(136)
	354, 398, 440	31,900, 24,200, 21,200	B	(136)
12α-bromo enol (Δ^{17}-21-al-20-ol)	284	10,900	M	(137)
3-acetate 12α-bromo	282	12,500	M	(137)
enol (Δ^{17}21-al-20-ol)	284	13,700	C	(137)
20-enol acetate	246	14,300	E	(137)
3-Acetate 12α-bromo 21-(2,4-dinitrophenylhydrazone) enol (Δ^{17}-21-al-20-ol)	268, 305, 379	13,000, 9,960, 26,400	C	(136)
	388	27,900	B	(136)
20-enol acetate	262, 289, 373	14,100, 8,600, 30,900	C	(136)
	381	30,700	B	(136)
21-Al-3,11,20-pregnanetrione 12α-bromo 20-(2,4-dinitrophenylhydrazone)	371, 400	20,400, 22,200	C	(136)
	374, 380–392	22,600, 22,400	B	(136)
12α-bromo 21,21-dimethoxy 20-(2,4-dinitrophenylhydrazone)	365	22,500	C	(136)
3β-Acetoxy-14-hydroxy-21-glyoxyloxy-20-keto-14-isopregnane	273	282	A	(276)

* A = ethanol; AA = alkaline ethanol, usually 0.1 *N*; B = acetone; C = chloroform; E = ethyl ether; M = methanol.

† The low extinction coefficient indicates that in solution the keto–enol equilibrium is in favor of the α-diketone

TABLE 28

Ultraviolet absorption of steroid β-diketone and its enol

COMPOUND	$\lambda_{max.}$	$\epsilon_{max.}$	SOLVENT*	REFERENCE
	mμ			
16,20-Diketone: 3α,12α-Dihydroxy-16,20-pregnanedione 3,12-diacetate 20-enol acetate (Δ^{17}-16-one-20-acetate)	249	11,200	A	(258)

* A = ethanol.

TABLE 29

Ultraviolet absorption of steroids containing two chromophoric systems

COMPOUND	$\lambda_{max.}$	$\epsilon_{max.}$	SOLVENT*	REFERENCES
	mμ			
Diene + α,β-conjugated ketone: 3,5,16-Pregnatrien-20-one	234, 318	30,200, 56	A	(333)
16-Isopropylidene-3,5-androstadien-17-one	~235, ~248, ~338	~30,200, ~25,100, ~63		(344)
4,7,9-Androstatriene-3,17-dione	236(i), 242, 249(i)†	24,700, 27,200, 22,400	A	(9)

TABLE 29—*Concluded*

COMPOUND	$\lambda_{max.}$	$\epsilon_{max.}$	SOLVENT[a]	REFERENCES
	mμ			
Diene + α,β-conjugated ketone:—Cont.				
4,7,9-Pregnatriene-3,20-dione	243	27,200	A	(9)
22-Iso-4,7,9-spirostatrien-3-one	242	32,400	A	(468)
4,7,9,22-Ergostatetraen-3-one	242	31,600	A	(166)
4,16,20-Pregnatrien-3-one	238	31,500	A	(292)
ω-Homo-4,17,21-pregnatrien-3-one	241, 310	28,000, 80	A	(77)
	236	42,100	E	(62)
Two α,β-conjugated ketones:				
4,7-Cholestadiene-3,6-dione				
7-bromo(?)‡	259	11,700	C	(83, 69)
4,7-dibromo(?)‡	259	11,000	C	(83, 69)
16-Dehydroprogesterone	234	26,100	E	(83, 66)
3-benzylthioenol ether	242, 268	18,600, 22,900	A	(333)
16-Methyl-16-dehydroprogesterone	250, 310	27,500, 260		(432)
17-(17²-Oxopropylidene)-4-androsten-3-one	242, 314	28,200, 220	A	(310)
α,β-Conjugated ketone + α,β-conjugated nitrile:				
20-Cyano-21-hydroxy-4,17-pregnadien-3-one	236	47,900	A	(161)
α,β-Conjugated ketone + dienone:				
1,4,16-Pregnatriene-3,20-dione	241	14,800	A	(347)
α,β-Conjugated ketone + trienone:				
1,4,6,16-Pregnatetraen-3,20-dione	234, 298	21,900, 15,500	A	(99)
Diene + cyclobutenolide:				
Anhydroadynerigenin	247	12,600		(418)
α,β-Conjugated ketone + cyclobutenolide:				
3-Keto-21-oxy-4,20(23)-norcholadienic acid lactone	241, 310	21,900, 69		(359)
α,β-Conjugated ketone + cyclopentenolide:				
Anhydrotelocinobufagon	240, 300	17,000, 5,250	A	(275)
α,β-Conjugated ketone + benzenoid ring A:				
3-Methoxy-1,3,5,14-estratetraen-16-one	227, 280	18,600, 2,510	A	(439)
17-Acetyl-3-hydroxy-1,3,5,16-estratetraene	230, 280	15,800, 2,950	A	(99)
20-semicarbazone	266	28,800	C	(99)
17-Acetyl-3-hydroxy-1-methyl-1,3,5,6,16-estrapentaene	228, 266, 306	33,900, 8,130, 1,780	A	(99)
β-Conjugated ketone + phenylketone				
24-Phenyl-4-cholene-3,24-dione	240, 280(i)†	25,100, 1,400	A	(245)

* A = ethanol; C = chloroform; E = ethyl ether.
† (i) signifies an inflection.
‡ Since a bromine atom on the double bond should cause a large bathochromic shift, it is unlikely that the structural assignment is correct.

