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OPTICAL ROTATORY DISPERSION STUDIES—CIII[1]

THIOSTEROIDS–XVI[2]
OPTICAL ROTATORY DISPERSION AND CIRCULAR DICHROISM OF TWISTED SULPHUR-CONTAINING CHROMOPHORIC SYSTEMS

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Abstract—The optical properties of a number of di- and trithiocarbonates, oxathiolanes, dithiolanes and oxathianes, have been examined. Optical rotatory dispersion and circular dichroism measurements have demonstrated the optical activity of the various absorption bands in these compounds and such data serve to generate a chirality rule in which the sense of twist of the chromophoric ring corresponds in sign to the measurements in question.

ALTHOUGH the initial and large amount of work in optical rotatory dispersion (ORD) proved very important in the formalization of the octant rule,[3] and there is still further work in progress stimulated by the success of such a rule, recently there has also been notable interest in the ORD and circular dichroism (CD) of dissymmetric chromophores,[4] and especially of those cases in which a distorted (twisted) π electron system is present.[5] In connection with our work on steroidal sulphur compounds,[6,7] we have had occasion to report briefly on the ORD and CD of trithiocarbonates[8] without, however, relating them to chirality or other geometrical features. In the course of further investigations of a large number of various steroidal sulphur compounds, some important generalizations have arisen—especially with regard to cyclic dithiocarbonates, trithiocarbonates and oxathiolanes and these are discussed herewith.

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[1] For paper CII, see K. Takeda, K. Kuriyama, T. Komeno, D. A. Lightner, R. Records and C. Djerassi, *Tetrahedron*, **21**, 1203 (1965).

[2] For paper XV, see T. Komeno, K. Tori and K. Takeda, *Tetrahedron*, submitted for publication.

[3] C. Djerassi, *Optical Rotatory Dispersion: Applications to Organic Chemistry*. McGraw-Hill, New York (1960).

[4] For leading Refs. see K. Mislow, *Annals of the New York Acad. of Sci.* **93**, 457 (1962).

[5] A. Moscowitz, K. Mislow, M. A. W. Glass and C. Djerassi, *J. Amer. Chem. Soc.* **84**, 1945 (1962). R. C. Cookson and J. Hudec, *J. Chem. Soc.* 429 (1962).

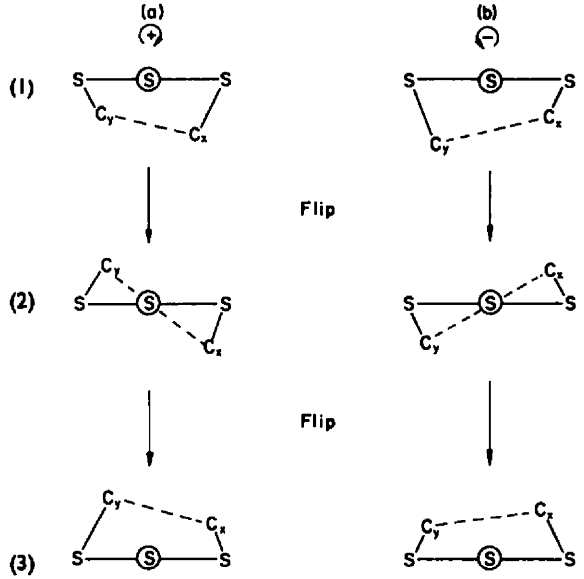
[6] D. A. Lightner and C. Djerassi, *Tetrahedron*, **21**, 583 (1965).

[7] K. Takeda, T. Komeno, J. Kawanami, S. Ishihara, H. Kadokawa, H. Tokura and H. Itani, *Tetrahedron*, **21**, 329 (1965).

[8] C. Djerassi, H. Wolf, D. A. Lightner, E. Bunnenberg, K. Takeda, T. Komeno and K. Kuriyama, *Tetrahedron* **19**, 1547 (1963).

