London) for stimulating correspondence. Grateful thanks are due to the many investigators mentioned in this paper who have supplied us promptly and generously with various specimens required in this study.

DETROIT, MICHIGAN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WAYNE STATE UNIVERSITY]

Optical Rotatory Dispersion Studies. VIII.[1] α,β-Unsaturated Ketones and Solvent Effects[2]

BY CARL DJERASSI, ROSEMARIE RINIKER AND BERNHARD RINIKER

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The rotatory dispersion curves of a variety of steroidal as well as of simpler alicyclic unsaturated ketones are reported and correlations of certain structural groupings with characteristic dispersion features are discussed. The rotatory dispersion method has been used to settle certain stereochemical ambiguities of 19-nor steroids, and attention is called to the remarkable rotatory dispersion changes—ascribable to conformational alterations—observed with certain Δ^4-3-ketosteroids. The fine structure of many of the dispersion curves is particularly well resolved in non-polar solvents and is almost completely obscured in methanol. It is proposed that dioxane be used as the solvent of choice for all rotatory dispersion work concerned with α,β-unsaturated ketones.

The striking correlations between shapes of rotatory dispersion curves and chemical structure—initially encountered with steroidal ketones[3]—have recently been shown[1] to be applicable also to simpler alicyclic ketones. This enormous extension of the "rotatory dispersion method" with its important bearing on assignment of absolute configuration[1,4] and detection of subtle conformational factors[1,5] has made it necessary to collect rotatory dispersion curves of as many reference compounds as possible. The dispersion curves of some unsaturated ketones—chiefly Δ^4-3-ketosteroids[3b]—have already been recorded in the preceding seven papers[1,3] of this series, but it is the purpose of the present article to discuss this particular subject more fully and to offer a large number of additional examples.

Solvent Effect.—The relationship between ultraviolet absorption and anomalous rotatory dispersion has already been discussed.[6] It was pointed out that the rotatory dispersion method will generally be of value only where the dispersion curve shows "maxima" and "minima,"[3a] and these in turn will be produced only by optically active chromophores which absorb in a suitable spectral range. This range should not be too far in the ultraviolet in order to preclude measurements because of experimental limitations nor should the absorption be so intense as to prevent measurements because of lack of light transmission. This explains why ketones and aldehydes are nearly ideally suited for our purposes since saturated carbonyl compounds show a definite but weak absorption in the 270–300 mμ region[7] which produces strong abnormal rotatory dispersion[1,3] amenable to precise experimental detection by means of a spectropolarimeter.[8] From a practical standpoint, we have found dioxane and methanol to be the most satisfactory solvents—methanol because of its great optical transparency and dioxane because of its great solvent power for the compounds under investigation. It has already been noted earlier[9] that the shapes of the dispersion curves of *saturated* carbonyl compounds are identical in those two solvents but that in dioxane, the entire curve is shifted to longer wave length by about 8 mμ, a correction factor which easily can be taken into consideration.

α,β-Unsaturated ketones exhibit maximal ultraviolet absorption in the 220–260 mμ region which is so intense as to prevent rotatory dispersion measurements beyond *ca.* 280 mμ with the equipment available at the present time. However, in addition these ketones also show a weak band[10] above 300 mμ, and it is this absorption which is probably responsible for the rotatory dispersion features associated[1,3] with this chromophore. Attention has been called to the fact[10] that this low-intensity long wave absorption maximum—usually ill defined and frequently only appearing as an inflection with ethanol as the solvent—is shifted to longer wave length with concomitant increased resolution when a hydrocarbon solvent is employed for the spectral measurements. Such an effect should also be noticeable in the rotatory dispersion curves of unsaturated ketones, and we have selected octane, dioxane and methanol as typical solvents with increasing polarity. Two examples—the bicyclic (−)-*trans*-3-keto-9-methyl-$\Delta^{1,6}$-hexahydronaphthalene

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[1] Paper VII, C. Djerassi, R. Riniker and B. Riniker, THIS JOURNAL, **78**, 6362 (1956).

[2] Supported by a research grant from the Damon Runyon Memorial Fund for Cancer Research.

[3] (a) C. Djerassi, E. W. Foltz and A. E. Lippman, THIS JOURNAL, **77**, 4350 (1955); (b) E. W. Foltz, A. E. Lippman and C. Djerassi, *ibid.*, **77**, 4359 (1955); (c) A. E. Lippman, E. W. Foltz and C. Djerassi, *ibid.*, **77**, 4364; (d) C. Djerassi and R. Ehrlich, *ibid.*, **78**, 440 (1956); (e) C. Djerassi, W. Closson and A. E. Lippman, *ibid.*, **78**, 3163 (1956); (f) C. Djerassi and W. Closson, *ibid.*, **78**, 3761 (1956).

[4] C. Djerassi and W. Klyne, *Chemistry & Industry*, 988 (1956).

[5] To be published.

[6] Reference 3a and leading review articles given therein.

[7] *Cf.* A. Gillam and E. S. Stern, "Electronic Absorption Spectroscopy in Organic Chemistry," Edward Arnold, Ltd., London, 1954, p. 48.

[8] H. Rudolph, *J. Optical Soc. Am.*, **45**, 50 (1955); E. Brand, E. Washburn, B. F. Erlanger, E. Ellenbogen, J. Daniel, F. Lippmann and M. Scheu, THIS JOURNAL, **76**, 5037 (1954).

[9] Reference 3f, especially footnote 11.

[10] *Cf.* R. C. Cookson and S. H. Dandegaonker, *J. Chem. Soc.*, 1651 (1955), and references cited therein.

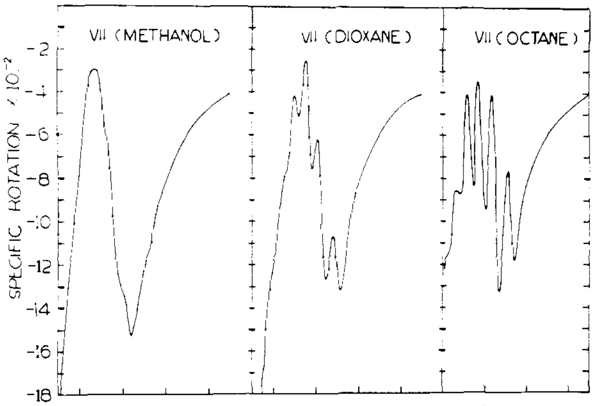

Fig. 1.—Rotatory dispersion curves of (−)-*trans*-3-keto-9-methyl-$\Delta^{1,8}$-hexahydronaphthalene (VII).

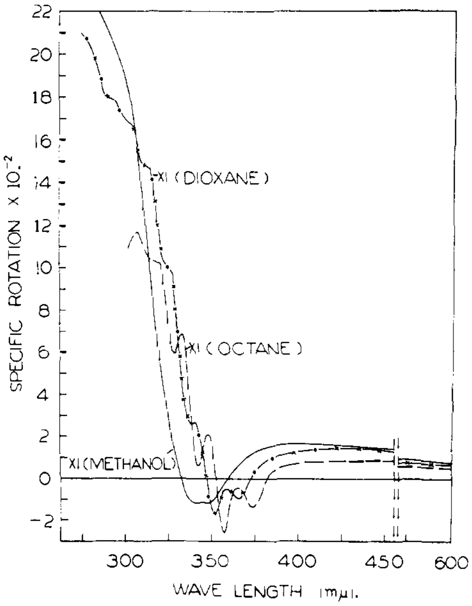

Fig. 2.—Rotatory dispersion curves of Δ^4-cholesten-3-one (XI).

(VII)[11,12] and the steroidal Δ^4-cholesten-3-one (XI)—are given in Figs. 1 and 2 and illustrate the impressive effect in going from the hydrocarbon solvent octane to the polar methanol. Essentially no resolution is effected with methanol, whereas a wealth of fine structure becomes apparent in octane. Furthermore, a bathochromic shift is observed by changing from a polar to a non-polar medium. While the resolution is not quite as satisfactory in dioxane, we have selected it as the solvent of choice for *unsaturated* ketones since many ketones (especially steroidal and triterpenoid) are not soluble in octane, and it is highly desirable to settle on one solvent for all measurements in order to eliminate this variable. As stated above,[9] either methanol or dioxane is suitable for *saturated* carbonyl compounds, and the former is probably to be recommended in these cases because it permits measurements farther into the ultraviolet (245–250 mμ). Fortunately, all of the earlier[1,3] measurements on conjugated ketones had been carried out in dioxane, but some of these were now repeated with a xenon lamp[3e] in order to go below 300 mμ, which had not been possible in the original investigations[3a–c] where only a zirconium lamp was available. The pertinent results will be discussed below.

Monocyclic and Bicyclic Ketones.—Several naturally occurring bi- and tricyclic terpenes and related compounds have already been investigated in the preceding paper[1] and the unsaturated ketones were usually bicyclic analogs of Δ^4-3-ketosteroids. Their rotatory dispersion curves were on the whole fully comparable to those of the corresponding steroids except where certain unusual conformational factors entered into the picture (*e.g.*, LVIII[1]). We should now like to record the rotatory dispersion curves of several mono- and bicyclic unsaturated ketones which can serve as reference compounds for future work.

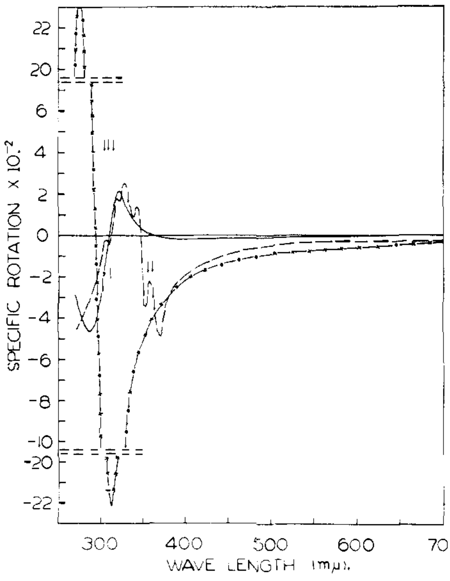

Fig. 3.—Rotatory dispersion curves of: (−)-menthone (I) (−)-piperitone (II), β-dihydroumbellulone (III).

An interesting series of compounds (I–VI), made available to us by Dr. R. H. Eastman[13] exemplifies the effect of a cyclopropane ring in conjugation with a carbonyl group (see also below for XLIII). (−)-Menthone (I) can be considered the parent ketone of this series,[14] and its rotatory dispersion curve (Fig. 3) is of the type to be expected from a cyclohexanone derivative.[3] (−)-Piperitone (II) is the simplest α,β-unsaturated alicyclic ketone which we have investigated so far, and it already shows the typical fine structure observed (Fig. 1) with the bicyclic ketone VII.[11] Introduction of a cyclopro-

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[11] A. J. Speziale, J. A. Stephens and Q. E. Thompson, THIS JOURNAL, **76**, 5011 (1954).

[12] We are greatly indebted to Drs. W. S. Knowles, Q. E. Thompson and O. Weinkauff (Monsanto Chemical Co., St. Louis, Mo.) for this substance.

[13] We are thankful to Dr. R. H. Eastman (Stanford University) for this gift. See Abstracts, Amer. Chem. Soc. Meeting, 1956, Dallas, p. 37-N; R. H. Eastman and S. K. Freeman, THIS JOURNAL, **77**, 6642 (1955), and earlier papers.

[14] For absolute configurations of monoterpenes, see A. J. Birch, *Ann. Repts.*, **47**, 192 (1951). It should be noted that I and II belong to enantiomeric series.

pane ring (Fig. 3) as in β-dihydroumbellulone (III) does not produce fine structure but only greatly magnified "maxima" and "minima" of over 2000°. This effect is most noticeable in umbellulone (IV) itself (Fig. 4) which shows a rather low specific rotation ($[\alpha]_D$ − 42.5 ± 2°) at the conventional sodium D line (589 mμ) while its rotation at 287.5 mμ amounts to −18400 ± 500°. The dispersion curves of two other cyclopropane-containing ketones (V and VI) derived from umbellulone are collected in Fig. 4, and while no definite configurational conclusions can be drawn from them at this time, they exemplify in a very striking manner the analytical applications which can be derived from a knowledge of such dispersion curves. All of the ketones shown in Fig. 4 possess only low rotation at the D line but extremely high values in the 300 mμ region. Clearly, if only one rotation value is given for characterization purposes, one of the "maxima" or "minima" should be picked rather than $[\alpha]_D$ which in these instances is relatively insignificant.

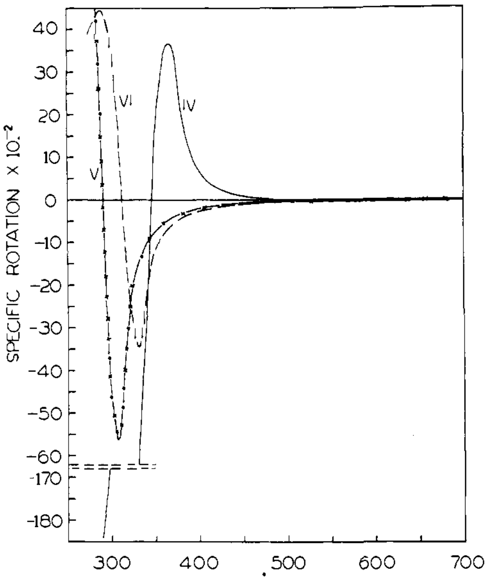
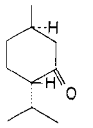
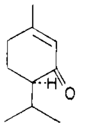


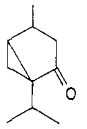
Fig. 4.—Rotatory dispersion curves of: umbellulone (IV), tricyclic ketone V from umbellulone, epoxyumbellulone (VI).