TABLE 30

Ultraviolet absorption of steroids containing a conjugated lactone ring

COMPOUND	$\lambda_{max.}$	$\epsilon_{max.}$	SOLVENT[a]	REFERENCES
Cyclobutenolides				
	mμ			
17-Cyclobutenolides:				
Acolongifloroside-E	217	15,100	A	(15)
Acolongifloroside-G	217	16,200	A	(15)
Acolongifloroside-H acetate	217	17,000	A	(15)
Acolongifloroside-J	217	15,500	A	(15)
Acolongifloroside-K acetate	217	16,200	A	(15)
Acovenoside-A	217	15,800	A	(118)
diacetate	217	~19,100	A	(416)
Acovenoside-B	217	~15,800	A	(118)
Acovenoside-C diacetate	217	17,800	A	(283)
Acovenosigenin-A diacetate	217	17,400	A	(118)
Adonitoxigenin	218	12,900	A	(225)
Al-dihydro-α-antiarin	217	10,500	A	(108)

TABLE 30—*Continued*

COMPOUND	$\lambda_{max.}$	$\epsilon_{max.}$	SOLVENT[a]	REFERENCES
Cyclobutenolides—*Continued*				
	mμ			
17-Cyclobutenolides:—Continued				
3β-Acetoxy-17α-hydroxy-20-allopregnene-21-acid lactone	215	8,300	A	(427)
Allouzarigenin-3 acetate	210	35,500[b]		(308)
α-Anhydrogenin acetate	217	16,200	A	(389)
α-Antiarin	217, 305[c]	12,000, 32	A	(108)
Corchortoxin	217		A	(221)
Courmontoside-A acetate	217, 280–290(i)[d]	15,900, ~79	A	(384)
Courmontoside-B acetate	217	15,500	A	(384)
Courmontoside-C	217, 280–300(p)[d]	15,500, ~50	A	(384)
Cryptograndoside-A	215, ~270[e]	13,500, ~500	A	(2)
Cryptograndoside-B	215, 270[e]	13,500, 2,200	A	(2)
16-acetate	215, 270[e]	14,100, 580	A	(2)
Cryptograndoside-C acetate	216, 275[e]	16,600, 850	A	(2)
Dehydroacovenoside-A diacetate	215, 292	17,400, 21	A	(416)
Desglucodigitalinum verum aus Adenium honghel	218	15,100	A	(196)
Digitalinum verum hexaacetate aus Adenium honghel	217	13,200	A	(196)
Desglucodigitalinum verum aus Adenium multiflorum	217	16,200	A	(197)
Digitoxigenin	216	16,600	A	(71)
β′-(3β,5α-Dihydroxyetioallocholanyl-17-$\Delta^{\alpha',\beta'}$-butenolide 3-acetate	219	20,000		(364)
3α,12β-Diacetoxy-21-oxy-20(22)-norcholenic acid lactone	220	20,000		(368)
3α,21-Diacetoxy-12β-oxy-20(22)-norcholenic acid lactone(23→12)	221	7,100		(305)
Emicymarin	217	16,200	A	(3)
Gofruside	217	10,000		(229)
Honghelοside-A	217, ~280(i)[d]	14,100, ~60	A	(196)
Honghelοside-C	217	14,100	A	(196)
acetate	216, ~280(i)	14,800, ~60	A	(196)
Honghelοside-D	217	14,100	A	(196)
Honghelοside-E	215	13,500	A	(196)
Honghelοside-G	217	15,800	A	(383)
β′-(Δ^5-3β-Acetatenorcholenyl-23)-$\Delta^{\alpha',\beta'}$-butenolide	217	11,200		(360)
α′-methyl	222	20,000		(362)
3β-Acetoxy-21-oxy-20(22)-norallocholenic acid lactone	220	25,100	A	(367)
3α-Hydroxy-21-oxy-20(22)-norcholenic acid lactone	221	22,400		(356)
3-acetate	220	25,100		(356)
3β-Acetoxy-21-oxy-5,20(22)-norcholadienic acid lactone	~222	~25,100		(358)
β′-(3β-Acetoxy-5-etiocholenyl-17)-α′-methyl-$\Delta^{\alpha',\beta'}$-butenolide	227	22,400		(362)
Monoanhydroconvallatoxigenin benzoate	270, 280		C	(419)
Neriifolin	217	10,200	A	(170)
Odorigenone-B	217, 280–290(i)	15,500, 43	A	(193)
Oleandrigenin	216, 270 (i)	14,000, —	A	(2)
Oleandrigenone	216, 270–290(i)	14,500, —	A	(2)
Ouabagenin-A acetate	217, 260(i)	14,100, —	A	(277)
Ouabagenin-B acetate	217, 305	14,100, 45	A	(277)
Pantroside acetate	215, 270–280(i)	17,400, 75	A	(119, 346)
Periplogenin	218	~15,800	A	(295)
acetate	~219	~12,600	A	(398)
Sarmentogenin 3β,11α-diacetate	218	~20,000		(224)
Sarmentoside-A acetate	217	18,200	A	(389)
Sarmentoside-A acetate acid methyl ester	217	16,600	A	(389)
Sarveroside	216, 280(i)	16,600, 80	A	(71)
Strophanthidin	216, 290–310(i)[c]	17,000, ~80	A	(3, 295)
Strophanthidol	217	15,500	A	(3)
Trianhydroperiplogen	285[f]	~400	D	(115)
Trianhydrostrophanthidin	279[f]	~400	A	(115)
β′-(3α,7α,12α-Trihydroxyetiocholanyl-17)-$\Delta^{\alpha',\beta'}$-butenolide	223	12,600		(184)
β′-(3α,7α,12β-Trihydroxynorcholanyl-23)-$\Delta^{\alpha',\beta'}$-butenolide-7,12-diacetate	217	12,600		(361)
Xysmalobigenin acetate	217	16,200	A	(193)
Xysmalobin	215	18,200	A	(193)
Conjugated cyclobutenolides				
Δ^{16}-*17-Cyclobutenolides:*				
Anhydroadynerigenin	280	25,100		(418)
16-Anhydrodesglucodigitalinum verum diacetate	270	18,600	A	(197)