Dithio- and Trithio-carbonates

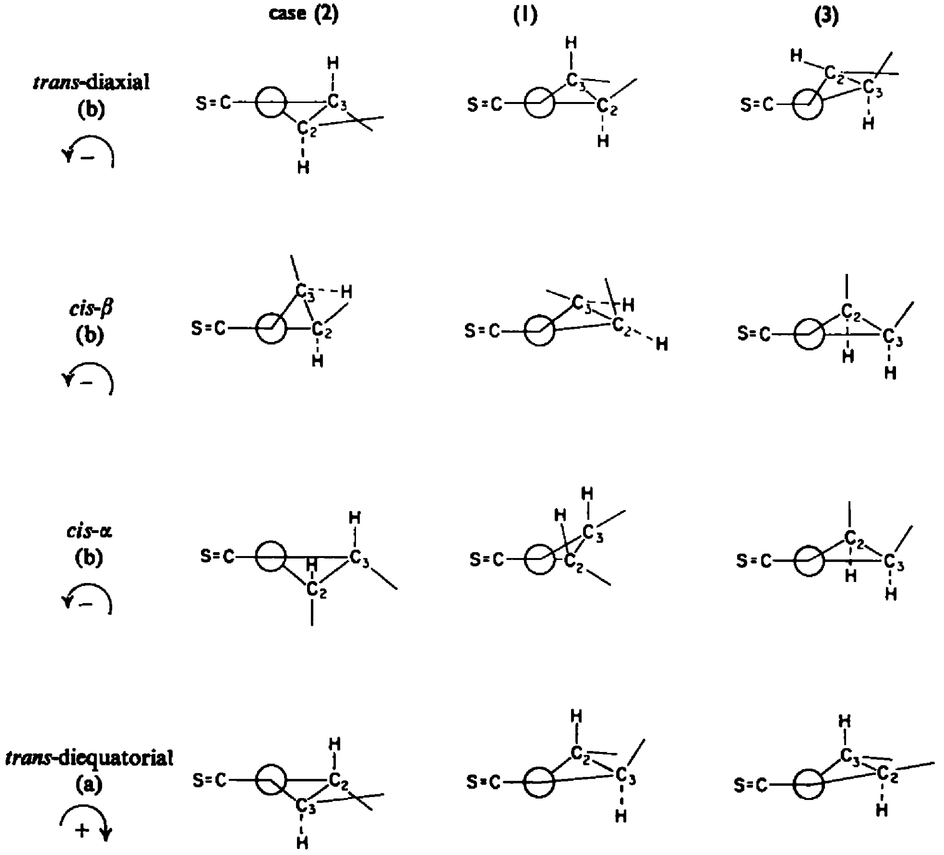
On the basis of a critical examination of the stereochemistry of steroidal cyclic dithio-and trithio-carbonates in which the 5-membered ring is fused onto a six membered ring and in which the thiocarbonyl group is located opposite and not adjacent to the commonly shared two carbon atoms of the bicyclic system, there are three possible stereochemical arrangements of the C═S groupings (denoted ⓢ in the following diagrams) in regard to its environment.



Thus, if the plane generated by the two ring hetero atoms and the carbon atom of the thiocarbonyl group (and thus also necessarily the sulphur of the thiocarbonyl) is viewed from the thiocarbonyl sulphur atom through its carbon atom, the plane is seen to intersect (2) or pass above (3) or below (1) the carbon-carbon bond of the bridgehead carbon atoms giving rise (case 2) to an apparent, non-interconvertible (a -||→ b) chirality as designated above. Moreover, forms (1) and (3) also possess a chirality, which is more easily seen with models, of the same nature as is obvious with case (2), e.g. (1a) goes to (2a); likewise, (3a) goes to (2a). All this may be seen from the diagrams if the S–ⓢ–S plane is moved upward so that it intersects the C_x—C_y bond. Thus a given dithio- or trithio-carbonate may possess an apparent right (a) or left (b) handed sense of twist in the chromophoric system.

This chirality becomes the most important factor in determining the sign of the Cotton effect or CD curve in the $\pi \rightarrow \pi^*$ transition of the thiocarbonyl chromophore, and it also no doubt influences the $n \rightarrow \pi^*$ transition to a very large extent. Consequently, it may be expected that in the case of a cyclic dithio- or trithio-carbonate the sign of the $\pi \rightarrow \pi^*$ transition of the Cotton effect and CD curve will be determined by the chirality of the chromophoric system, and this in turn is of direct stereochemical importance with regard to the location of the chromophoric ring on the steroid perimeter, and to the relative stereochemistry of the ring heteroatoms with respect to the steroid moiety.