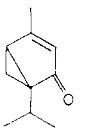
I



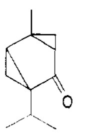
II



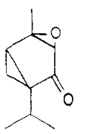
III



IV



V



VI

The dispersion curves of the five bicyclic unsaturated ketones VII–X again show an abundance of fine structure in the ultraviolet region. The curves of VII (Fig. 1) and VIII[12] (Fig. 5) do not resemble those of their steroid counterparts (Δ^1-cholesten-3-one and Δ^2-cholesten-1-one (XXXVIII)), but this may very well be due to conformational changes produced by the additional unsaturation in the second ring. The effect of a β-methoxy substituent is shown by comparing IX[12] with VIII (note antipodal relationship) while α-(Xa) and β-vetivone (Xb) represent the first examples of a cycloheptenone whose rotatory dispersion has been measured. This constitutes another example for the remarkable susceptibility (see below) of cyclic α,β-unsaturated ketones to conformational changes.

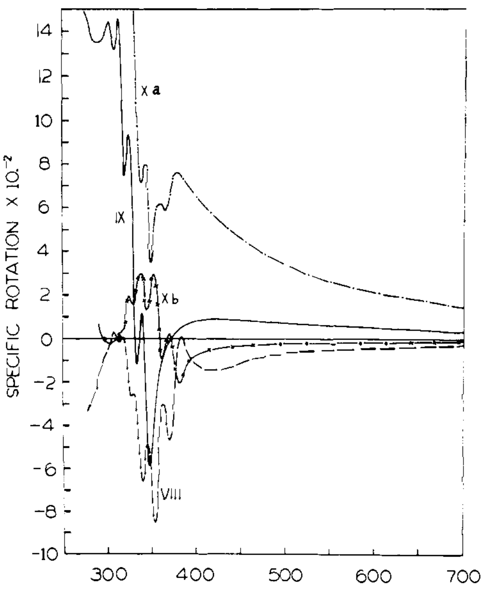
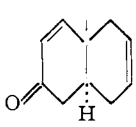
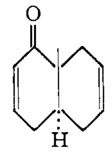


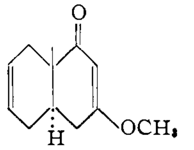
Fig. 5.—Rotatory dispersion curves of: (−)-*trans*-1-keto-9-methyl-$\Delta^{2,6}$-hexahydronaphthalene (VIII), (+)-*trans*-1-keto-3-methoxy-9-methyl-$\Delta^{2,6}$-hexahydronaphthalene (IX), α-vetivone (Xa), β-vetivone (Xb).



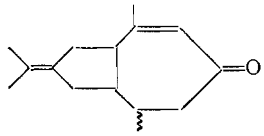
VII



VIII



IX



Xa, "α"
b, "β"

Steroidal α,β-Unsaturated Ketones.—Most of the Δ^4-3-ketones studied earlier[3] possessed additional, strongly active carbonyl chromophores which tended to overshadow the low wave length portion of the rotatory dispersion curve. The only examples where there were not present additional structural complications were represented by Δ^4-cholesten-3-one (XI)[3c] and by testosterone (XIII).[3b] Attention was called to the fact that in addition to the very characteristic fine structure between 350–380 mμ (which was observed in all Δ^4-3-ketosteroids[1,3]) there was present a flat peak near 300 mμ. The importance of this "maximum" could not be assessed at that time,[3c] particularly since it was usually only defined by one or two inaccurate readings at the extreme lower limit of the zirconium lamp. We have now repeated these measurements with a xenon lamp[3e] and as shown in Fig. 2 with Δ^4-cholesten-3-one (XI), there is, in fact, no "maximum" associated with the Δ^4-3-keto moiety at 300 mμ but rather just a drift to increasingly positive rotation with some inflections indicative of fine structure which could be resolved somewhat in octane solution. The dispersion curve of testosterone (XIII) determined with a xenon lamp is reproduced in Fig. 6 and is essentially identical with the earlier reported one[3b] except for the absence of a peak near 300 mμ. At the same time, there have been determined the dispersion curves of a variety of substituted testosterones and as is apparent from Fig. 6 and/or the Experimental section, substitution of halogen (XIV, XV) or methyl (XVI) at C-4[15] has very little effect on the over-all shape of the curve except for some intensity variations. Some loss in fine structure in the 350 mμ region is noticeable in 2α-acetoxytestosterone acetate (XVIII) but not in 2α-methyltestosterone (XVII).

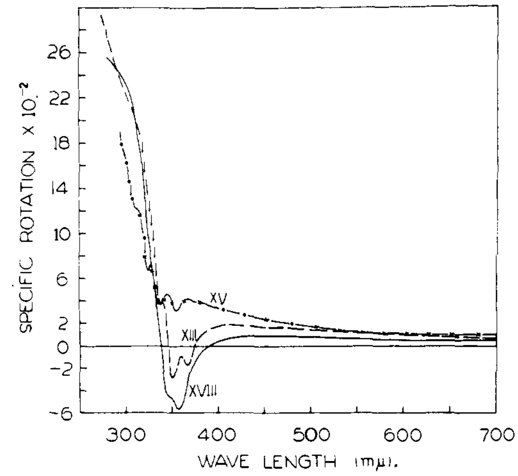
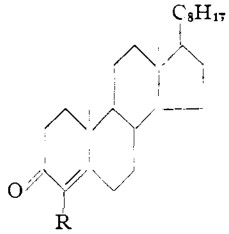
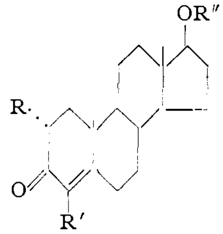


Fig. 6.—Rotatory dispersion curves of: testosterone (XIII), 4-bromotestosterone (XV), 2α-hydroxytestosterone 2,17-diacetate (XVIII).





XI, R = H
XII, R = CH$_3$

XIII, R = R′ = R″ = H
XIV, R′ = Cl; R = R″ = H
XV, R′ = Br; R = R″ = H
XVI, R′ = CH$_3$; R = R″ = H
XVII, R = CH$_3$; R′ = R″ = H
XVIII, R = OAc; R′ = H; R″ = Ac

Support for the important generalization that an angular hydrogen or methyl are equivalent insofar as the characteristic rotatory dispersion features of Δ^4-3-ketosteroids are concerned was presented in an earlier paper[1] where the striking similarity of the rotatory dispersion curves of testosterone (XIII) and 19-nortestosterone (XIX) was noted. The utility of this observation is illustrated in Fig. 7 where are reproduced the curves of two 19-nortestosterone derivatives about which there existed some uncertainty with respect to the configuration at C-10. The first of these was 1-methyl-19-nortestosterone (XX)[16] and the other 10-hydroxy-19-nortestosterone (XXI), a microbiological oxidation product[17] of 19-nortestosterone. The close similarity of their respective dispersion curves with those of

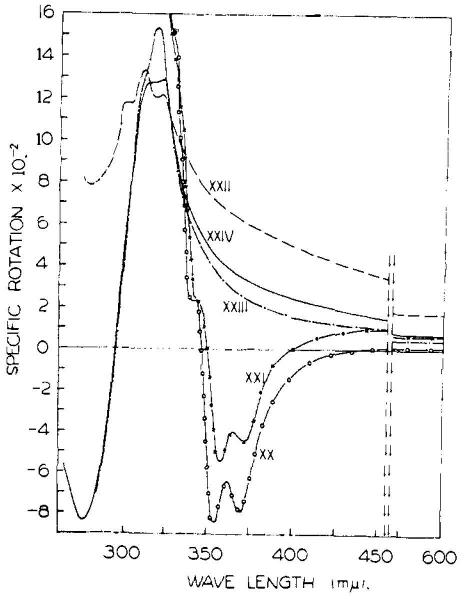
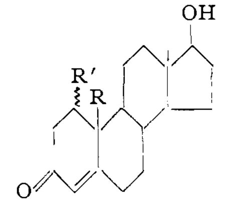
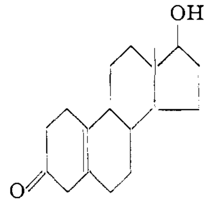


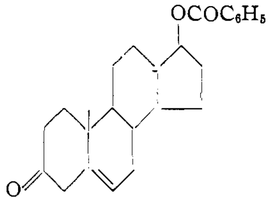
Fig. 7.—Rotatory dispersion curves of: 1-methyl-19-nortestosterone (XX), 10β-hydroxy-19-nortestosterone (XXI), $\Delta^{5(10)}$-estren-17β-ol-3-one (XXII), Δ^5-androsten-17β-ol-3-one benzoate (XXIII), $\Delta^{5,14}$-androstadien-3β-ol-17-one acetate (XXIV).



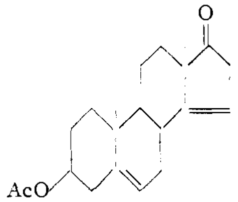
XIX, R = R′ = H
XX, R = H; R′ = CH$_3$
XXI, R = OH; R′ = H



XXII



XXIII



XXIV

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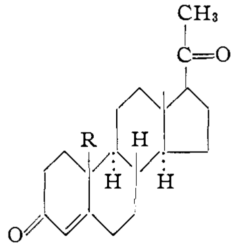
[15] The dispersion curve of 4-methyl-Δ^4-cholesten-3-one (XII) is also very similar to that of Δ^4-cholesten-3-one (XI) (*cf.* ref. 1).

(16) H. J. Ringold, G. Rosenkranz and F. Sondheimer, THIS JOURNAL, **78**, 2477 (1956).

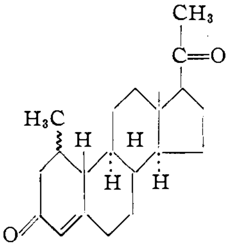
(17) R. L. Pederson, J. A. Campbell, J. C. Babcock, S. H. Eppstein, H. C. Murray, A. Weintraub, R. C. Meeks, P. D. Meister, L. M. Reineke and D. H. Peterson, *ibid.*, **78**, 1512 (1956).

testosterone (XIII) (Fig. 6) and 19-nortestosterone (XIX)[1] leaves little doubt as to the β-configuration of the C-10 substituent. In Fig. 7 are also given the dispersion curves of three β,γ-unsaturated ketones, and it is interesting to note that while the curves of the Δ^5-3-ketone XXIII and the Δ^{14}-17-ketone XXIV do not differ very much from those of the corresponding dihydro-*trans*-ketones, this is not the case with the $\Delta^{5(10)}$-isomer XXII of 19-nortestosterone.

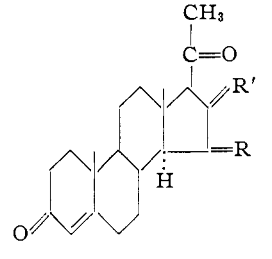
The great resemblance of the dispersion curve (Fig. 8) of 19-norprogesterone (XXVa) to that of progesterone (XXVb)[3b] represents a further illustration of the unimportance of the angular substituent in Δ^4-3-ketosteroids. This provided another opportunity to achieve a stereochemical assignment by the rotatory dispersion method. In a recent synthesis[18] of 1-methyl-19-norprogesterone (XXVI), there were isolated two isomers of which only one (m.p. 152°) exhibited progestational activity. The rotatory dispersion curve (see Experimental) of the m.p. 152° isomer (XXVIa) is very similar to that of 19-norprogesterone (XXVa) while the m.p. 171° isomer (XXVIb) exhibits a completely different curve (Fig. 8) which will be discussed below in connection with 8α-steroids. Since the dispersion curve of Δ^4-3-ketosteroids is rather sensitive to conformational changes (see Fig. 15 and appropriate discussion), it can be concluded that the biologically active 1-methyl-19-norprogesterone (XXVIa) possesses the same conformation and stereochemistry at all relevant asymmetric centers as do 19-norprogesterone (XXVa) and progesterone (XXVb). As far as the orientation of the 1-methyl group is concerned, we believe that it is α since models indicate considerable interference between the equatorially oriented 1β-methyl substituent and the 11-methylene group. The same statement can also be made about the configuration of the 1-methyl function in 1-methyl-19-nortestosterone (XX.)[16]



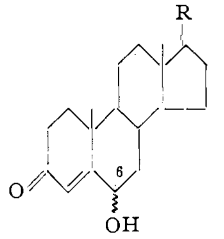
XXVa, R = H
b, R = CH_3



XXVIa, m.p. 152°
XXVIb, m.p. 171°



XXVII, R = O; R' = H_2
XXVIII, R = H_2; R' = O



XXIX, R = C_8H_{17}; 6α
XXX, R = C_8H_{17}; 6β
XXXI, R = OH; 6β

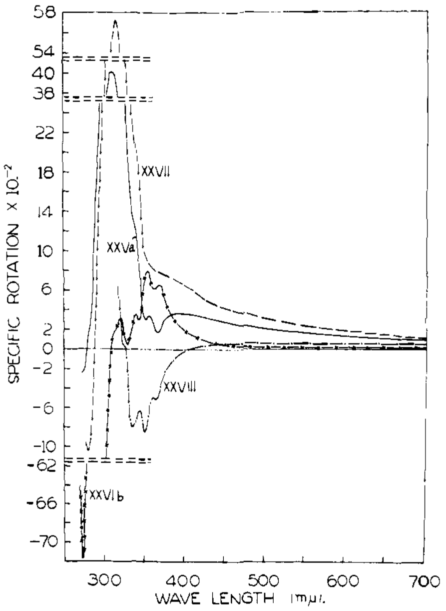


Fig. 8.—Rotatory dispersion curves of: 19-norprogesterone (XXVa), 1-methyl-19-norprogesterone (m.p. 171°) (XXVIb), 15-ketoprogesterone, (XXVII) 16-ketoprogesterone (XXVIII).

The effect of additional ketonic substitution in the progesterone molecule can be discerned from two examples given in Fig. 8. The 15-keto group (XXVII) simply obliterates the fine structure in the 350–380 mμ region, while a completely different type of curve is encountered in the case of 16-ketoprogesterone (XXVIII), a change which may in part be attributable to the enolized β-diketone system, although the strong, initial negative drift may well be due to the 16-keto function.[1]

An interesting effect of a conformational nature is shown in Fig. 9 which includes the curves of the two epimeric 6-hydroxy-Δ^4-cholesten-3-ones. The equatorial 6α-hydroxy derivative XXIX is very similar to Δ^4-cholestenone (XI) (Fig. 2) while the axial 6β-epimer XXX exhibits major differences in the 300 mμ range as well as some variations in the fine structure between 350–380 mμ. The corresponding testosterone derivative XXXI possesses almost the identical dispersion curve (see Experimental).