TABLE 30—*Concluded*

COMPOUND	$\lambda_{max.}$	$\epsilon_{max.}$	SOLVENT[a]	REFERENCES
Conjugated cyclobutenolides—*Continued*				
	mμ			
Δ^{16}-17-Cyclobutenolides:—Continued				
16-Anhydrodigitalinum verum	272	17,000	A	(196)
16-Anhydrogitoxigenin acetate	271	18,600	A	(2, 272)
Desacetylanhydrocryptograndoside-A	220, 277[g]	5,000, 17,800	A	(2)
16-Desacetylanhydroöleandrin	~220, 270[g]	~ 5,000, 17,400	A	(2)
acetate	~220, 270[g]	~ 5,000, 17,000	A	(2)
16-Desacetylanhydrocryptograndoside-B	~220, 270[g]	~ 5,000, 16,200	A	(2)
Desacetylanhydrohongheloside-A	~220, 270[g]	~ 5,000, 16,600	A	(196)
Hongheloside-F	~220, 270[g]	~ 5,000, 16,600	A	(196)
β'-(3β-Acetoxy-16-etioallocholenyl-17)-$\Delta^{\alpha',\beta'}$-butenolide	273	22,400		(369, 363)
$\Delta^{14,16}$-17-Cyclobutenolides:				
Anhydro-16-dehydrodigoxigenin diacetate	332	17,800		(299)
14,16-Dianhydrogitoxigenin	223, 338	11,500, 20,400	A	(385, 417)
β'-(3β-Acetoxy-14,16-etioallocholadienyl-17)-$\Delta^{\alpha',\beta}$-butenolide	332	22,400		(299)
Dianhydroöleandrigenone	337	~50,100[b]	A	(417)
Cyclopentenolides				
17-Cyclopentenolides:[f]				
Bufotalin	303	5,900		(83, 129, 274, 434)
Cinobufagin	293		C	(83, 420)
Cinobufotalin	295			(238)
Desglucohellebrin acid acetate methyl ester	308	5,020		(72)
γ-Bufogenin	300			(434)
Hellebrigenol 3-acetate	300	7,080	A	(387)
Hellebrin	300	6,300	A	(386, 223)
Marinobufagin	300		C	(420)
14-Monoanhydrobufotalin acetate	296	5,100	A	(274)
Scillaren-A	300	~11,000	A	(410)
Scillarenin	300	5,250	A	(410)
Scillarenone	240, 300[h]	17,800, 5,500	A	(410)
Scillaridin-A	230, 300[i]	17,000, 5,010	A	(410)
Scilliroside	300	~ 6,300	A	(409)
tetraacetate	300	3,980	A	(411)
Scillirosidin	~300	~ 6,300	A	(409)
Tetraacetylanhydrodehydroscilliroside	~287[j]	~15,800	A	(411)
Tetraacetyldehydroscilliroside	300	5,000	AD	(411)
$\Delta^{14,16}$-17-Cyclopentenolides:				
Bufotalien	300			(129)
Bufotalienone	300			(129)
16-Desacetyl-14,16-bufotalin acetate	300[k]	16,600	A	(274)