For any vicinal di-substituted system (dithiol, β-hydroxymercaptan) on a cyclohexane ring in a chair conformation in the steroid there may exist a maximum of four possible relative stereochemical arrangements of these groups: two *cis* (α,α and β,β) and two *trans* (α,β and β,α). The vicinal groups of the two *cis* forms are always arranged axial-equatorial or equatorial-axial; whereas, the two *trans* forms are equatorial-equatorial and axial-axial. When these vicinal atoms are joined in a five membered ring, there may arise four possible fused cyclic systems: two *cis* and two *trans*, where in the latter the cyclohexane ring of the *trans* diaxial arrangement must be flexible enough to flip into a boat or twist conformer in order to allow the heretofore *trans*-diaxial arrangement to become more nearly in position for ring formation. *In three of these four possible cases the chirality of the chromophoric ring will always be of the same sign: whereas the fourth case will always be oppositely signed.* The three cases which always possess the same sign are the two *cis* and the *trans*-diaxial arrangements; the *trans*-diequatorial is always oppositely signed from these. All this may be seen easily as shown below with a 2,3-substituted steroid if one looks through the nodal plane of the thiocarbonyl group (which also contains the two ring hetero atoms) and orthogonally at its π orbitals:



Moreover, as the vicinal substitutents move about the perimeter of the steroid skeleton, the chirality reverses sign in the respective groups.

TABLE 1. PREDICTED SIGN OF COTTON EFFECT OF DI- AND TRI-THIOCARBONATES IN 5α-ANDROSTANE SKELETON[a]

Position	*Cis*, and *Trans*-diaxial	*Trans*-diequatorial
1, 2	+	−
2, 3	−	+
3, 4	+	−
4, 5	−	
5, 6	+	
6, 7	−	+
7, 8	+	
9, 11	−	
11, 12	+	
14, 15	+	
15, 16	−	
16, 17	−	

[a] The same steroid of the opposite absolute configuration would have correspondingly opposite chiralities.

The predictions of chirality in Table 1 are borne out in the cases of the four isomers of cholestane at C-2, C-3 (Table 2), and as predicted from the generalizations and Table 1, the 3,4-dithiocarbonate is also in complete agreement (Table 2).

In order to show that these predictions are valid for systems other than steroids, data for simpler compounds[6,9] are presented in Table 3.

Experimental optical rotatory dispersion (and in several cases also circular dichroism) data together with appropriate spectral measurements are collected in Figs. 1–8. It should be noted that in the case of the dithiocarbonates the relevant π–π^* Cotton effect is the one centered near 280 mμ.

In summary, it may be seen that chirality effects dominate. In these twisted chromophores the electric and magnetic dipole moments associated with the π–π^* transition have non-zero parallel components; hence, the transition is optically active as such. The situation in the n–π^* transition is similar to that of β,γ-unsaturated ketones[5] in that due to the twisted chromophore, the so-called n- and π-systems are not orthogonal to each other. As in β,γ-unsaturated ketones, the erstwhile n–π^* transition will borrow electric dipole transition moment from the π–π^* transition, resulting in the high intensity CD curve for the n–π^* promotion. Again as in unsaturated ketones, the sign of the mixing coefficient (hence the sign of the n–π^* Cotton effect) is determined by the chirality. It may be noted that there is also a one-to-one correspondence between the relative sign of the π–π^* and n–π^* Cotton effects, as there must be if chirality dominates.

Oxathiolanes

Oxathiolanes show an electronic absorption maximum in the range 240–250 mμ ($\epsilon \sim 30$), and it would appear from the cases examined by us to date that this transition is an optically active one. On intensity grounds the transition considered is electric dipole forbidden and is probably related to the weak transition seen as a shoulder near 240 mμ in tetrahydrothiophene.[10] However, instead of it being a

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[9] G. E. McCasland, S. Furuta, A. Furst and J. N. Shoolery, *J. Org. Chem.* **28**, 456 (1963).

[10] R. E. Davis, *J. Org. Chem.* **23**, 1380 (1958).