The rotatory dispersion method lends itself very conveniently to determine fairly accurately whether certain ring ketones should be treated as enantiomeric types in the sense proposed by Klyne,[19] especially when comparing terminal with non-terminal rings. Thus, it was possible to show[1] that saturated steroidal 4- and 6-ketones could not be considered to be enantiomeric in contrast to the corresponding unsaturated ketones (Δ^5-4-one *vs.* Δ^4-6-one). Two additional and important examples of enantiomeric non-terminal rings are given in Fig. 10. The two Δ^5-7-ketosteroids 7-ketocholesteryl acetate (XXXII) and the 3,20-bis-ketal of 7-ketodesoxycorticosterone acetate (XXXIII)[20] exhibit

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[18] C. Djerassi, A. E. Lippman and J. Grossman, THIS JOURNAL, **78**, 2479 (1956).

[19] W. Klyne, *J. Chem. Soc.*, 2916 (1952).

[20] R. H. Lenhard and S. Bernstein, THIS JOURNAL, **78**, 989 (1956).

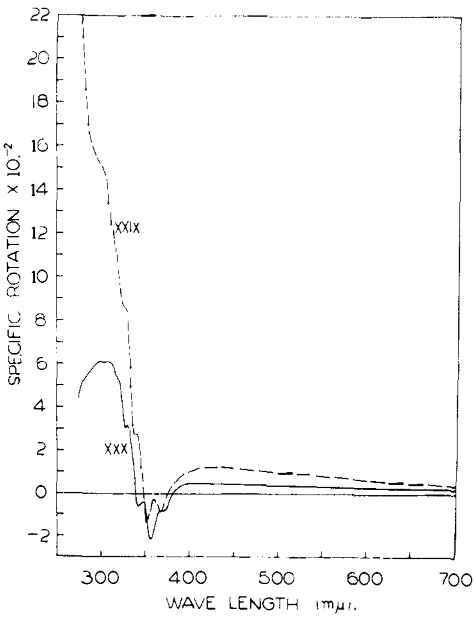


Fig. 9.—Rotatory dispersion curves of: 6α-hydroxy-Δ^4-cholesten-3-one (XXIX), 6β-hydroxy-Δ^4-cholesten-3-one (XXX).

curves which are virtually mirror images of those of Δ^4-3-ketosteroids (*e.g.*, XI, XIII); this, interestingly enough, also applies to Δ^7-6-ketones such as $\Delta^{7,22}$-ergostadien-3β-ol-6-one acetate (XXXIV).

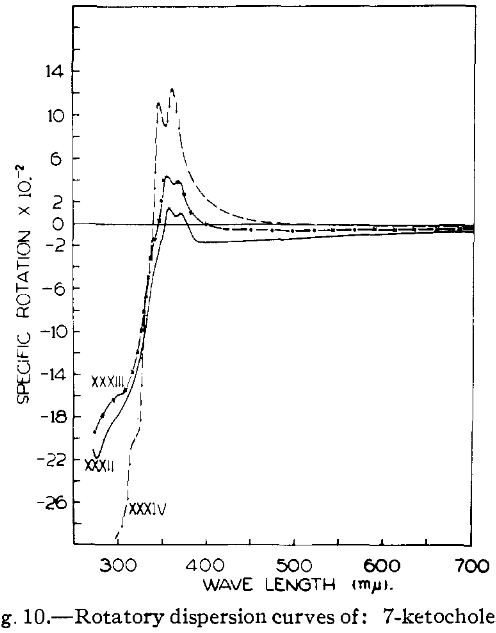
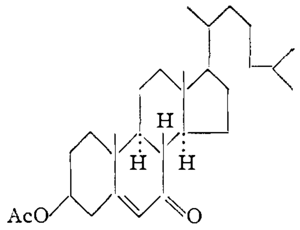


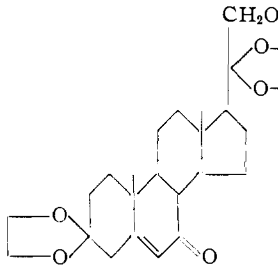
Fig. 10.—Rotatory dispersion curves of: 7-ketocholesterol acetate (XXXII), 7-ketodesoxycorticosterone acetate 3,20-biscycloethylene ketal (XXXIII), $\Delta^{7,22}$-ergostadien-3β-ol-6-one acetate (XXXIV).

These two observations imply: (a) that comparisons of terminal with non-terminal ring systems are valid in such cases and (b) that Δ^6-7-ketones and Δ^7-6-ketones are of the same type which in turn is enantiomeric with Δ^4-3-ketosteroids.

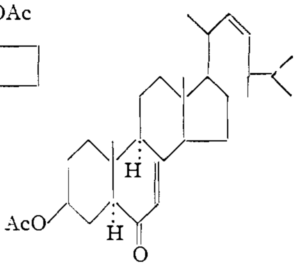
The dispersion curves of some miscellaneous steroidal α,β-unsaturated ketones are collected in Fig. 11. The two $\Delta^{8(9)}$-7-ketosteroids XXXV and XXXVI demonstrate the strong influence of the A/B ring juncture upon the rotatory dispersion of this type of chromophore, while inspection of the curve of a $\Delta^{8(9)}$-7-ketone (XXXVI) *vs.* that of its $\Delta^{8(14)}$-isomer (XXXVII) shows that the marked rotatory dispersion changes could also be used for purposes of characterization in addition to the ultraviolet absorption spectra. The dispersion curve of Δ^2-cholesten-1-one (XXXVIII)[21] does not show any fine structure and is quite different from that of the bicyclic analog VIII. Whether this is due to the presence of the additional double bond in VIII or whether it is a reflection of the earlier noted[1,3e] peculiar dispersion associated with saturated 1-ketosteroids remains to be seen.



XXXII



XXXIII



XXXIV

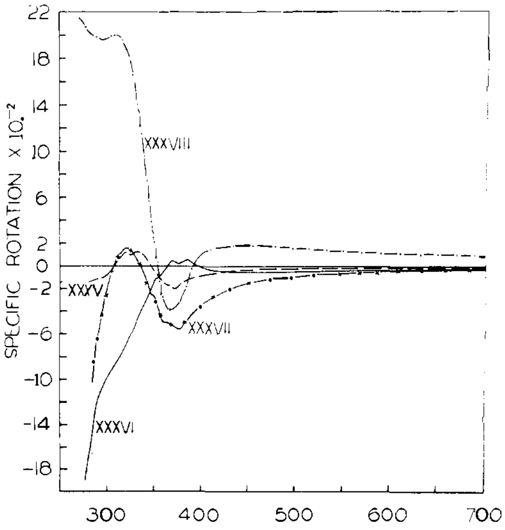


Fig. 11.—Rotatory dispersion curves of: methyl Δ^8-3α-acetoxy-7-ketocholenate (XXXV), Δ^8-cholesten-3β-ol-7-one acetate (XXXVI), $\Delta^{8(14)}$-cholesten-3β-ol-7-one acetate (XXXVII), Δ^2-cholesten-1-one (XXXVIII).

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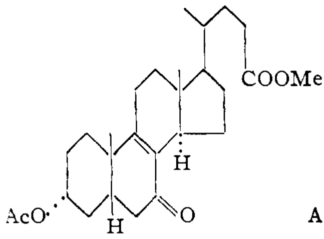
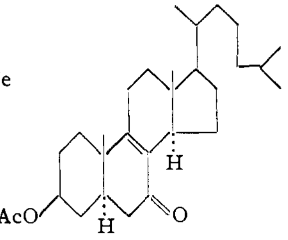
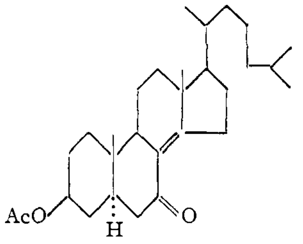
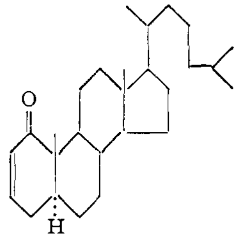
[21] P. Striebel and C. Tamm, *Helv. Chim. Acta*, **37**, 1094 (1954).


XXXV


XXXVI


XXXVII


XXXVIII

The situation with respect to Δ^{16}-20-ketosteroids is summarized in Fig. 12. Such unsaturated ketones do not show any fine structure but rather are characterized by a moderate, positive peak near 360 mμ which may be shifted somewhat in intensity depending upon the "background" rotation of the rest of the system. An illustration of the influence of the 16–17 double bond is afforded by a comparison of the dispersion curves of Δ^{5}-pregnen-3β-ol-20-one (XXXIX) and $\Delta^{5,16}$-pregnadien-3β-ol-20-one acetate (XL), and it should be noted that their specific rotations differ by about 3850° at 310 mμ. These two substances are commercially important steroids, and for characterization purposes it would obviously be more significant to report their rotations at 310 rather than at 589 mμ. The dispersion curve of Δ^{16}-pregnen-3α-ol-20-one acetate (XLI) (see Experimental) is somewhat more positive (this being a reflection of the absence of the negative "background" rotation ascribable to the Δ^{5}-double bond) while the curve of Δ^{16}-allopregnen-15β-ol-20-one acetate (XLII) is shifted considerably to the negative side and thus explains the anomalous results observed[22] in molecular rotation calculations involving 15β-acetoxy-Δ^{16}-20-ketosteroids. The cyclopropyl ketone XLIII[23] demonstrates quite clearly that in this instance (insofar as rotatory dispersion is concerned) conjugation of a cyclopropane ring with a 20-ketone does not resemble at all the Δ^{16}-20-keto chromophore. The dispersion curve of 16-dehydroprogesterone (XLIV) is also included and appears to be roughly the summation of the contributions of the two separate unsaturated ketone moieties.

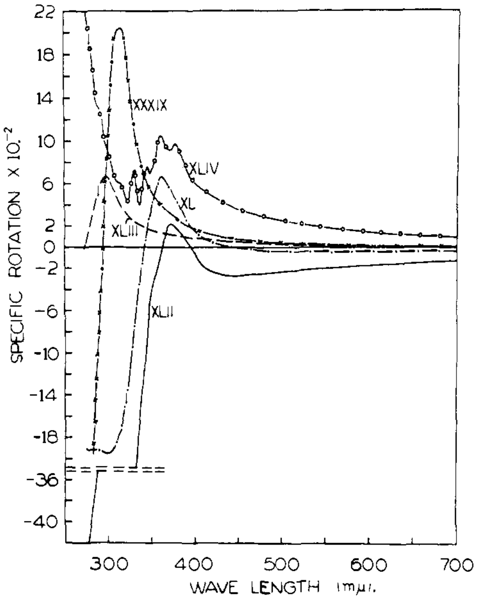
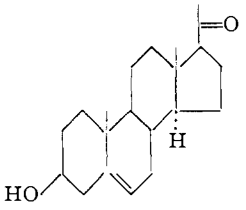
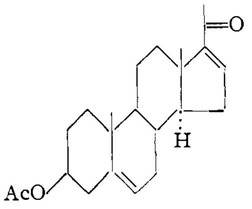
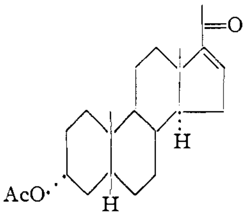


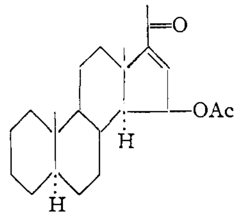
Fig. 12.—Rotatory dispersion curves of: Δ^{5}-pregnen-3β-ol-20-one (XXXIX), $\Delta^{5,16}$-pregnadien-3β-ol-20-one acetate (XL), Δ^{16}-allopregnen-15β-ol-20-one acetate (XLII), 16,17-methylene-Δ^{5}-pregnen-3β-ol-20-one acetate (XLIII), 16-dehydroprogesterone (XLIV).

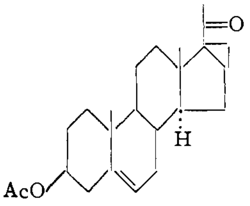
A rather unexpected effect of ring C substituents upon dispersion characteristics of ring A unsaturated ketones is considered in Figs. 13 and 14. The rotatory dispersion of cortisone has been reported earlier,[3b] and we have now measured cortisone acetate (XLVa) (Fig. 13) in order to define the low wave length "minimum" which could not be reached earlier[3b] with a zirconium lamp. At the same time, there were also investigated the 9α-fluoro (XLVb), 9α-chloro (XLVc) and 9α-bromo (XLVd) derivatives and the surprising observation was made that while 9α-fluorocortisone acetate (XLVb) (see Experimental) still retained the characteristic[3b] fine structure between 350–400 mμ (except for some intensity changes), the 9α-chloro derivative (XLVc) (see Experimental) showed only a faint inflection and the 9α-bromo analog (XLVd) (Fig. 13) possessed a perfectly smooth curve in that

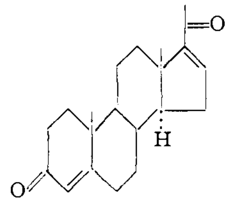

XXXIX


XL


XLI


XLII


XLIII


XLIV

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(22) C. Djerassi and T. T. Grossnickle, *Chemistry & Industry*, 728 (1954).

(23) A. Sandoval, G. Rosenkranz and C. Djerassi, THIS JOURNAL, **73**, 2383 (1951).

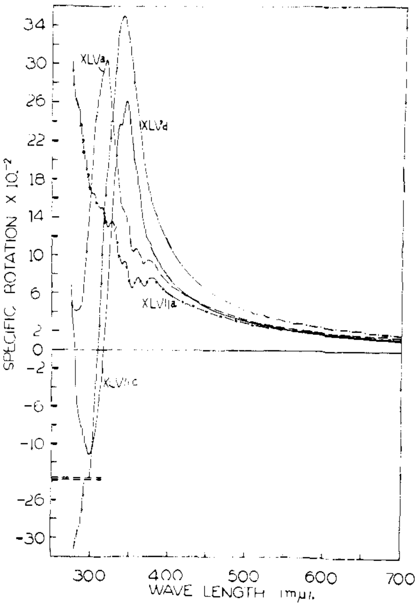


Fig. 13.—Rotatory dispersion curves of: cortisone acetate (XLVa), 9α-bromocortisone acetate (XLVd), 11-ketotestosterone (XLVIIa), 9α-bromo-17α-methyl-Δ^4-androstene-3,11-dione-17β-ol (XLVIIc).