[a] A = ethanol; AC = sample dissolved in a minimum of chloroform and diluted with ethanol; C = chloroform.
[b] The extinction coefficient is too high.
[c] The band at 305 mμ can probably be attributed to an aldehyde group.
[d] (i) signifies an inflection; (p) signifies a plateau.
[e] The band at 270–275 mμ is due to the presence of a small amount of the C_{16}-anhydro compound.
[f] There is indication of a band below 220–230 mμ.
[g] The band at 220 mμ indicates the presence of starting material, a non-conjugated cyclobutenolide.
[h] The band at 240 mμ is due to the presence of a Δ^4-en-3-one component.
[i] The broad band at 230 mμ is due to the presence of a $\Delta^{3,5}$-diene component.
[j] The band at approximately 287 mμ is a composite curve of two isolated chromophoric systems of which one is the cyclopentenolide and the second must be a conjugated system that absorbs at 270–280 mμ.
[k] The band at 300 mμ is quite broad, continuing in a shallow decline from 340 to 380 mμ.

TABLE 31

Ultraviolet absorption of steroids containing benzenoid rings

COMPOUNDS	$\lambda_{max.}$	$\epsilon_{max.}$	SOLVENT†	REFERENCES
Benzenoid ring A*				
	mμ			
17-Desoxyestrone	280	2,510		(315, 200)
1,3,5,16-Estratetraen-3-ol	280	2,510		(315)
17α-Estradiol	280		A	(129)
17β-Estradiol	280	2,000	A	(83, 113)
	300		AA	(83)
17-acetate	280	2,640	A	(100)
3,17-diacetate	268	700		(208)
3,17-dibenzoate	230, 265(i)‡	17,400, —	A	(77)

TABLE 31—*Continued*

COMPOUNDS	$\lambda_{max.}$	$\epsilon_{max.}$	SOLVENT†	REFERENCES
Benzenoid ring A*—*Continued*				
	mμ			
"α"-Dihydroequilin	281, 290(i)	1,960, ~1,800	A	(75, 16)
3-Hydroxy-1,3,5-estratrien-16-one	281	2,190	A	(439)
Estrone	280	2,300	A	(83, 73)
	300		AA	(83, 73)
3-acetate	260	1,040	A	(83)
3-methoxy	280		A	(83, 73)
3-sodium sulfonate	272	850	M	(83, 59)
17-ethylene hemithioketal	282	1,950	A	(335)
Equilin	280	2,000	A	(83,270)
16-Epiestriol (isoestriol-A)	280	2,300	A	(195)
Estriol (theelol)	280	2,300	A	(83, 73)
	300		AA	(83, 73)
17-Ethynylestradiol	280	2,140	A	(77)
3-acetate	268	850	A	(77)
3-methoxy	280	2,280	A	(77)
3-Hydroxy-1,3,5-estratriene-17-carboxylic acid	280	2,120	A	(106)
17-methyl ester	280	2,460	A	(106)
17-ethyl ester	282	2,075	A	(113)
3-methoxy 17-methyl ester	280	2,290	A	(106)
17-Acetyl-3-hydroxy-1,3,5-estratriene	222, 280	6,610, 2,510	A	(99)
17-Acetyl-3-hydroxy-16-methoxy-1,3,5-estratriene	280	2,140	A	(99)
17-Acetyl-3,17α-dihydroxy-1,3,5-estratriene	280	1,950	A	(99)
17-(β-Acetoxyacetyl)-3-methoxy-1,3,5-estratriene	220(i)‡, 278	—, 2,450	A	(106)
19-Nor-1,3,5-cholestatrien-3-ol	284	1,590	A	(334)
3-acetate	265	430	A	(334)
1-Methyl-1,3,5-cholestatrien-7-one	285		A	(222)
Doisynolic acid	281	1,820	A	(77)
methyl ester	282	2,050		(157)
Marianolic acid dimethyl ester	282	1,580		(157)
1-Methyldoisynolic acid (?)§	285	1,410	A	(103)
1-Methylestradiol	284	1,910	A	(100a)
17-acetate (?)§	282	2,300	A	(208)
3,17-diacetate	268	340	A	(100a)
3,17-dipropionate	268	340	A	(100a)
2-bromo (?)§	289	2,630	A	(104)
2-bromo 3,17-diacetate (?)§	273	470	A	(104)
1-Methylestrone	282	1,820	A	(100a)
3-acetate	268	330	A	(100a)
3-Hydroxy-1-methyl-1,3,5-estratriene-17-carboxylic acid (?)§	283	2,340	A	(102)
3-acetate 17-methyl ester (?)§	267	301	A	(102)
3-methoxy (?)§	278–284	2,040	A	(106)
17-Acetyl-3-hydroxy-1-methyl-1,3,5-estratriene	284	2,040	A	(99)
3-acetate	268	390	A	(99)
17-(β-Acetoxyacetyl)-3-methoxy-1-methyl-1,3,5-estratriene (?)§	278–284	2,140	A	(106)
3-Hydroxy-1-methyl-19-nor-1,3,5-cholatrienic acid (?)§	283	2,400		(205)
3-Hydroxy-1-methyl-19-nor-1,3,5-cholestatriene (?)§	284	2,000	A	(331)
Conjugated benzenoid ring A				
Δ^6				
6-Dehydroestradiol	262, 302	10,000, 2,950	A	(100)
17-acetate	222, 262, ~270, 302	28,800, 8,510, ~6,920, 2,950	A	(100)
3,17-diacetate	264	10,200	A	(100)
6-Dehydroestrone	220, 262, ~272(i), 304	30,900, 8,910, ~6,300, 2,750	A	(228, 296)
19-Nor-1,3,5,6-cholestatraen-3-ol	224, 266, 304	30,900, 9,120, 1,620	A	(334)
3-acetate	226, 264	31,600, 12,300	A	(334)
3-benzoate	230, 262	30,900, 10,700	A	(334)
3-(*p*-nitrobenzoate)	264	23,400	C	(334)
1-Methyl-6-dehydroestradiol	226, 266	37,200, 8,900	A	(100a)
3,17-diacetate	222, 264	28,800, 9,100	A	(100a)
1-Methyl-6-dehydroestrone	228, 268, 306	30,900, 7,940, 1,910	A	(100a)
3-acetate	222, 264	27,500, 8,510	A	(100a)
1-Methyl-19-nor-1,3,5,6-cholestatetraen-3-ol	228, 266, ~275(i), 304	~25,000, ~7,900, ~6,300, ~1,600	A	(331)
3-acetate	224, 266	26,300, 8,710	A	(331)