TABLE 2. OBSERVED AND PREDICTED COTTON EFFECT OF DI- AND TRI-THIOCARBONATES OF THE CHOLESTANE SERIES

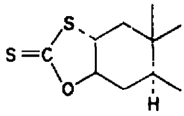
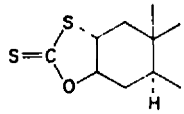
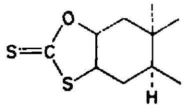
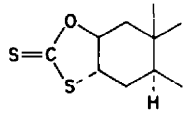
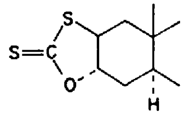
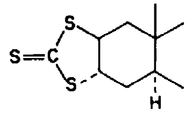
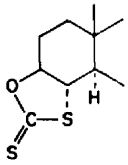
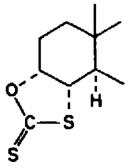
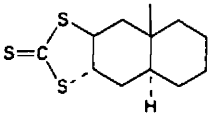
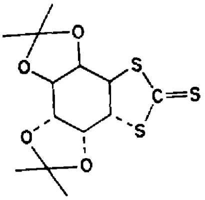
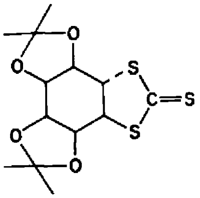
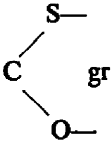
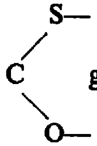
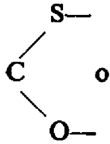
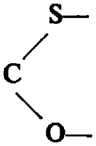
Stereochemistry		Observed chirality	Experimentally observed Cotton effect sign π–π^*
 4	*trans*-diequatorial	+ (Fig. 1)	+
 5	*cis*-α,α	− (Fig. 2)	−
 6	*cis*-β,β	− (Fig. 3)	−
 7	*trans*-diaxial (A boat)	− (Fig. 4)	−
 8	*trans*-diaxial (A boat)	− (Fig. 5)	−
 9	*trans*-diaxial (A boat)	− (Fig. 6)[8]	−
 10	*trans*-diequatorial	− (Fig. 7)	−
 11	*cis*-α,α	+ (Fig. 8)	+

TABLE 3. OBSERVED AND PREDICTED EFFECTS OF SOME NON-STEROIDAL TRITHIOCARBONATES

Stereochemistry		Observed chirality	Experimentally observed Cotton effect sign
 12	*trans*-diaxial (A boat)	−	−
 13	*trans*-diaxial (boat)	+	+
 14	*trans*-diequatorial	−	−

promotion from a sulphur 3p to a sulphur 3d orbital, the upper state M.O. is probably composed of 3d sulphur and 3d oxygen atomic orbitals; hence, there is a lowering of the upper-state orbital and concomitantly a reduction in the transition energy to near 250 mμ. In the present instance there is clearly no strong electric dipole allowed transition that is significantly mixed in ($\epsilon \sim 30$), unlike the previously mentioned inherently dissymmetric cases of the dithio- and trithio-carbonates and the β,γ-unsaturated ketones.[5] Hence, although there is an apparent correlation here, too, of chirality with sign of the Cotton effect, the present situation represents a different and somewhat new circumstance, as is evident not only by the small extinction coefficient, but also by the relativity small (for inherent chirality) rotational strength.

It is expected that the relatively small, signed magnitude of the isolated, twisted  grouping would be of the same order as vicinal contributions. Therefore, if the correlation between chirality and sign of the Cotton effect is to be maintained when the  group is no longer isolated, there must be a secondary correlation between the chirality and the geometry of the most important vicinal perturbers relative to the chromophore. This, in fact, is the case, i.e. the positions relative to  of the carbon atoms which make up the rest of the five membered ring are also determined by the chirality of  albeit secondarily, so that there is an overall correlation between chirality and sign, even though the magnitude of the rotational strength involved is relatively small.

For those examples in which the oxathiolane ring is fused to the steroid skeleton in a vicinal manner (in contrast to geminal or spiro), it would appear that the sign of the ORD Cotton effect and the CD curve is dependent to a large extent on the chirality of the chromophoric ring, the direction of which is assigned as done previously with dithio- and trithio-carbonates. It may be noted from the succeeding data that in each example the experimentally observed sign of the Cotton effect has always the opposite sign as assigned in Table 1 for the position and stereochemistry of the attached atoms. However, if the model is placed so that one looks through sulphur in much the same manner as was done by looking through the thione group in dithio- and trithiocarbonates, the sense of chirality is also uniformly opposite to that indicated in Table 1 and, in this sense, there is correlation between Cotton effect sign and chirality. The analogy of "looking through sulphur" is in no way meant to imply any similarity in the nature of the electronic transition, but is done for convenience.