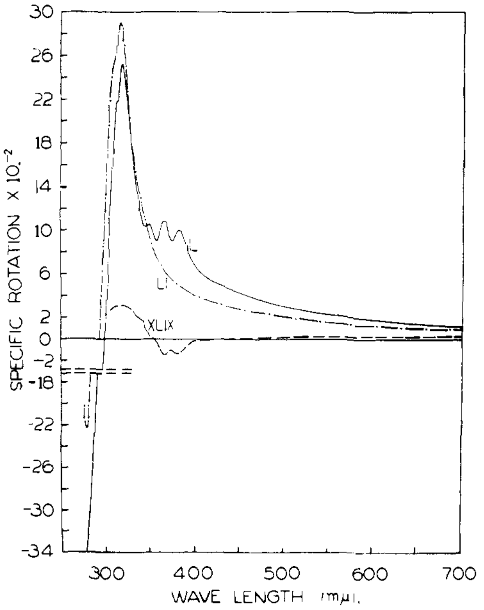
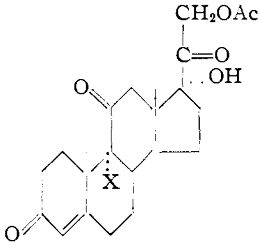


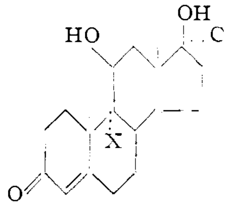
Fig. 14.—Rotatory dispersion curves of: 1,4-androstadien-17β-ol-3-one (XLIX), 1,4-pregnadiene-3,11,20-trione-17α,21-diol acetate (L), 1,4-pregnadiene-3,20-dione-11β,17α,21-triol acetate (LI).

region. Furthermore, there was observed a progressive bathochromic shift of *ca.* 32 mμ of the main "maximum" on going from fluorine to bromine and the intensity of this "maximum" was also very much higher in the case of the chloro- and bromocortisone acetates as compared to 9α-fluorocortisone acetate.[24]

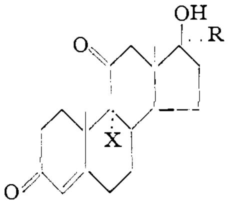
The availability[25] of a series of 9α-halo-11β-hydroxy (XLVI) and 11-keto-17α-methyltestosterones (XLVII)[26] permitted a closer examination of this effect of a 9α-halogen atom upon the rotatory dispersion characteristics of the Δ^4-3-keto grouping without the interference of the 20-ketone present in XLV. The curves of the various 11β-hydroxy-17α-methyltestosterones (XLVIa-c) were very similar (see Experimental) to that of testosterone (XIII) thus demonstrating conclusively that it could not have been an effect of the halogen atom *per se.* On the other hand, in the 11-keto series (XLVII) while the curves of 11-ketotestosterone (XLVIIa) (Fig. 13) and 9α-fluoro-11-keto-17α-methyltestosterone (XLVIIb) (see Experimental) were similar, the 9α-bromo-11-ketone (XLVIIc) exhibited a very different curve (Fig. 13), the most notable feature being a pronounced "maximum" and "minimum" in the 300–350 mμ range and the absence of the typical Δ^4-3-keto fine structure. It is clear, therefore, that the 11-ketone is implicated and subsequent work[27] has shown that the type of curve exhibited by XLVIIc is rather characteristic of 9α-bromo-11-ketones (*e.g.*, 9α-bromoergostan-11-one-3β-ol), and its effect is so powerful as to overshadow even the typical features of the Δ^4-3-ketone grouping. Unfortunately, a 9α-fluoro-11-ketosteroid lacking additional ketonic substituents is not known at the present time, but from our results it can be predicted that the substitution of the fluorine atom should produce a rather different rotatory dispersion effect as compared to a chlorine or bromine atom.



XLVa, X = H
b, X = F
c, X = Cl
d, X = Br



XLVIa, X = H
b, X = F
c, X = Br



XLVIIa, X = R = H
b, X = F; R = CH_3
c, X = Br; R = CH_3

In Fig. 14 is shown a somewhat different effect produced by an 11-keto group. 1,4-Cholestadien-3-one (XLVIII)[1] and 1,4-androstadien-17β-ol-3-one (XLIX) possess essentially identical dispersion curves involving fine structure around 375 mμ and a broad "maximum" of rather low intensity near 320 mμ, and these features can be considered to be

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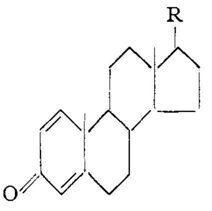
[24] No such marked effect was noted with 4-chlorocortisone acetate (see Experimental) as was to be anticipated in view of the earlier mentioned results with 4-chlorotestosterone (XIV).

[25] M. E. Herr, J. A. Hogg and R. H. Levin, THIS JOURNAL, **78**, 500 (1956).

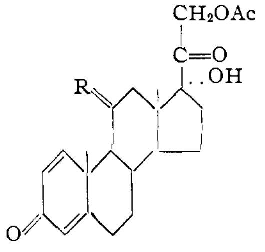
[26] The 9α-bromo-11-ketone XLVIIc was not described (ref. 25), but it was prepared (see Experimental section) by oxidation of the corresponding 11β-alcohol XLVIc.

[27] This will be reported in a detailed paper dealing with the rotatory dispersion results of various saturated steroidal halo-ketones.

typical of the 1,4-dien-3-one grouping. It is now interesting to note that while the corresponding dienone L of cortisone acetate still exhibits fine structure between 350–400 mμ, this is completely obliterated in the hydrocortisone acetate analog LI, and no explanation can be offered at the present time for this phenomenon.



XLVIII, R = C_8H_{17}
XLIX, R = OH



L, R = O
LI, R = $\langle^{OH}_{\cdot H}$

A most dramatic effect—due to conformational alteration—is presented in Fig. 15 and would not have been detectable to any appreciable extent by any other physical method. A series of 8α-steroids have recently been synthesized in this Laboratory,[28] the consequence of this stereochemical change (B/C ring juncture *cis* rather than *trans*) being the requirement that either ring B or ring C must exist in a boat form rather than in the conventional all-chair arrangement. The dispersion curves (see Experimental) of a saturated 20- (LII) or 17- (LIV) ketosteroid or of a Δ^{16}-20-ketone (LIII) with such a B/C *cis* juncture do not differ greatly from those of the natural (B/C *trans*-8β,9α) isomers, but a remarkable effect is noted with the analogous Δ^4-3-ketones. The rotatory dispersion curves (Fig. 15) of 8-isotestosterone (LV), 8-iso-Δ^4-androstene-3,17-dione (LVI)[29] and 8-isoprogesterone (LVII) have rather similar shapes which are completely unlike those of the parent hormones.[3a,b] In fact, the effect is so powerful that it completely overshadows the strong positive peak associated with 17- and 20-keto groups[3] as observed in Δ^4-androstene-3,17-dione[3a] and in progesterone.[3b] In view of the fact that epi-α-cyperone (LVIII) has a very similar dispersion curve,[1,30] it is conceivable that the common conformational feature producing this dispersion effect is the 9-methyloctalone system with the saturated ring existing as a partial or complete boat.

It should be noted that the dispersion curve (Fig. 8) of the biologically inactive 1-methyl-19-norprogesterone (XXVIb) resembles greatly (except for intensity variations) that of 8-isoprogesterone (LVII). This would suggest that the C-10 hydrogen atom of XXVIb is β-oriented (by analogy to the angular methyl group of LVII) and that the structural factor responsible for the major change in the rotatory dispersion picture (XXVIa *vs.* XXVIb) is the C-1 methyl group which probably possesses the β-configuration. This in turn involves steric interaction with the C-11 methylene function, and to relieve this strain, a conformational (partial conversion to boat?) change is produced in rings B and/or C which now resembles closely the 8α-steroids LV–LVII. It is also quite striking that a similar dispersion curve (Fig. 15) is obtained when ring B becomes five-membered as in B-nor-Δ^4-cholesten-3-one[31] (LIX) which might imply that the increased strain due to the five-membered B ring might have produced the same type of conformational alteration mentioned above. As demonstrated in the Experimental section, unsaturation at 9–11 as in the cortisone intermediates[12,32] LX and LXI does not affect the characteristic rotatory dispersion features of Δ^4-3-ketosteroids.

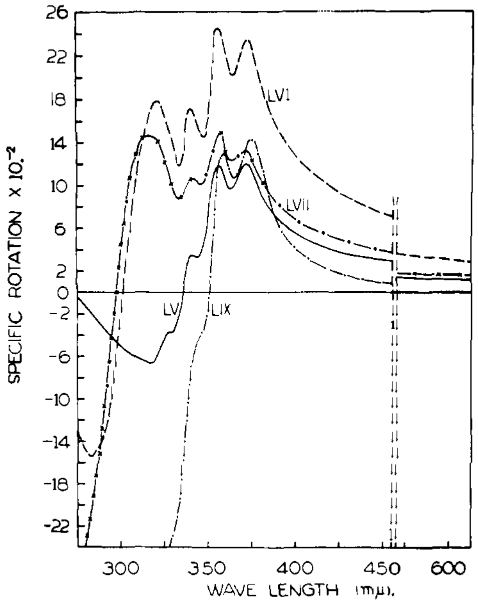


Fig. 15.—Rotatory dispersion curves of: 8α-testosterone (LV), Δ^4-8α-androstene-3,17-dione (LVI), 8α-progesterone (LVII), B-nor-Δ^4-cholesten-3-one (LIX).

The dispersion curves of some miscellaneous conjugated, unsaturated ketones are reproduced in Fig. 16. Steroidal Δ^4-3,6-diones such as Δ^4-cholestene-3,6-dione (LXII) or 6-ketotestosterone (LXIII) (see Experimental) exhibit none of the fine structure observed in the corresponding Δ^4-3-ketone (Fig. 2), but the situation is changed completely when ring B is five-membered (LXIV).[31] 16-Methylene-17-ketosteroids (LXV)[33] show a characteristic doublet in the 375–300 mμ range which is even retained (see Experimental) in the presence of an additional Δ^4-3-keto moiety (LXVI).[32] Jervine (LXVII) represents another cyclopentenone, but its chromophore is unique and no generalizations can be made from its dispersion curve. The last curve shown in Fig. 16 is that of $\Delta^{1,4,6}$-androstatrien-17β-ol-3-one acetate (LXVIII), and all of its

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[28] C. Djerassi, A. J. Manson and A. Segaloff, *J. Org. Chem.*, **21**, 490 (1956), and C. Djerassi, H. Bendas and A. Segaloff, *ibid.*, **21**, 1056 (1956).

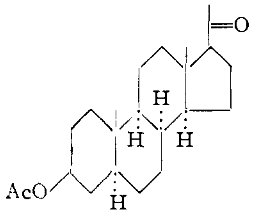
[29] The shape of this dispersion curve represents almost the exact summation of the two individual chromophores (LII and LV).

[30] In contrast to that of the epimeric α-cyperone with the equatorial isopropenyl group which behaves like an ordinary Δ^4-3-ketosteroid.

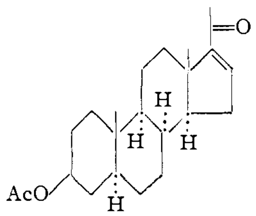
[31] F. Sorm and H. Dykova, *Collection Czechoslov. Chem. Communs.*, **13**, 407 (1948); *C. A.*, **43**, 1789 (1949). We are grateful to Dr. W. G. Dauben (University of California) for a specimen (*cf.* W. G. Dauben and G. J. Fonken, THIS JOURNAL, **78**, 4736 (1956).)

[32] L. B. Barkley, M. W. Farrar, W. S. Knowles, H. Raffelson and Q. E. Thompson, *ibid.*, **76**, 5014 (1954).

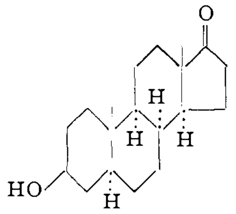
[33] F. Neumann, O. Mancera, G. Rosenkranz and F. Sondheimer, *ibid.*, **77**, 5676 (1955).



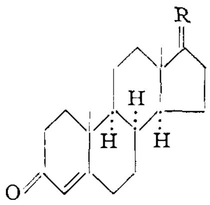
LII



LIII



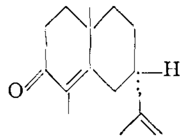
LIV



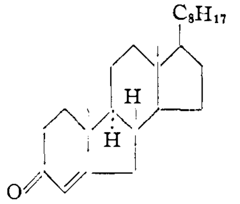
LV, R = $<^{\mathrm{OH}}_{\cdot\mathrm{H}}$

LVI, R = O

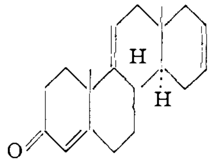
LVII, R = $\underset{\mathrm{H}}{\vdots}$—COCH$_3$



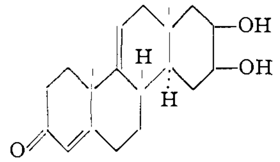
LVIII



LIX



LX



LXI

features are typical of the 1,4,6-trien-3-one grouping since it is quite similar to the other trienones[3a,3d] measured earlier. These substances possessed, respectively, a 17-keto or spiroketal substituent in ring D, but it is clear that the effect of the trienone grouping is so powerful as to overshadow such additional chromophores.