TABLE 31—*Continued*

COMPOUNDS	$\lambda_{max.}$	$\epsilon_{max.}$	SOLVENT†	REFERENCES
		Conjugated benzenoid ring A—*Continued*		
	mμ			
$\Delta^{3(9)}$				
2-Methyl-7-methoxy-1,2,3,4,9,10-hexahydrophenanthrene-1,2-dicarboxylic acid dimethyl ester	275	18,500	A	(16, 159)
α-Monodehydrodoisynolic acid 7-methyl ether	~275	~15,800	A	(160)
3-Hydroxy-1,3,5,8-estratetraen-16-one	273, 336, 363	14,500, 230, 170	A	(439)
3-methoxy	273	17,800	A	(439)
8-Dehydro-14-isoestrone (isoequilin-A)	275	16,000	A	(16, 160, 190)
3-methoxy	275	16,000	A	(16, 160)
3-methoxy (racemic mixture)	270, 335	15,800, 32	A	(160)
$\Delta^{9(11)}$				
2-Methyl-7-methoxy-1,2,3,9,10,11-hexahydrophenanthrene-1,2-dicarboxylic acid dimethyl ester	264, 299	20,900, ~3,200	A	(159, 16)
β-9-Dehydro-14-isoestradiol	264, 300	18,000, 3,000	A	(16)
9-Dehydro-14-isoestrone	264, 299	~18,000, ~3,000	A	(16)
3-methoxy	264, 299	~18,000, ~3,000	A	(16)
8-Hydroxy-9-dehydro-14-isoequilin	270	16,500	A	(83, 190)
6-keto:				
β-Estradiol-6-one	256, 326	8,000, 3,000		(250, 83)
3,17-diacetate	~250, ~300	~9,000, ~1,900		(250)
Miscellaneous:				
$\Delta^{1,1'}$-2'-Keto-2-methyl-7-methoxy-3,4,9,10-tetrahydro-1,2-cyclopentanophenanthrene	258, 280(i)‡, 360	10,700, 5,000, 27,500	A	(439)
		Benzenoid ring B		
3-Hydroxy-5,7,9-estratrien-17-one	270, 278	345, 240	A	(152, 151)
22-Dihydroneoergostatriene	~224, ~269, ~277	~10,000, ~400, ~250	A	(149)
Epineoergosterol	270	500	E	(83, 442)
Neoergosterol	268	500	A	(83, 269)
Norsterol	270			(83, 381)
		Conjugated benzenoid ring B		
Δ^{3}				
3-Methoxy-3,5,7,9,22-ergostapentaene	270, ~280	16,200, ~15,000	E	(442, 83)
3-Methoxy-3,5,7,9-ergostatetraene	270	20,500	E	(83, 442)
3,5,7,9-Ergostatetraen-17-one	268	4,600		(152)
Neoergostapentaene	~224, ~231, ~268, ~308, ~314, ~323	~25,100, ~27,000, ~6,300, ~200, ~80, ~100	A	(149)
22-Dihydroneoergostatetraene	~224, ~230, ~268, 308, ~314, ~323	~20,000, ~18,000, ~8,000, ~400, ~200, ~250	A	(149)
Δ^{11}				
3-Acetoxy-11-dehydroneoergosterol	270	11,500		(454)
		Benzenoid rings AB		
β-*dl*-Equilenane	231, 282, 322	93,300, 5,760, 910	A	(215)
3-Desoxyequilenin	~282, ~321	~5,000, ~600	A	(312)
cis-3-Methoxy-16-equilenone	229, 265, 275 283(i)‡, 319, 334	64,600, 5,890, 5,750, 3,890, 1,860, 2,340	A	(440)
trans-3-Methoxy-16-equilenone	232, 269, 278, 287(i), 323, 336	64,600, 5,130, 5,620, 3,890, 2,040, 2,450	A	(440)
Equilenin	230, 270, 282, 292, 328, 340	—, 7,080, 7,420, 5,500, 3,800, 4,790	A	(228, 14, 16)
17-(2,4-dinitrophenylhydrazone)	370	102,000¶	C	(186)
Isoequilenin	267, 278, 289, 325, 338		A	(16)
α-6-Methoxy-17-equilenone	225, 240, 303	28,800, 42,700, 6,460	A	(214)