In the set of cases examined, there is consistent agreement with the predicted sign according to observed chirality (Table 4). However, the case of the 2α(S), 3α(O)-acetonide (17), which shows two differently signed weak CD curves (Fig. 11), is extremely interesting and perhaps indicates that either solvation effects[11] are giving two different species, each having an electronic transition maximum at different wavelengths, or that there are in reality two different electronic transitions in the range 240–255 mμ heretofore undetected in solution spectra. In any case, the CD spectrum has detected a difference which was not otherwise noticeable in the ultraviolet spectrum.

The relevant optical rotatory dispersion and other spectral measurements are collected in Figs. 9–15. While in most cases the ORD results are unambiguous, Fig. 10 represents a good example where the CD curve is superior, since the ORD is characterized by a weak negative Cotton effect superimposed on a steeply positive

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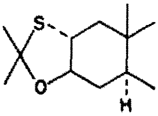
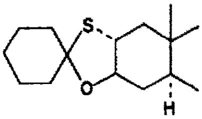
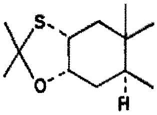
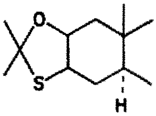
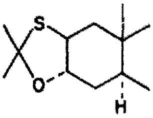
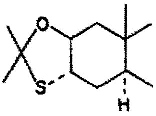
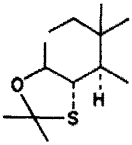
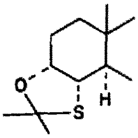
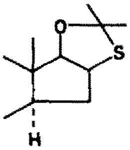
[11] K. M. Wellman, P. H. Laur, W. S. Briggs, A. Moscowitz and C. Djerassi, *J. Amer. Chem. Soc.* **87**, 66 (1965).

TABLE 4. SPECTRAL DATA AND CHIRALITY RELATIONSHIP OF OXATHIOLANES

	UV		ORD Cotton	CD		
	λ	(ε)	effect	λ	([θ])	Chirality
 15	250	(31)	− (Fig. 9)	251	(−3400)	−
 16			− (Fig. 10)	252	(−1370)	−
 17	245	(27)	? (Fig. 11)	240 255	(+180) (−680)	+
 18	243	(27)	+ (Fig. 12)	243	(+1450)	+
 19	248	(28)	+ (Fig. 13)	251	(+2620)	+
 20	249	(31)	+ (Fig. 14)	252	(+2200)	+
 21	240	(70)	+ (Fig. 15)			+
 22	243	(70)	− (Fig. 15)			−
 23			+ (Fig. 15)			+

background. Even more complicated is the evaluation of the ORD spectrum in Fig. 11 because of the two closely spaced Cotton effects noted in the corresponding CD.

In the case of spiro-oxathiolanes, such as the ethylene hemithioketals of steroid ketones, the aforesaid arguments also obtain. The major stereochemical difference is the greater flexibility of these hemithioketals, which may undergo facile conformational twisting (with accompanying reversing chirality), and because of this flexibility less can be said now in regard to the contribution of both chirality and substituent effects to the sign of the Cotton effect. Nevertheless, when the exact nature of the contributions which determine the sign are known, these flexible examples may prove even more interesting than the more rigid counterparts.

The appropriate spectral data are collected in Table 5, and in almost all cases the Cotton effects are unambiguously defined by the CD curves. The curves are not reproduced, with one exception, and the exact values are listed in the experimental section. The exception is Fig. 16 dealing with the two isomeric hemithioketals,[12] 27a and 27b, of cholestan-3-one. These isomeric substances both exhibit positive Cotton effect curves; however, the CD maxima are of unequal magnitude and the wavelengths of these maxima are significantly displaced from one another (Table 5). The differences in environment of the sulphur atoms in 27a (sulphur equatorial) and 27b (sulphur axial) and possibly different chiral forms evidently have significant effect.