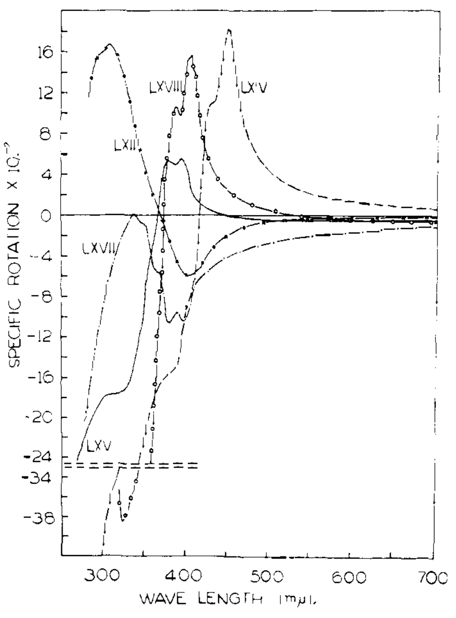
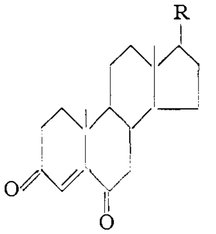
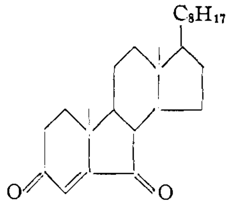


Fig. 16.—Rotatory dispersion curves of: Δ^4-cholestene-3,6-dione (LXII), B-nor-Δ^4-cholestene-3,6-dione (LXIV), 16-methylene-Δ^5-androsten-3β-ol-17-one (LXV), jervine (LXVII), $\Delta^{1,4,6}$-androstatrien-17β-ol-3-one acetate (LXVIII).

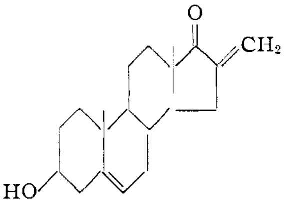
In the Experimental section are given pertinent dispersion data for a variety of Δ^1-3-ketosteroids with or without halogens at C-2. Neither the halogen atom nor diverse non-ketonic substituents at C-17 altered to any large extent the typical shape of the dispersion curve which has been ascribed[3] to the Δ^1-3-keto chromophore.



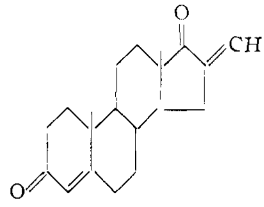
LXII, R = C$_8$H$_{17}$
LXIII, R = OH



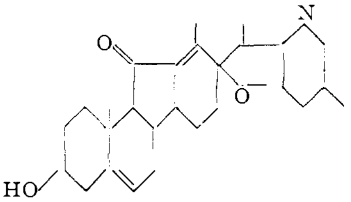
LXIV



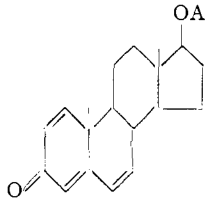
LXV



LXVI



LXVII



LXVIII

Experimental[34]

(−)-Menthone (I) (R. H. Eastman[13]), R.D. (Fig. 3), c 0.182: $[\alpha]_{700}$ 0°, $[\alpha]_{589}$ −9°, $[\alpha]_{270}$ −286°, "max." $[\alpha]_{322.5}$ +216°, "min." $[\alpha]_{287.5}$ −450°.

(−)-Piperitone (II) (R. H. Eastman), R.D. (Fig. 3), c 0.054 on freshly distilled sample: $[\alpha]_{700}$ −27°, $[\alpha]_{589}$ −27°, $[\alpha]_{272.5}$ −450°, "min." $[\alpha]_{370}$ −486°, "max." $[\alpha]_{358}$ −227°, "min." $[\alpha]_{252.5}$ −336°, "max." $[\alpha]_{342.5}$ +139°, "min." $[\alpha]_{337.5}$ +93°, "max." $[\alpha]_{329}$ +252°, "shoulder" $[\alpha]_{320-325}$ +178°, "shoulder" $[\alpha]_{305-310}$ −30°.

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[34] The rotatory dispersion measurements were carried out by the procedures outlined in earlier papers (ref. 1 and 3). Unless noted otherwise, dioxane was used which is transparent (under our experimental conditions) to *ca.* 270 mμ, but this limit was hardly ever reached with conjugated ketones because of earlier, strong absorption.

β-Dihydroumbellulone (III) (R. H. Eastman), R.D. (Fig. 3), *c* 0.103: $[\alpha]_{700}$ −35°, $[\alpha]_{589}$ −64°, $[\alpha]_{271.25}$ +2140°, “min.” $[\alpha]_{312}$ −2220°, “max.” $[\alpha]_{275}$ +2300°.

Umbellone (IV) (R. H. Eastman), R.D. (Fig. 4), *c* 0.094 on freshly distilled material: $[\alpha]_{700}$ −34°, $[\alpha]_{589}$ −42.5° ± 2°, $[\alpha]_{290}$ −18400 ± 500°, “max.” $[\alpha]_{367}$ +3670°.

Tricyclic ketone V from umbellulone (R. H. Eastman), R.D. (Fig. 4), *c* 0.098 on freshly distilled material: $[\alpha]_{700}$ −3°, $[\alpha]_{589}$ −12°, $[\alpha]_{275}$ +7570°, “min.” $[\alpha]_{307.5}$ −5630°.

Epoxyumbellulone (VI) (R. H. Eastman), R.D. (Fig. 4), *c* 0.09 on freshly distilled material: $[\alpha]_{700}$ +3°, $[\alpha]_{589}$ −4°, $[\alpha]_{275}$ +3900°, “min.” $[\alpha]_{332}$ −3450°, “max.” $[\alpha]_{290}$ +4470°.

(−)-*trans*-**3-Keto**-9-methyl-$\Delta^{1,6}$-**hexahydronaphthalene** (**VII**),[11,12] R.D. (Fig. 1), *c* 0.088 in *methanol:* $[\alpha]_{700}$ −162°, $[\alpha]_{589}$ −234°, $[\alpha]_{270}$ −2130°, “min.” $[\alpha]_{361}$ −1530°, “inflect.” $[\alpha]_{350}$ −1311°, “max.” $[\alpha]_{319}$ −298°, *c* 0.0525 in *dioxane:* $[\alpha]_{700}$ −145°, $[\alpha]_{589}$ −225°, $[\alpha]_{280}$ −1955°, “min.” $[\alpha]_{379}$ −1330°, “max.” $[\alpha]_{370}$ −1070°, “min.” $[\alpha]_{362.5}$ −1270°, “max.” $[\alpha]_{352.5}$ −620°, “min.” $[\alpha]_{345}$ −758°, “max.” $[\alpha]_{338}$ −257°, “min.” $[\alpha]_{330}$ −515°, “max.” $[\alpha]_{325}$ −412°, “inflect.” $[\alpha]_{315}$ −758°, *c* 0.0736 in *octane:* $[\alpha]_{700}$ −143°, $[\alpha]_{589}$ −223°, $[\alpha]_{302.5}$ −1220°, “min.” $[\alpha]_{386}$ −1180°, “max.” $[\alpha]_{377.5}$ −766°, “min.” $[\alpha]_{367.5}$ −1330°, “max.” $[\alpha]_{359}$ −408°, “min.” $[\alpha]_{351}$ −944°, “max.” $[\alpha]_{342.5}$ −344°, “min.” $[\alpha]_{336}$ −831°, “max.” $[\alpha]_{330}$ −404°, “min.” $[\alpha]_{320}$ −868°, “max.” $[\alpha]_{315}$ −858°, “inflect.” $[\alpha]_{307}$ −1145°.

(−)-*trans*-1-**Keto**-**9**-**methyl**-$\Delta^{2,6}$-**hexahydronaphthalene** (**VIII**),[12] R.D. (Fig. 5), *c* 0.073 on freshly distilled sample (b.p. 88–90° at 23 mm.): $[\alpha]_{700}$ −31°, $[\alpha]_{589}$ −49°, $[\alpha]_{272.5}$ −407°, “min.” $[\alpha]_{410-420}$ −140°, “max.” $[\alpha]_{383}$ +9°, “min.” $[\alpha]_{370}$ −469°, “max.” $[\alpha]_{363}$ −306°, “min.” $[\alpha]_{355}$ −847°, “max.” $[\alpha]_{345}$ −495°, “min.” $[\alpha]_{340}$ −655°, “max.” $[\alpha]_{330}$ −253°, “min.” $[\alpha]_{327}$ −262°, “max.” $[\alpha]_{319}$ + 5°, “min.” $[\alpha]_{314}$ −13°, “max.” $[\alpha]_{307.5}$ +30°.

(+)-*trans*-1-**Keto**-**3**-methoxy-9-methyl-$\Delta^{2,6}$-**hexahydronaphthalene** (IX),[12] R.D. (Fig. 5), *c* 0.10 in *dioxane:* $[\alpha]_{700}$ +33°, $[\alpha]_{589}$ +52°, $[\alpha]_{275}$ +1445°, “max.” $[\alpha]_{410-430}$ +90°, “min.” $[\alpha]_{349}$ −587°, “max.” $[\alpha]_{339}$ +110°, “min.” $[\alpha]_{334}$ −119°, “max.” $[\alpha]_{324}$ +930°, “min.” $[\alpha]_{320}$ +745°, “max.” $[\alpha]_{312.5}$ +1450°, “min”. $[\alpha]_{307.5}$ +1320°, “max.” $[\alpha]_{302.5}$ +1440°, “min.” $[\alpha]_{290}$ + 1350°. *c* 0.11 in *octane:* $[\alpha]_{700}$ +38°, $[\alpha]_{589}$ +53°, $[\alpha]_{297.5}$ +436°, “max.” $[\alpha]_{415-440}$ +110°, “min.” $[\alpha]_{352.5}$ −532°, “max.” $[\alpha]_{346}$ +315°, “min.” $[\alpha]_{339}$ −294°, “max.” $[\alpha]_{330}$ +518°, “min.” $[\alpha]_{325}$ +36°, “max.” $[\alpha]_{317.5}$ +810°, “min.” $[\alpha]_{312.5}$ +336°, “max.” $[\alpha]_{305}$ +618°.

α-**Vetivone** (**Xa**) (Y. R. Naves), R.D. (Fig. 5), *c* 0.088: $[\alpha]_{700}$ +142°, $[\alpha]_{589}$ +218°, $[\alpha]_{295}$ +3750°, “max.” $[\alpha]_{380}$ +759°, “min.” $[\alpha]_{365}$ +583°, “max.” $[\alpha]_{358}$ +610°, “min.” $[\alpha]_{350}$ +352°, “max.” $[\alpha]_{343}$ +797°, “min.” $[\alpha]_{337.5}$ +716°, “max.” $[\alpha]_{327.5}$ +1700°, “min.” $[\alpha]_{325}$ +1660°, “inflect.” $[\alpha]_{310}$ +2660°.

β-**Vetivone** (**Xb**) (Y. R. Naves), R.D. (Fig. 5), *c* 0.10: $[\alpha]_{700}$ −12°, $[\alpha]_{589}$ −19°, $[\alpha]_{290}$ +68°, “min.” $[\alpha]_{382.5}$ −207°, “max.” $[\alpha]_{370}$ +18°, “min.” $[\alpha]_{362.5}$ −90°, “max.” $[\alpha]_{352.5}$ +291°, “min.” $[\alpha]_{345}$ +133°, “max.” $[\alpha]_{339}$ +294°, “min.” $[\alpha]_{330}$ +154°, “max.” $[\alpha]_{325}$ +194°, “min.” $[\alpha]_{304}$ −25°.

Δ^{4}-**Cholesten-3-one** (**XI**) R.D. (Fig. 2), *c* 0.10 in *methanol:* $[\alpha]_{700}$ +56°, $[\alpha]_{589}$ +86°, $[\alpha]_{280}$ +2410°, “max.” $[\alpha]_{395-410}$ +167°, “min.” $[\alpha]_{340-350}$ −116°; *c* 0.10 in *dioxane:* $[\alpha]_{700}$ +53°, $[\alpha]_{589}$ +73°, $[\alpha]_{275}$ +2100°, “max.” $[\alpha]_{410-425}$ +145°, “min.” $[\alpha]_{366}$ −93°, “max.” $[\alpha]_{359}$ −51°, “min.” $[\alpha]_{352}$ −164°, “shoulder,” $[\alpha]_{337-340}$ +265°, “inflect.” $[\alpha]_{325}$ +1000°, “inflect.” $[\alpha]_{311}$ +1480°; *c* 0.077 in *octane:* $[\alpha]_{700}$ +20°, $[\alpha]_{589}$ +52°, $[\alpha]_{302.5}$ +1090°, “max.” $[\alpha]_{415-450}$ +88°, “min.” $[\alpha]_{373}$ −130°, “max.” $[\alpha]_{365}$ −43°, “min.” $[\alpha]_{357.5}$ −258°, “max.” $[\alpha]_{350}$ +201°, “min.” $[\alpha]_{342.5}$ +66°, “max.” $[\alpha]_{332.5}$ +685°, “min.” $[\alpha]_{328.5}$ +598°, “inflect.” $[\alpha]_{315}$ +1042°, “max.” $[\alpha]_{307.5}$ +1170°.

Testosterone (**XIII**), R.D. (Fig. 6), *c* 0.10 in *dioxane:* $[\alpha]_{700}$ +62°, $[\alpha]_{589}$ +103°, $[\alpha]_{275}$ +2935°, “max.” $[\alpha]_{405-425}$ +180°, “min.” $[\alpha]_{366}$ −177°, “max.” $[\alpha]_{360}$ −95°, “min.” $[\alpha]_{352}$ −282°, “shoulder” $[\alpha]_{337-340}$ +390°, “inflect.” $[\alpha]_{325}$ +1339°, *c* 0.10 in *methanol:* $[\alpha]_{700}$ +74°, $[\alpha]_{589}$ +111°, $[\alpha]_{275}$ +3210°, “max.” $[\alpha]_{390-425}$ +220°, “min.” $[\alpha]_{347.5}$ −140°, “max.” $[\alpha]_{284}$ +3455°.