TABLE 31—*Continued*

COMPOUNDS	$\lambda_{max.}$	$\epsilon_{max.}$	SOLVENT†	REFERENCES
		Benzenoid rings AB—*Continued*		
	mμ			
Tetradehydroneoergosterol	250, 280, >340		E	(83, 192)
3-acetate	240, 280			(83, 192)
22-Dihydrotetradehydroneoergosterol acetate	280	4,900	E	(83, 442)
7-Methylbisdehydrodoisynolic acid methyl ester	268, 276, 286, 315, 333	~5,600, 6,580, ~4,500 ~2,000, 2,720	A	(156)
1-Methyl-17β-dihydroequilenin	~236, ~272, ~284, ~295, ~329, ~344	~79,000, ~7,000, ~6,900, ~5,600, ~2,000, ~2,500	A	(100a)
3,17-diacetate	~234, ~278, ~316, ~330	~100,000, ~8,900, ~2,200, ~2,500	A	(100a)
1-Methylequilenin	~235, ~273, ~285, ~297, ~330, ~344	~63,000, ~5,600, ~6,300, ~4,500, ~2,000, ~2,500	A	(100a)
3-acetate	~236, ~278, ~316, ~330	~80,000, ~7,100, ~,1800, ~2,500	A	(100a)
1-Methyl-19-nor-1,3,5,6,8-cholestapentaen-3-ol(?)§	~240, ~258, ~264, ~282, ~299, ~315, ~340	~32,000, ~16,000, ~16,000, ~5,000, ~7,900, ~4,000, ~2,000	A	(96)
6-Methoxy-17-equilenone-15-carboxylic acid	243, 300	38,900, 6,160	A	(214)
		Conjugated benzenoid rings AB		
Δ^{14}				
14-Dehydroequilenane	255, 285, 295, 305	45,700, 12,600, 15,500, 12,900	A	(440)
3-Methoxy-14-dehydroequilenane	245(i), 254, 263, 281, 292, 303	33,900, 45,700, 44,700, 13,800, 18,600, 17,800	A	(440)
16-Hydroxy-14-dehydroequilenane	245(i), 254, 262, 283, 292, 305	34,700, 46,800, 41,700, 13,500, 16,600, 13,500	A	(440)
14-Dehydro-17-equilenone	251, 281, 292, 303	49,000, 12,300, 14,400, 11,500	A	(215)
3-Methoxy-14-dehydroequilenin	253, 262, 294, 305, 333, 350	46,800, 45,700, 15,800, 14,800, 2,190, 1,740	A	(216)
6-Methoxy-14-dehydro-17-equilenone	260, 302, 330, 347	44,700, 8,710, 4,170, 2,950	A	(214)
$\Delta^{14(20)}$				
3'-Keto-3,4-dihydro-1,2-cyclopentanophenanthrene	219, 241, 250(i), 260(i), 270, 280, 324, 335, 360(i)	38,000, 6,610, 7,240 17,000, 38,000, 46,800, 14,200, 15,500, 8,910	A	(436)
$\Delta^{1,1'}$-2'-Keto-3,4-dihydro-1,2-cyclopentanophenanthrene	219, 238, 245, 255(i), 266, 276, 316, 360(i)	20,900, 13,200, 13,300, 18,600, 36,300, 42,700, 29,500, 4,900	A	(436)
$\Delta^{1,1'}$-2'-Keto-2-methyl-3,4-dihydro-1,2-cyclopentanophenanthrene	220, 231, 246, 257(i), 266, 275, 315, 360(i)	21,900, 16,200, 11,600, 16,600, 32,400, 38,000, 25,700, 4,070	A	(436)
$\Delta^{1,1'}$-2'-Keto-2-methyl-7-hydroxy-3,4-dihydro-1,2-cyclopentanophenanthrene	226, 263(i), 268(i), 283, 342	19,500, 20,000, 27,500, 28,800, 24,500,	A	(436)
7-acetate	222, 235(i), 258(i), 268, 277, 318, 353(i)	20,900, 12,900, 19,100, 33,900, 39,800, 26,900, 6,030	A	(436)
7-methoxy	226, 262(i), 274(i), 281, 333	21,900, 22,400, 28,200, 31,600, 27,500	A	(436)
$\Delta^{1,1'}$-2'-Keto-3'-hydroxy-2-methyl-3,4-dihydro-1,2-cyclopentanophenanthrene	219, 239, 247, 260(i), 268, 277, 318, 360(i)	20,900, 12,000, 12,200, 17,800, 30,900, 36,300, 27,500, 4,790	A	(436)
$\Delta^{1,1'}$-2',3'-Diketo-2-methyl-3,4-dihydro-1,2-cyclopentanophenanthrene	220(i), 236, 271, 280, 291, 333(i) 345	18,200, 23,400, 15,800, 18,200, 14,100, 16,600, 17,000	A	(436)