Dithiolanes

Dithiolanes appear to exhibit an electronic transition maximum at about 245 mμ ($\epsilon \sim 350$),[13] which is possibly of the same type as that of oxathiolanes. Its optical activity is now demonstrated as shown in the examples collected in Table 5. In contrast to oxathiolanes, however, dithiolanes generally show two absorptions in their circular dichroism spectra; one appears near 260 mμ, whereas a second more intense one is noted near 240 mμ. These two transitions always appear oppositely signed (Figs 17 and 18), while in the UV spectra there is detected only one transition, generally near 240 mμ. Attention should be called to the C-5 epimeric dithiolanes (33a and 33b) where the C-5 stereochemistry affects the ORD and CD spectra. The marked effect of a substituent making an "octant" contribution is seen in the corresponding 5α- and 5β-cyano compounds (34a and 34b) in which the Cotton effects are essentially of mirror image type.

Dithiolanes and oxathiolanes of α,β-unsaturated ketones

It is known that a carbon–carbon double bond attached to sulphur has a marked effect on the electronic transitions associated with sulphur over that of an attached saturated substituent.[13] Thus, it might be expected that the CD maxima of allylic unsaturated systems could differ from those of the saturated ones. As will be noted from Table 6, this expectation is borne out. In the case of the oxathiolanes (40 and 41) there is no apparent shift in wavelength, and the Cotton effect sign does not change from that of the saturated analog 27. The dithiolanes 42–45, however, do

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[12] E. L. Eliel, L. A. Pilato and V. G. Badding, *J. Amer. Chem. Soc.* **84**, 2377 (1962).

[13] H. H. Jaffé and M. Orchin, *Theory and Application of Ultraviolet Spectroscopy*, p. 475. J. Wiley, New York (1962).

TABLE 5. SPECTRAL DATA OF OXATHIOLANES AND DITHIOLANES

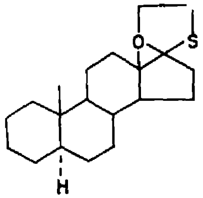
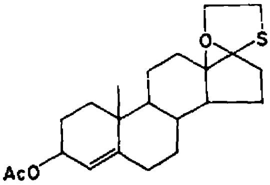
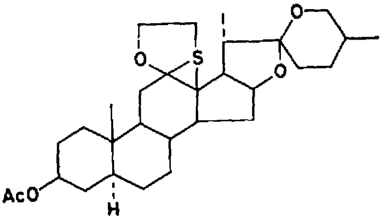
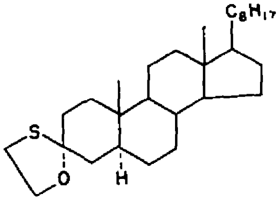
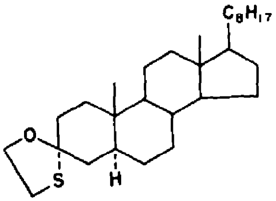
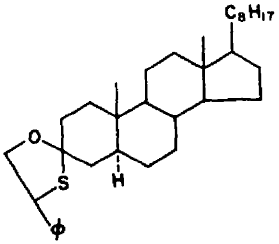
	ORD	CD		UV	
	Cotton effect	λ	([θ])	λ	(ε)
 **24**	−	242	(−3567)		
 **25**	−	240	(−4524)		
 **26**	+	244	(+4900)		
 **27a**	+ (Fig. 16)	255	(+195)	242	(45)
 **27b**	+ (Fig. 16)	245	(+646)	235	(50) shoulder
 **28**	+				

Table 5 (*contd.*)

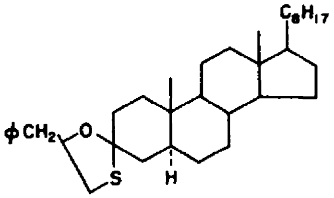
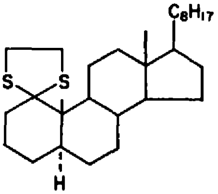
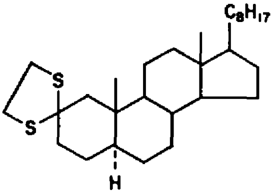
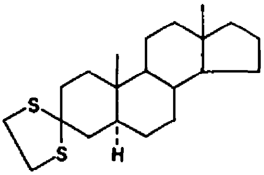
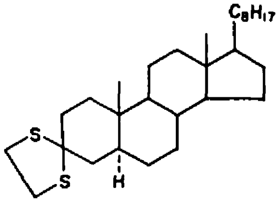
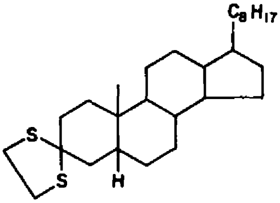
	ORD	CD		UV	
	Cotton effect	λ	([θ])	λ	(ε)
 29	+	247	(+6250)	247	(318)
 30	(Fig. 18)	245	(+11,865)	244	(279)
 31	(Fig. 18)	263 240	(+3100) (−20,000)	240	(393)
 32	−	262·5 235	(+255) (−510)	243	(300)
 33a	− (Fig. 17)	261 239	(+816) (−2176)	243	(372)
 33b	? (Fig. 17)			243	(374)