4-Chlorotestosterone (**XIV**)[35] (H. J. Ringold), R.D., *c* 0.10: $[\alpha]_{700}$ +96°, $[\alpha]_{589}$ +111°, $[\alpha]_{290}$ +2255°, “max.” $[\alpha]_{382.5}$ +315°, “min.” $[\alpha]_{372.5}$ +290°, “max.” $[\alpha]_{365}$ +305°, “min.” $[\alpha]_{352.5}$ +164°, “max.” $[\alpha]_{345}$ +363°, “min.” $[\alpha]_{337.5}$ +223°, “inflect.” $[\alpha]_{325}$ +705°.

4-Bromotestosterone (**XV**)[35] (H. J. Ringold), R.D. (Fig. 6), *c* 0.10: $[\alpha]_{700}$ +92°, $[\alpha]_{589}$ +113°, $[\alpha]_{295}$ +1880°, “shoulder” $[\alpha]_{375-382}$ +390°, “max.” $[\alpha]_{367.5}$ +419°, “min.” $[\alpha]_{355}$ +312°, “max.” $[\alpha]_{346}$ +463°, “min.” $[\alpha]_{337.5}$ +369°, “max.” $[\alpha]_{327.5}$ +715°, “min.” $[\alpha]_{325}$ +670°, “inflect.” $[\alpha]_{312.5}$ +1210°.

4-Methyltestosterone (**XVI**)[35] (H. J. Ringold), R.D., *c* 0.051: $[\alpha]_{700}$ +69°, $[\alpha]_{589}$ +122°, $[\alpha]_{280}$ +3640°, “max.” $[\alpha]_{405-420}$ +265°, “min.” $[\alpha]_{369}$ +14°, “max.” $[\alpha]_{365}$ +22°, “min.” $[\alpha]_{354}$ −188°, “shoulder” $[\alpha]_{338-343}$ +275°, “inflect.” $[\alpha]_{325}$ +1350°.

2α-**Methyltestosterone** (**XVII**)[35] (H. J. Ringold), R.D., *c* 0.11: $[\alpha]_{700}$ +64°, $[\alpha]_{589}$ +99°, $[\alpha]_{285}$ +3440°, “max.” $[\alpha]_{425-475}$ +157°, “min.” $[\alpha]_{363}$ −631°, “max.” $[\alpha]_{356}$ −496°, “min.” $[\alpha]_{350}$ −603°, “inflect.” $[\alpha]_{337.5}$ +481°, “inflect.” $[\alpha]_{322.5}$ +2061°.

2α-**Hydroxytestosterone 2,17-diacetate** (**XVIII**) (O. Mancera), R.D. (Fig. 6), *c* 0.10: $[\alpha]_{700}$ +48°, $[\alpha]_{589}$ +54°, $[\alpha]_{280}$ +2547°, “max.” $[\alpha]_{425-475}$ +90°, “min.” $[\alpha]_{357.5}$ −568°, “inflect.” $[\alpha]_{350}$ −476°.

1-Methyl-19-nortestosterone (**XX**)[16] (H. J. Ringold), R.D. (Fig. 7), *c* 0.078: $[\alpha]_{700}$ −14°, $[\alpha]_{589}$ +9°, $[\alpha]_{275}$ +3050°, “min.” $[\alpha]_{370}$ −785°, “max.” $[\alpha]_{362.5}$ −643°, “min.” $[\alpha]_{355}$ −837°, “shoulder” $[\alpha]_{340-343}$ +231°, “inflect.” $[\alpha]_{327.5}$ +1500°, “inflect.” $[\alpha]_{300}$ +2450°.

10β-Hydroxy-19-nortestosterone (**XXI**)[17] (D. H. Peterson), R.D. (Fig. 7), *c* 0.088: $[\alpha]_{700}$ +51°, $[\alpha]_{589}$ +65°, $[\alpha]_{302.5}$ +2340°, “max.” $[\alpha]_{440-500}$ +97°, “min.” $[\alpha]_{372.5}$ −451°, “max.” $[\alpha]_{365}$ −402°, “min.” $[\alpha]_{357.5}$ −540°, “inflect.” $[\alpha]_{345}$ +212°, “inflect.” $[\alpha]_{327.5}$ +1440°.

$\Delta^{5(10)}$-**Estren-17β-ol-3-one** (**XXII**) (J. A. Hartman), R.D. (Fig. 7), *c* 0.10: $[\alpha]_{700}$ +131°, $[\alpha]_{589}$ +175°, $[\alpha]_{275}$ +820°, “shoulder” $[\alpha]_{317.5-322.5}$ +1210°, “max.” $[\alpha]_{311}$ +1322°, “shoulder” $[\alpha]_{300-304}$ +1172°, “min.” $[\alpha]_{282}$ +760°.

Δ^{5}-**Androsten-17β-ol-3-one benzoate** (**XXIII**), R.D. (Fig. 7), *c* 0.10: $[\alpha]_{700}$ +31°, $[\alpha]_{589}$ +46°, $[\alpha]_{285}$ −705°, “max.” $[\alpha]_{319}$ +1528°, “inflect.” $[\alpha]_{310}$ +1246°.

$\Delta^{5,14}$-**Androstadien-3β-ol-17-one acetate** (**XXIV**), R.D. (Fig. 7), *c* 0.11: $[\alpha]_{700}$ +40°, $[\alpha]_{589}$ +76°, $[\alpha]_{265}$ −559°, “max.” $[\alpha]_{322.5}$ +1286°, “shoulder” $[\alpha]_{315-318}$ +1272°, “min.” $[\alpha]_{277.5}$ −840°.

19-Norprogesterone (**XXVa**), R.D. (Fig. 8), *c* 0.10: $[\alpha]_{700}$ +92°, $[\alpha]_{589}$ +142°, $[\alpha]_{272.5}$ −250°, “max.” $[\alpha]_{390-400}$ +368°, “min.” $[\alpha]_{367}$ +178°, “max.” $[\alpha]_{357}$ +340°, “min.” $[\alpha]_{352}$ +290°, “inflect.” $[\alpha]_{340}$ +1212°, “max.” $[\alpha]_{310}$ +4010°.

1-Methyl-19-norprogesterone (m.p. 152°) (**XXVIa**),[18] R.D., *c* 0.107: $[\alpha]_{700}$ +91°, $[\alpha]_{589}$ +134°, $[\alpha]_{270}$ +2000°, “max.” $[\alpha]_{425-435}$ +242°, “min.” $[\alpha]_{371}$ −346°, “max.” $[\alpha]_{362}$ −114°, “min.” $[\alpha]_{355}$ −229°, “inflect.” $[\alpha]_{340}$ +1320°, “max.” $[\alpha]_{311}$ +5060°, “min.” $[\alpha]_{277.5}$ +1600°.

1-Methyl-19-norprogesterone (m.p. 171°) (**XXVIb**),[18] R.D. (Fig. 8), *c* 0.103: $[\alpha]_{700}$ +5°, $[\alpha]_{589}$ +11°, $[\alpha]_{270}$ −6410°, “max.” $[\alpha]_{367.5}$ + 653°, “min.” $[\alpha]_{362.5}$ + 614°, “max.” $[\alpha]_{355}$ +795°, “min.” $[\alpha]_{343}$ +301°, “max.” $[\alpha]_{340}$ +349°, “min.” $[\alpha]_{330}$ +56°, “max.” $[\alpha]_{320}$ +315°, “min.” $[\alpha]_{272.5}$ −7180°.

15-Ketoprogesterone (**XXVII**) (J. Fried), R.D. (Fig. 8), *c* 0.050; $[\alpha]_{700}$ +112°, $[\alpha]_{589}$ +188°, $[\alpha]_{277.5}$ −960°, “inflect.” $[\alpha]_{375}$ +750°, “inflect.” $[\alpha]_{340}$ +2062°, “max.” $[\alpha]_{315}$ +5718°, “min.” $[\alpha]_{280}$ −1040°.

16-Ketoprogesterone (**XXVIII**) (J. Fried), R.D. (Fig. 8), *c* 0.066: $[\alpha]_{700}$ +52°, $[\alpha]_{589}$ +45°, $[\alpha]_{317.5}$ +636°, “min.” $[\alpha]_{365}$ −512°, “max.” $[\alpha]_{360}$ −495°, “min.” $[\alpha]_{351}$ −840°,

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The accuracy of the readings under our experimental conditions has already been discussed in detail in ref. 3a (especially under “mathematical results” and under “experimental results”), and it was pointed out that the percentage accuracy was rather poor in those cases where the concentration was *c* 0.1 rather than *c* 1.0 and the rotation was small. It should be noted that in the present work, nearly all of the concentrations were *c* 0.1 or even smaller because of the stronger absorption of these substances. In fact, the region 280–310 mμ could usually only be investigated with α,β-unsaturated ketones at *c* 0.02 but since the rotations are usually very high in that spectral range, the percentage accuracy is still within the desired 3% (see for instance $[\alpha]_{287.5}$ −18,400 ± 500° for umbellulone (IV)). For the purpose of our work—correlation of shape of dispersion curve with chemical structure—the 450–700 mμ region is rather unimportant, and this is almost invariably the region where the rotations are small and the percentage errors higher (up to 10%) at the low concentration employed.

(35) H. J. Ringold, E. Batres, O. Mancera and G. Rosenkranz to be published.

‘max.” $[\alpha]_{345}$ −636°, “min.” $[\alpha]_{336}$ −792°, “inflect.” $[\alpha]_{325}$ +30°.

6α-Hydroxy-Δ^{4}-cholesten-3-one (XXIX) (L. F. Fieser), R.D. (Fig. 9), *c* 0.052: $[\alpha]_{700}$ +38°, $[\alpha]_{589}$ +67°, $[\alpha]_{277.5}$ +2190°, “max.” $[\alpha]_{425-460}$ +110°, “min.” $[\alpha]_{367.5}$ −83°, “max.” $[\alpha]_{360}$ −27°, “min.” $[\alpha]_{352.5}$ −135°, “shoulder” $[\alpha]_{337-340}$ +277°, “inflect.” $[\alpha]_{325}$ +871°.

6β-Hydroxy-Δ^{4}-cholesten-3-one (XXX) (O. Mancera), R.D. (Fig. 9), *c*, 0.10 in *dioxane:* $[\alpha]_{700}$ +18, $[\alpha]_{589}$ +32°, $[\alpha]_{275}$ +438°, “max.” $[\alpha]_{400-450}$ +45°, “shoulder” $[\alpha]_{367-373}$ −83°, “min.” $[\alpha]_{357.5}$ −220°, “max.” $[\alpha]_{348}$ −40°, “min.” $[\alpha]_{343}$ −57°, “shoulder” $[\alpha]_{327-330}$ +310°, “inflect.” $[\alpha]_{317}$ +545°, “max.” $[\alpha]_{305}$ +613°; *c* 0.10 in *methanol:* $[\alpha]_{700}$ +38°, $[\alpha]_{589}$ +43°, $[\alpha]_{292.5}$ −320°, “max.” $[\alpha]_{425-500}$ +57°, min.” $[\alpha]_{350}$ −171°, “max.” $[\alpha]_{315}$ +285°.

6β-Hydroxytestosterone (XXXI) (O. Mancera), R.D., *c* 0.10; $[\alpha]_{700}$ +12°, $[\alpha]_{589}$ +23°, $[\alpha]_{270}$ +551°, “max.” $[\alpha]_{425-475}$ +40°, “min.” $[\alpha]_{371}$ −128°, “max.” $[\alpha]_{367.5}$ −120°, “min.” $[\alpha]_{357.5}$ −300°, “max.” $[\alpha]_{349}$ −66°, “min.” $[\alpha]_{343}$ −106°, “inflect.” $[\alpha]_{327.5}$ +374°, “inflect.” $[\alpha]_{317.5}$ +654°, “max.” $[\alpha]_{302.5}$ +768°.

7-Ketocholesterol Acetate (XXXII) (R. C. Cookson), R.D. (Fig. 10), *c* 0.105: $[\alpha]_{700}$ −66°, $[\alpha]_{589}$ −85°, $[\alpha]_{275}$ −2178°, “min.” $[\alpha]_{395-425}$ −175°, “max.” $[\alpha]_{371}$ +98°, “min.” $[\alpha]_{365}$ +69°, “max.” $[\alpha]_{357.5}$ +151°, “inflect.” $[\alpha]_{345}$ −309°.

7-Ketodesoxycorticosterone Acetate 3,20-Biscycloethylene Ketal (XXXIII)[20] (S. Bernstein), R.D. (Fig. 10), *c* 0.104: $[\alpha]_{700}$ −29°, $[\alpha]_{589}$ −45°, $[\alpha]_{275}$ −1985°, “max.” $[\alpha]_{370}$ +394°, “min.” $[\alpha]_{364}$ + 369°, “max.” $[\alpha]_{355}$ +440°, “inflect.” $[\alpha]_{342.5}$ −107°.

$\Delta^{7,22}$-Ergostadien-3β-ol-6-one Acetate (XXXIV) (R. C. Cookson), R.D. (Fig. 10), *c* 0.076: $[\alpha]_{700}$ −24°, $[\alpha]_{589}$ −14°, $[\alpha]_{300}$ −2950°, “max.” $[\alpha]_{362.5}$ +1237°, “min.” $[\alpha]_{355}$ +900°, “max.” $[\alpha]_{347.5}$ +1104°, “inflect.” $[\alpha]_{335}$ −458°, “inflect.” $[\alpha]_{320}$ −2014°.

Methyl Δ^{8}-3α-acetoxy-7-ketocholenate (XXXV) (L. F. Fieser), R.D. (Fig. 11), *c* 0.102: $[\alpha]_{700}$ −12°, $[\alpha]_{589}$ −19°, $[\alpha]_{280}$ −148°, “min.” $[\alpha]_{370}$ −193°, “max.” $[\alpha]_{332.5}$ +128°, “min.” $[\alpha]_{325}$ +93°, “max.” $[\alpha]_{320}$ +123°.

Δ^{8}-Cholesten-3β-ol-7-one acetate (XXXVI) (L. F. Fieser), R.D. (Fig. 11), *c* 0.10: $[\alpha]_{700}$ −29°, $[\alpha]_{589}$ −30°, $[\alpha]_{277.5}$ −1865, “min.” $[\alpha]_{425-450}$ −55°, “max.” $[\alpha]_{385}$ +52°, “min.” $[\alpha]_{375}$ +31°, “max.” $[\alpha]_{369}$ +49°, “inflect.” $[\alpha]_{352.5}$ −117°.