TABLE 31—*Concluded*

COMPOUNDS	$\lambda_{max.}$	$\epsilon_{max.}$	SOLVENT†	REFERENCES
Conjugated benzenoid rings AB—*Continued*				
	mμ			
Δ^{14}-*15-carboxylic acid:*				
Methyl 14-dehydro-17-equilenone-15-carboxylate	219, 243, 247, 264, 310	29,500, 20,000, 20,000, 26,900, 17,800	A	(216)
Methyl 3-methoxy-14-dehydroequilenin-15-carboxylate	223, 265, 323	30,200, 25,100, 18,200	A	(216)
Methyl 6-methoxy-14-dehydro-17-equilenone-15-carboxylate	213, 224, 269, 311, 354	24,500, 25,100, 24,000, 12,900, 5,890	A	(214)
Methyl-11,12,13,17-tetrahydro-16*H*-cyclopentanophenanthrene-16-keto 15-acetate	220, 236, 267, 277, 316	24,600, 10,000, 38,000, 45,700, 25,700	A	(421)
Δ^{15}-*17-one:*				
15-Dehydro-17-equilenone	230, 270, 321	77,600, 6,760, 660	A	(215)
Δ^{15}-*carboxylic acid-17-one:*				
15-Dehydro-17-equilenone-15-carboxylic acid	228, 273	89,100, 7,760	A	(214)
3-Hydroxy-15-dehydroequilenin-15-carboxylic acid				
3-methoxy	235, 318, 334	77,600, 2,880, 2,690	A	(214)
3-methoxy methyl ester	235, 275, 318, 333	57,500, 5,370, 2,090, 2,090	A	(214)
6-Hydroxy-15-dehydroequilenone-15-carboxylic acid				
6-methoxy	215, 243, 296, 327	39,800, 43,700, 5,890, 3,240	A	(214)
6-methoxy methyl ester	242, 296, 325	41,700, 5,890, 2,570	A	214)
$\Delta^{11(12),14(18)}$:				
3′,5-Dimethyl-1,2-cyclopentanophenanthrene	260, 280, 298	~58,000, ~13,000, ~9,500		(206)

* Many of the compounds in this group have an inflection near 220 mμ.
† A = ethanol; AA = alkaline ethanol, usually 0.1 *N*; C = chloroform; E = ethyl ether; M = methanol.
‡ (i) signifies an inflection.
§ It has been shown (101a) that these compounds are probably 4-hydroxy-1-methyl or 1-hydroxy-4-methyl derivatives, the latter structure being the more probable.
¶ The extinction coefficient is too high.

TABLE 32

Ultraviolet absorption of steroids containing phenyl chromophores

COMPOUNDS	$\lambda_{max.}$	$\epsilon_{max.}$	SOLVENT*	REFERENCES
	mμ			
Diphenylcarbinol:				
3α-Acetoxy-24,24-diphenylcholane-12α,24-diol	255	780	A	(77)
(3α,12β-Dihydroxypregnyl-20)-diphenylcarbinol	~262	~600	A	(397)
3α-Acetoxy-12α,22-oxido-22,22-diphenylbisnorcholane	~260	~600	A	(397)
Phenyl ketone:				
24-Keto-24-phenylnorcholane	243, 280	12,800, 1,030	A	(249)
3α,11α-Diacetoxy-24-keto-24-phenylnorcholane	243, 280	12,500, 980	A	(249)
Diphenylethylene:				
1′-Methyl-1′-(3α,11α-diacetoxyetiocholanyl-17)-2′,2′-diphenylethylene	245	11,800	A	(249)
1′-Methyl-1′-(3α,12 -dihydroxyetiocholanyl-17)-2′,2′-diphenylethylene				
3-acetate	~252	~12,200	A	(397)
3,12-diacetate	~252	~12,200	A	(397)
1′-Methoxy-1′-(3α,12β-dihydroxyetiocholanyl-17)-2′,2′-diphenyl ethylene	~250(p)†	~20,000	A	(397)