$\Delta^{8(14)}$-Cholesten-3β-ol-7-one acetate (XXXVII) (L. F. Fieser), R.D. (Fig. 11), *c* 0.106: $[\alpha]_{700}$ −37°, $[\alpha]_{589}$ −59°, $[\alpha]_{285}$ −1034°, “min.” $[\alpha]_{375}$ −554°, “shoulder” $[\alpha]_{360-362}$ −496°, “max.” $[\alpha]_{320}$ +160°.

Δ^{2}-Cholesten-1-one (XXXVIII)[21] (C. Tamm and T. Reichstein), R.D. (Fig. 11), *c* 0.10: $[\alpha]_{700}$ +87°, $[\alpha]_{589}$ +116°, $[\alpha]_{272.5}$ +2159°, “max.” $[\alpha]_{440-460}$ +180°, “min.” $[\alpha]_{366}$ −397°, “max.” $[\alpha]_{311}$ +1997°, “min.” $[\alpha]_{295}$ +1965°.

Δ^{5}-Pregnen-3β-ol-20-one (XXXIX) R. D. (Fig. 12), *c* 0.115 in *dioxane:* $[\alpha]_{700}$ +3°, $[\alpha]_{589}$ +16°, $[\alpha]_{282.5}$ −1914°, $[\alpha]_{315}$ +2041°; *c* 0.10 in *methanol:* $[\alpha]_{700}$ +13°, $[\alpha]_{589}$ +27°, $[\alpha]_{255}$ −3039°, “max.” $[\alpha]_{307.5}$ +2356, “min.” $[\alpha]_{262.5}$ −3301°.

$\Delta^{5,16}$-Pregnadien-3β-ol-20-one acetate (XL) R.D. (Fig. 12), *c* 0.11: $[\alpha]_{700}$ −26°, $[\alpha]_{589}$ −43°, $[\alpha]_{275}$ −1900°, “max.” $[\alpha]_{362.5}$ +657°, “min.” $[\alpha]_{298}$ −1959°.

Δ^{16}-Pregnen-3α-ol**-20-one acetate (XLI)** (O. Mancera), R.D. *c* 0.10: $[\alpha]_{700}$ +49°, $[\alpha]_{589}$ +83°, $[\alpha]_{272.5}$ −580°, “max.” $[\alpha]_{362.5}$ +995°, “min.” $[\alpha]_{304}$ −1045°.

Δ^{16}-Allopregnen-15β-ol-20-one acetate (XLII), R.D. (Fig. 12), *c* 0.156: $[\alpha]_{700}$ −129°, $[\alpha]_{589}$ −170°, $[\alpha]_{275}$ −4320°, “min.” $[\alpha]_{440-475}$ −260°, “max.” $[\alpha]_{372.5}$ +224°, “inflect.” $[\alpha]_{300}$ −3260°.

16,17-Methylene-Δ^{5}-pregnen-3β-ol-20-one acetate (XLIII)[23] R.D. (Fig. 12), *c* 0.10: $[\alpha]_{700}$ +6°, $[\alpha]_{589}$ +24°, $[\alpha]_{272.5}$ −15°, “max.” $[\alpha]_{297.5}$ +665°.

16-Dehydroprogesterone (XLIV), R.D. (Fig. 12), *c* 0.10: $[\alpha]_{700}$ +99°, $[\alpha]_{589}$ +154°, $[\alpha]_{275}$ +2305°, “max.” $[\alpha]_{377}$ +959°, “min.” $[\alpha]_{370}$ +920°, “max.” $[\alpha]_{360}$ +1050°, “min.” $[\alpha]_{347.5}$ +703°, “max.” $[\alpha]_{345}$ +755° “min.” $[\alpha]_{336}$ +415°, “max.” $[\alpha]_{330}$ +725°, “min.” $[\alpha]_{322.5}$ +425°, “shoulder” $[\alpha]_{312-315}$ +600°.

Cortisone acetate (XLVa) (A. L. Nussbaum) R.D. (Fig. 13), *c* 0.101: $[\alpha]_{700}$ +134°, $[\alpha]_{589}$ +218°, $[\alpha]_{275}$ +674°, “max.” $[\alpha]_{375}$ +946°, “min.” $[\alpha]_{367.5}$ +912°, “max.” $[\alpha]_{360}$ +1065°, “min.” $[\alpha]_{355}$ +1042°, “inflect.” $[\alpha]_{340}$ +1510°, “max.” $[\alpha]_{320}$ +3040°, “min.” $[\alpha]_{281}$ +416°.

9α-Fluorocortisone acetate (XLVb) (J. Fried), R.D., *c* 0.091: $[\alpha]_{700}$ +113°, $[\alpha]_{589}$ +180°, $[\alpha]_{275}$ +1180°, “max.” $[\alpha]_{380-385}$ +1524°, “min.” $[\alpha]_{370}$ +474°, “max.” $[\alpha]_{362.5}$ +537°, “min.” $[\alpha]_{355}$ +479°, “inflect.” $[\alpha]_{342.5}$ +775°, “max.” $[\alpha]_{310}$ +2890°.

9α-Chlorocortisone acetate (XLVc) (J. Fried), R.D., *c* 0.0674: $[\alpha]_{700}$ +159°, $[\alpha]_{589}$ +258°, $[\alpha]_{275}$ −1461°, “max.” $[\alpha]_{327.5}$ +3661°, “min.” $[\alpha]_{280}$ −1820°.

9α-Bromocortisone acetate (XLVd) (J. Fried), R.D. (Fig. 13), *c* 0.10: $[\alpha]_{700}$ +162°, $[\alpha]_{589}$ +261°, $[\alpha]_{280}$ −3120°, “max.” $[\alpha]_{342}$ +3497°.

4-Chlorocortisone acetate[35] (H. J. Ringold), R.D., *c* 0.046: $[\alpha]_{700}$ +81°, $[\alpha]_{589}$ +148°, $[\alpha]_{275}$ +1110°, “inflect.” $[\alpha]_{367.5}$ +775°, “max.” $[\alpha]_{352.5}$ +869°, “min.” $[\alpha]_{340}$ +733°, “max.” $[\alpha]_{310}$ +2010°, “min.” $[\alpha]_{280}$ +643°.

17α-Methyl-Δ^{4}-androstene-11β,17β-diol-3-one (XLVIa)[25] (J. A. Hogg), R.D., *c* 0.090: $[\alpha]_{700}$ +90°, $[\alpha]_{589}$ +133°, $[\alpha]_{275}$ +3200°, “max.” $[\alpha]_{400-425}$ +250°, “min.” $[\alpha]_{365}$ −116°, “max.” $[\alpha]_{358}$ −16°, “min.” $[\alpha]_{350}$ −141°, “inflect.” $[\alpha]_{340}$ +396°, “shouder” $[\alpha]_{322-327}$ +1490°.

9α-Fluoro-17α-methyl**-Δ^{4}-androstene-11β,17β-diol-3-one (XLVIb)**[25] (J. A. Hogg), R.D., *c* 0.11: $[\alpha]_{700}$ +77°, $[\alpha]_{589}$ +114°, $[\alpha]_{275}$ +3410°, “max.” $[\alpha]_{410-430}$ +199°, “min.” $[\alpha]_{367.5}$ −165°, “max.” $[\alpha]_{360}$ −79°, “min.” $[\alpha]_{353}$ −198°, “inflect.” $[\alpha]_{340}$ +484°, “inflect.” $[\alpha]_{325}$ +1450°.

9α-Bromo-17α-methyl**-Δ^{4}-androstene-11β,17β-diol-3-one (XLVIc)**[25] (J. A. Hogg), R.D., *c* 0.106: $[\alpha]_{700}$ +66°, $[\alpha]_{589}$ +97°, $[\alpha]_{275}$ +3550°, “max.” $[\alpha]_{425-450}$ +180°, “min.” $[\alpha]_{370}$ −195°, “max.” $[\alpha]_{362.5}$ −98°, “min.” $[\alpha]_{355}$ −227°, “shoulder” $[\alpha]_{340-342.5}$ +530°, “inflect.” $[\alpha]_{325}$ +1630°.

11-Ketotestosterone (XLVIIa) (J. A. Hogg), R.D. (Fig. 13), *c* 0.10: $[\alpha]_{700}$ +122°, $[\alpha]_{589}$ +196°, $[\alpha]_{275}$ +3030°, “max.” $[\alpha]_{377.5}$ +774°, “min.” $[\alpha]_{369}$ +683°, “max.” $[\alpha]_{360}$ +770°, “min.” $[\alpha]_{352.5}$ +659°, “max.” $[\alpha]_{343}$ +928°, “min.” $[\alpha]_{340}$ +912°, “max.” $[\alpha]_{327}$ +1353°, “min.” $[\alpha]_{320}$ +1314°, “shoulder” $[\alpha]_{310-315}$ +1500°, “shoulder” $[\alpha]_{300-303}$ +1650°, “inflect.” $[\alpha]_{290}$ +2065°.

9α-Fluoro-17α-methyl**-Δ^{4}-androstene-3,**11**-dione-17β-ol (XLVIIb)**[25] (J. A. Hogg), R.D., *c* 0.12: $[\alpha]_{700}$ +86°, $[\alpha]_{589}$ +128°, $[\alpha]_{280}$ +2885°, “max.” $[\alpha]_{390-400}$ +292°, “min.” $[\alpha]_{368}$ +131°, “max.” $[\alpha]_{364}$ +164°, “min.” $[\alpha]_{353}$ +12°, “shoulder” $[\alpha]_{343-348}$ +185°, “inflect.” $[\alpha]_{327.5}$ +771°.

9α-Bromo-17α-methyl-Δ^{4}-androstene-3,11**-dione-17β-ol (XLVIIc)**.—A solution of 50 mg. of the bromohydrin XLVIc in 3 cc. of glacial acetic acid and 2 cc. of carbon tetrachloride was treated with 11 mg. of chromium trioxide in 2 cc. of 95% acetic acid, and the mixture was warmed at 50° for 5 minutes. Water was added, the neutral product was isolated by means of ether and recrystallized twice from methylene chloride; yield 30 mg., m.p. 168–170° dec.; $\lambda_{\max}^{\mathrm{CHCl_3}}$ 2.80, 5.81, 5.98 and 6.13 μ. *Anal.* Calcd. for $C_{20}H_{27}BrO_3$: Br, 20.21. Found: Br, 19.67. R.D. (Fig. 13), *c* 0.115: $[\alpha]_{700}$ +122°, $[\alpha]_{589}$ +190°, $[\alpha]_{275}$ +487°, “inflect.” $[\alpha]_{355}$ +1985°, “max.” $[\alpha]_{345}$ +2605°, “shoulder” $[\alpha]_{337-340}$ +2375°, “min.” $[\alpha]_{298}$ −1104°.

1,4-Androstadien-17β-ol-3-one (XLIX), R.D. (Fig. 14), *c* 0.148: $[\alpha]_{700}$ +30°, $[\alpha]_{589}$ +27°, $[\alpha]_{305}$ +262°, “min.” $[\alpha]_{380}$ −131°, “max.” $[\alpha]_{374}$ −108°, “min.” $[\alpha]_{366}$ −142°, “inflect.” $[\alpha]_{352.5}$ +18°, “shoulder” $[\alpha]_{337-340}$ +191°, “max.” $[\alpha]_{315}$ +318°.

1,4-Pregnadiene-3,11,20-trione-17α,21-diol **acetate (L)** (E. B. Hershberg, K. Pfister), R.D. (Fig. 14), *c* 0.114 in *dioxane:* $[\alpha]_{700}$ +114°, $[\alpha]_{589}$ +187°, $[\alpha]_{277.5}$ −3400°, “max.” $[\alpha]_{382}$ +1009°, “min.” $[\alpha]_{375}$ +909°, “max.” $[\alpha]_{365}$ +1090°, “min.” $[\alpha]_{357.5}$ +900°, “shoulder” $[\alpha]_{343-350}$ +1045°, “max.” $[\alpha]_{320}$ +2522°, “inflect.” $[\alpha]_{315}$ +2200°; *c* 0.102 in *methanol:* $[\alpha]_{700}$ +125°, $[\alpha]_{589}$ +188°, $[\alpha]_{285}$ −1755°, “inflect.” $[\alpha]_{335}$ +1455°, “max.” $[\alpha]_{319}$ +2200°, “min.” $[\alpha]_{287.5}$ −2520°.

1,4-Pregnadiene-3,20-dione-11β,17α,21-triol acetate (LI) (E. B. Hershberg, K. Pfister), R.D. (Fig. 14), *c* 0.064 in *dioxane:* $[\alpha]_{700}$ +86°, $[\alpha]_{589}$ +132°, $[\alpha]_{277.5}$ −2060°, “max.” $[\alpha]_{317.5}$ +2890°, “min.” $[\alpha]_{280}$ −2230°; *c* 0.087 in *methanol:* $[\alpha]_{700}$ +91°, $[\alpha]_{589}$ +137°, $[\alpha]_{285}$ +706°, “max.” $[\alpha]_{314}$ +2800°, “min.” $[\alpha]_{287.5}$ −684°.

8α-Allopregnan-3β-ol-20-one acetate (LII),[28] R.D., *c* 0.10: $[\alpha]_{700}$ +109°, $[\alpha]_{589}$ +193°, $[\alpha]_{270}$ −355°, “max.” $[\alpha]_{314}$ +2522°, “min.” $[\alpha]_{277}$ −1081°.

Δ^{16}-8α-Allopregnen-3β-ol-20-one acetate (LIII),[28] R.D., *c* 0.10: $[\alpha]_{700}$ +68°, $[\alpha]_{589}$ +124°, $[\alpha]_{272.5}$ +141°, “max.” $[\alpha]_{360}$ +1090°, “min.” $[\alpha]_{307.5}$ −703°.

8α-Androstan-3β-ol-17-one (LIV),[28] R.D., *c* 0.10: $[\alpha]_{700}$ +130°, $[\alpha]_{589}$ +200°, $[\alpha]_{272.5}$ −400°, "max." $[\alpha]_{320}$ +2776°, "min." $[\alpha]_{281}$ −1160°.

8α-Testosterone (LV),[28] R.D. (Fig. 15), *c* 0.035: $[\alpha]_{700}$ +65°, $[\alpha]_{589}$ +134°, $[\alpha]_{275}$ −51°, "max." $[\alpha]_{372}$ +1190°, "min." $[\alpha]_{362.5}$ +970°, "max." $[\alpha]_{355}$ +1173°, "shoulder" $[\alpha]_{340-345}$ +345°, "shoulder" $[\alpha]_{327-330}$ −374°, "min." $[\alpha]_{317}$ −662°.

Δ^4-8α-Androstene-3,17-dione (LVI),[28] R.D. (Fig. 15), *c* 0.90; $[\alpha]_{700}$ +215°, $[\alpha]_{589}$ +329°, $[\alpha]_{275}$ −1305°, "max." $[\alpha]_{372.5}$ +2330°, "min." $[\alpha]_{365}$ +2020°, "max." $[\alpha]_{356}$ +2440°, "min." $[\alpha]_{347.5}$ +1450°, "max." $[\alpha]_{340}$ +1705°, "min." $[\alpha]_{332.5}$ +1185°, "max." $[\alpha]_{321}$ +1780°, "min." $[\alpha]_{282.5}$ −1550°.

8α-Progesterone (LVII),[28] R.D. (Fig. 15), *c* 0.055: $[\alpha]_{700}$ +96°, $[\alpha]_{589}$ +169°, $[\alpha]_{270}$ −2700°, "max." $[\alpha]_{371}$ +1311°, "min." $[\alpha]_{363}$ +1238°, "max." $[\alpha]_{357.5}$ +1490°, "min." $[\alpha]_{345}$ +1010°, "max." $[\alpha]_{342}$ +1060°, "min." $[\alpha]_{334}$ +873°, "max." $[\alpha]_{315}$ +1460°.

B-Nor-Δ^4-cholesten-3-one (LIX)[31] (W. G. Dauben), R.D. (Fig. 15), *c* 0.10: $[\alpha]_{700}$ −7°, $[\alpha]_{589}$ −4°, $[\alpha]_{275}$ −4280°, "max." $[\alpha]_{375}$ +1420°, "min." $[\alpha]_{365}$ +1065°, "max." $[\alpha]_{358}$ +1275°, "inflect." $[\alpha]_{345}$ −431°, "inflect." $[\alpha]_{330}$ −2288°.

$\Delta^{4,9(11),16}$-D-Homoandrostatrien-3-one (LX),[12,32] R.D., *c* 0.010: $[\alpha]_{700}$ −23°, $[\alpha]_{589}$ −28°, $[\alpha]_{285}$ +905°, "min." $[\alpha]_{367}$ −440°, "max." $[\alpha]_{361}$ −400°, "min." $[\alpha]_{352.5}$ −590°, "max." $[\alpha]_{342.5}$ −166°, "min." $[\alpha]_{340}$ −180°, "max." $[\alpha]_{327.5}$ +570°, "min." $[\alpha]_{325}$ +480°, "inflect." $[\alpha]_{310}$ +945°, "max." $[\alpha]_{304}$ +1055°, "min." $[\alpha]_{299}$ +970°, "max." $[\alpha]_{294}$ +1025°.

$\Delta^{4,9(11)}$-D-Homoandrostadiene-16β,17β-diol-3-one (LXI)[12,32] R.D., *c* 0.109: $[\alpha]_{700}$ +2°, $[\alpha]_{589}$ +5°, $[\alpha]_{280}$ +931°, "min." $[\alpha]_{366}$ −326°, "max." $[\alpha]_{361}$ −280°, "min." $[\alpha]_{353}$ −450°, "max." $[\alpha]_{342.5}$ −47°, "min." $[\alpha]_{340}$ −58°, "inflect." $[\alpha]_{325}$ +528°, "inflect." $[\alpha]_{310}$ +1019°, "max." $[\alpha]_{303}$ +1126°, "shoulder" $[\alpha]_{290-297}$ +1030°.

Δ^4-Cholestene-3,6-dione (LXII) (L. F. Fieser), R.D. (Fig. 16), *c* 0.144: $[\alpha]_{700}$ −13°, $[\alpha]_{589}$ −19°, $[\alpha]_{285}$ +1142°, "min." $[\alpha]_{402.5}$ −599°, "max." $[\alpha]_{307.5}$ +1662°.

6-Ketotestosterone (LXIII) (O. Mancera), R.D., *c* 0.113: $[\alpha]_{700}$ −18°, $[\alpha]_{589}$ −40°, $[\alpha]_{285}$ +1679°, "min." $[\alpha]_{402}$ −680°, "max." $[\alpha]_{302.5}$ +1937°.

B-Nor-Δ^4-cholestene-3,6-dione (LXIV)[31] (W. G. Dauben), R.D. (Fig. 16), *c* 0.10: $[\alpha]_{700}$ +68° $[\alpha]_{589}$ +143°, $[\alpha]_{287.5}$ −5600°, "max." $[\alpha]_{450}$ +1806°, "shoulder" $[\alpha]_{428-432}$ +1086°, "inflect." $[\alpha]_{405}$ −798°, "inflect." $[\alpha]_{380}$ −1561°.

16-Methylene-Δ^5-androsten-3β-ol-17-one (LXV)[33] (O. Mancera), R.D. (Fig. 16), *c* 0.123: $[\alpha]_{700}$ −39°, $[\alpha]_{589}$ −53°, $[\alpha]_{270}$ −2438°, "max." $[\alpha]_{394}$ +544°, "min." $[\alpha]_{385}$ +495°, "max." $[\alpha]_{379}$ +536°, "inflect." $[\alpha]_{310}$ −1771°.

16-Methylene-Δ^5-androstene-3,17-dione (LXVI)[33] (O. Mancera), R.D., *c* 0.089: $[\alpha]_{700}$ +55°, $[\alpha]_{589}$ +89°, $[\alpha]_{285}$ +197°, "max." $[\alpha]_{393}$ +783°, "shoulder" $[\alpha]_{380-385}$ +705°, "inflect." $[\alpha]_{360}$ −176°, "min." $[\alpha]_{350}$ −938°, "max." $[\alpha]_{342.5}$ −675°, "min." $[\alpha]_{337.5}$ −871°, "max." $[\alpha]_{327.5}$ +202°, "min." $[\alpha]_{322.5}$ −259°, "shoulder" $[\alpha]_{307-311}$ +185°, "max." $[\alpha]_{300}$ +300°.

Jervine (LXVII) (O. Wintersteiner), R.D. (Fig. 16), *c* 0.10: $[\alpha]_{700}$ −113°, $[\alpha]_{589}$ −167°, $[\alpha]_{280}$ −2020°, "min." $[\alpha]_{397}$ −1041, "max." $[\alpha]_{389}$ −965°, "min." $[\alpha]_{380}$ −1058°, "inflect." $[\alpha]_{365}$ −562°, "inflect." $[\alpha]_{347.5}$ −86°, "max." $[\alpha]_{337}$ +4°.

$\Delta^{1,4,6}$-Androstatrien-17β-ol-3-one acetate (LXVIII), R.D. (Fig. 16), *c* 0.104: $[\alpha]_{700}$ −60°, $[\alpha]_{589}$ −47°, $[\alpha]_{320}$ −3505°, "max." $[\alpha]_{404}$ +1564°, "min." $[\alpha]_{392.5}$ +975°, "max." $[\alpha]_{387.5}$ +1051°, "inflect." $[\alpha]_{352.5}$ −2782°, "min." $[\alpha]_{325}$ −3840°.

Δ^1-Cholesten-3-one.—The earlier reported[3c] measurements were repeated using a xenon lamp in order to define more precisely the 280–300 mμ region which could not be measured with the zirconium lamp. R.D. *c* 0.081 in *methanol:* $[\alpha]_{700}$ +54°, $[\alpha]_{589}$ +79°, $[\alpha]_{275}$ +2400°, "max." $[\alpha]_{425-460}$ +122°, "min." $[\alpha]_{365}$ −222°, "inflect." $[\alpha]_{300}$ +1741°; *c* 0.081 in *dioxane:* $[\alpha]_{700}$ +36°, $[\alpha]_{559}$ +56°, $[\alpha]_{280}$ +1302°, "max." $[\alpha]_{440-460}$ +90°, "min." $[\alpha]_{382.5}$ −211°, "max." $[\alpha]_{272.5}$ −78°, "min." $[\alpha]_{365}$ −124°, "shoulder" $[\alpha]_{349-352}$ +375°, "shoulder" $[\alpha]_{335-338}$ +865°, "max." $[\alpha]_{325}$ +1083°, "min." $[\alpha]_{320}$ +1058°, "max." $[\alpha]_{312.5}$ +1088°, "min." $[\alpha]_{305}$ +1053.

Δ^1-2-Chlorocholesten-3-one, R.D., *c* 0.061 in *methanol:* $[\alpha]_{700}$ +30°, $[\alpha]_{589}$ +64°, $[\alpha]_{425-450}$ +100°, $[\alpha]_{365}$ −249°; *c* 0.107 in *dioxane:* $[\alpha]_{700}$ +37°, $[\alpha]_{589}$ +50°, $[\alpha]_{280}$ +2380°, "min." $[\alpha]_{380}$ −208°, "max." $[\alpha]_{372.5}$ −178°, "min." $[\alpha]_{364}$ −247°, "shoulder" $[\alpha]_{348-352}$ +105°, "inflect." $[\alpha]_{335}$ +696°.

Δ^1-2-Bromocholesten-3-one, R.D., *c* 0.092 in *methanol:* $[\alpha]_{700}$ +42°, $[\alpha]_{589}$ +55°, $[\alpha]_{290}$ +2164°, "max." $[\alpha]_{440-475}$ +76°, "min." $[\alpha]_{367}$ −186°; *c* 0.085 in *dioxane:* $[\alpha]_{700}$ +47°, $[\alpha]_{589}$ +42°, $[\alpha]_{285}$ +1930°, "min." $[\alpha]_{382.5}$ −180°, "max." $[\alpha]_{375}$ −129°, "min." $[\alpha]_{365}$ −192°, "inflect." $[\alpha]_{350}$ +109°, "inflect." $[\alpha]_{335}$ +600°, "inflect." $[\alpha]_{322.5}$ +1020°.

Δ^1-Androsten-17β-ol-3-one 17-hexahydrobenzoate, R.D. *c* 0.0886 in *methanol:* $[\alpha]_{700}$ +5°, $[\alpha]_{589}$ +7°, $[\alpha]_{280}$ +2037°, "min." $[\alpha]_{365}$ −262°, "inflect." $[\alpha]_{300}$ +1680°, *c* 0.043 in *dioxane:* $[\alpha]_{700}$ +68°, $[\alpha]_{589}$ +104°, $[\alpha]_{280}$ +2660°, "max." $[\alpha]_{450-500}$ +135°, "min." $[\alpha]_{382.5}$ −528°, "max." $[\alpha]_{372.5}$ −258°, "min." $[\alpha]_{366}$ −370°, "shoulder" $[\alpha]_{350-355}$ +655°, "shoulder" $[\alpha]_{335-340}$ +1660°, "shoulder" $[\alpha]_{320-325}$ +2130°.

Δ^1-2-Bromoandrosten-17β-ol-3-one 17-hexahydrobenzoate, R.D., *c* 0.0936 in *methanol:* $[\alpha]_{700}$ +38°, $[\alpha]_{589}$ +56°, $[\alpha]_{290}$ +2042°, "max." $[\alpha]_{425-475}$ +85°, "min." $[\alpha]_{367}$ −156°; *c* 0.10 in *dioxane:* $[\alpha]_{700}$ +34°, $[\alpha]_{589}$ +38°, $[\alpha]_{285}$ +1825°, "max." $[\alpha]_{475-500}$ +62°, "min." $[\alpha]_{382.5}$ −136°, "max." $[\alpha]_{375}$ −108°, "min." $[\alpha]_{365}$ −165°, "inflect." $[\alpha]_{350}$ +177°, "inflect." $[\alpha]_{335}$ +640°.

Δ^1-2,4-Dibromoandrosten-17β-ol-3-one 17-hexahydrobenzoate, R.D., *c* 0.0966 in *methanol:* $[\alpha]_{700}$ +24°, $[\alpha]_{589}$ +29°, $[\alpha]_{290}$ −48°, "max." $[\alpha]_{475-550}$ +33°, "min." $[\alpha]_{372.5}$ −264°, "max." $[\alpha]_{307.5}$ +1315°; *c* 0.103 in *dioxane:* $[\alpha]_{700}$ +20°, $[\alpha]_{589}$ +22°, $[\alpha]_{287.5}$ +1720°, "inflect." $[\alpha]_{382.5}$ −226°, "min." $[\alpha]_{372.5}$ −271°, "inflect." $[\alpha]_{355}$ −65°.

Δ^1-Allopregnene-3,20-dione-21-ol acetate, R.D., *c* 0.103 in *methanol:* $[\alpha]_{700}$ +97°, $[\alpha]_{589}$ +151°, $[\alpha]_{295}$ +3200°, "max." $[\alpha]_{400-410}$ +345°, "min." $[\alpha]_{366}$ +188°, "max." $[\alpha]_{303}$ +3992°; *c* 0.10 in *dioxane:* $[\alpha]_{700}$ +79°, $[\alpha]_{589}$ + 120°, $[\alpha]_{290}$ +1343°, "max." $[\alpha]_{408-420}$ +252°, "min." $[\alpha]_{382.5}$ +33°, "max." $[\alpha]_{371}$ +230°, "min." $[\alpha]_{366}$ +210°, "inflect." $[\alpha]_{352.5}$ +829°, "inflect." $[\alpha]_{337.5}$ +1581°, "max." $[\alpha]_{309}$ +3018°.

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DETROIT, MICHIGAN