TABLE 32—*Concluded*

COMPOUNDS	$\lambda_{max.}$	$\epsilon_{max.}$	SOLVENT*	REFERENCES
	mμ			
Diphenylethylene:—Continued				
3-acetate	~250(p)	~20,000	H	(397)
3,12-diacetate	~250(p)	~20,000	H	(397)
3α,11α-Diacetoxyternorcholanyldiphenylethylene	250	17,200	A	(249)
3α,11α-Diacetoxybisnorcholanyldiphenylethylene	250	17,200	A	(249)
3α,12β-Diacetoxy-24,24-diphenyl-23-cholene	~250(p)	~20,000	C	(278)
Diphenylbutadiene:				
3α,12β-Diacetoxy-24,24-diphenyl-20(22),23-choladiene	~310(p)	~17,800	C	(278)
3α-Acetoxy-12,21-dibromo-11-keto-24,24-diphenyl-20(22),23-choladiene	325			(77)
Diphenylhexatriene:				
3α-Acetoxy-20-keto-21-(1,1-diphenylacrylal)pregnane 20-enol acetate	245, 335	16,200, 47,600	A	(141)
3α,12α-Diacetoxy-20-keto-21-(1,1-diphenylacrylal)pregnane 20-enol acetate	245, 335	18,500, 51,000	A	(141)
Conjugated phenylenone:				
Dehydroepiandrosterone-16-benzylidene	223, 295	8,300, 24,600	A	(370a)
3β,14-Dihydroxy-17-keto-5-androstene-16-benzylidene	221, 290	8,300, 24,700	A	(77)
3β,11α-Diacetoxy-20-ketopregnane-21-benzal				
-17α	294	23,400	A	(257, 249)
-17α	294	22,900	A	(257, 249)
-17β	294	22,500	A	(257, 249)
-17β	294	24,000	A	(257, 249)
3α,12α,20-Triacetoxy-17-pregnene-21-benzal	~294, ~304, ~320	~33,000, ~33,500, ~22,750		(259)
Conjugated phenyldienone:				
3β-Acetoxy-17-keto-14-epiandrostene-16-benzylidene	234, 256, 335	12,600, 8,500, 22,400	A	(370a)
3β-Acetoxy-17-keto-5,14-androstadiene-16-benzylidene	234, 256, 335	12,600, 8,710, 23,500	A	(370a)
3α-Hydroxy-20-keto-21-(1,1-diphenylacrylal)pregnane	242, 338	13,900, 31,800	A	(141)
3α,12α-Dihydroxy-20-keto-21-(1,1-diphenylacrylal)pregnane	242, 338	12,300, 29,000	A	(141)

* A = ethanol; C = chloroform; H = hexane.
† (p) signifies a plateau.

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ADDENDUM

It is interesting to note that the absorption (ϵ_{226} = 20,000; ϵ_{298} = 7000) of the $\Delta^{8(14),15}$-dien-7-ones is similar to that of the $\Delta^{8(14),9(11)}$-dien-7-ones (ϵ_{223} = 15,600; ϵ_{298} = 5000) given in the main body of the review. The structural assignment of the latter compounds has been open to question. This author preferred a $\Delta^{8(9),14}$-dien-7-one assignment, while Woodward (footnote in reference 404) preferred the $\Delta^{8(14),15}$-7-one structure. It appears that the latter assignment is correct. The conjugated double bond position can be definitely established if the carbonyl moiety is reduced by lithium aluminum hydride and the extinction coefficient of the resulting diene is determined. Though both the $\Delta^{8(14),15}$-diene and the $\Delta^{8(9),14}$-diene absorb at nearly the same point (248 mμ), there is a great difference in their extinction coefficients, the values being 8000 and 18,500, respectively.

COMPOUND	$\lambda_{max.}$	$\epsilon_{max.}$	SOLVENT*	REFERENCES
	m			
Diene:				
$\Delta^{8(14),15}$				
3β,7,20β-Trihydroxy-8,15-allopregnadiene	247	7,900	A	(472)
3,20-diacetate	246	7,100	A	(472)
3,7,20-triacetate	246	7,900	A	(472)
Triene:				
$\Delta^{6,8(14),9(11)}$				
3β-Acetoxy-6,8,9,22-ergostatetraene	233, 288	17,800, 6600	E	(471)
Enone:				
Δ^{4}-one-3				
6α-Acetoxyprogesterone	236	14,910	A	(469)
6α-Acetoxy-4-androsten-3,17-dione	235	15,520	A	(469)
Dienone:				
$\Delta^{6,8(9)}$-11-one				
3β-Acetoxy-14-hydroxy-6,8,22-ergostatrien-11-one	308	6,900	E	(471)
$\Delta^{8(14),15}$-7-one				
3β,20β-Dihydroxy-8,15-allopregnadien-7-one	226, 298	20,000, 6500	A	(472, 473)
3,20-diacetate	226, 297	21,400, 7600	A	(472, 473)
7-oxime	228, 298	20,000, 5360	A	(472, 473)
3α-Acetoxy-22,23-dibromo-8,15-ergostadien-7-one	224, 296	18,000, 6000	A	(470)
$\Delta^{8(9),14}$-11-one				
3β-Acetoxy-8,14-22-ergostatrien-11-one	291	11,500	E	(471)
Trienone:				
$\Delta^{6,8(9),14}$-11-one				
3β-Acetoxy-6,8,14,22-ergostatetraen-11-one	233, 326	15,100, 8900	E	(471)

* A = ethanol; E = diethyl ether.

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