TABLE 5 (*contd.*)

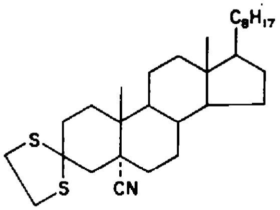
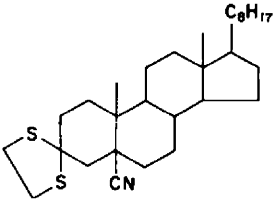
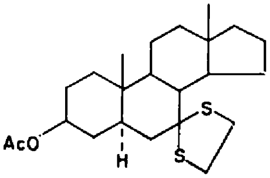
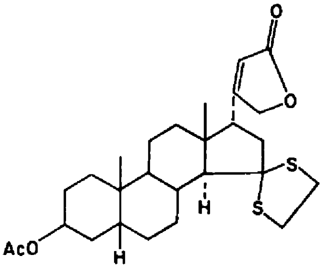
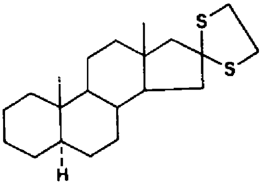
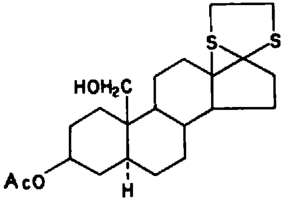
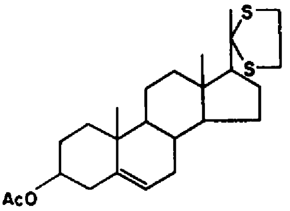
	ORD	CD		UV	
	Cotton effect	λ	([θ])	λ	(ε)
 34a	–				
 34b	+				
 35		277 245	(+106) (−10,070)	242	(331)
 36	+				
 37		276 248	(+348) (−13,500)	240	(81) shoulder

TABLE 5 (*contd.*)

	ORD	CD		UV	
	Cotton effect	λ	([θ])	λ	(ε)
 38	+	247	(+6250)	247	(318)
 39	+				

show more noticeable differences over the oxathiolanes 40 and 41, in a manner similar to that shown (Table 5) in the saturated oxathiolanes and dithiolanes. Again, in the same dithiolanes, there are two transitions (~240 mμ and ~270 mμ) of opposite sign, which have not yet been assigned, but it is likely that the sulphur atoms interact with themselves as well as with the allylic double bond. These are clearly visible in the CD spectra (Figs. 20 and 21), but not in the corresponding ORD curves. Only the ORD curve (Fig. 21) of 44 (Δ^1) shows an irregularity in the 290 mμ region indicative of another Cotton effect on the long wavelength side of the powerful 245 mμ Cotton effect. Moreover, as seen from the CD curves (Figs. 20 and 21), the signs change respectively in the Δ^1-(44) and Δ^4-(42) isomers. In the case of the oxathiolane (40 or 41), it is not altogether certain that the transition near 240 mμ corresponds to that at 240 mμ of the dithiolanes (42–45). It probably corresponds better in nature to the 270 mμ transition of dithiolanes, in which case the CD absorptions are of the same sign. In comparing saturated (Table 5) and unsaturated (Table 6) dithiolanes, it may be noted that the transitions occur at similar wavelengths but may differ in intensity and in corresponding signs (35 and 45), (33 and 42, 43), or they may be similar (33 and 44). Also, in the spiroketal (40) the well-known[14] strong negative background effect of the ether rings comes into play, a feature which, of course, is not operative in the corresponding CD curve (Fig. 19).

Oxathianes

The oxathianes presented in Table 7 give what are apparently at least two transitions very near 300 mμ as seen in the CD curves (Figs. 22 and 24). This is remarkable in that the absorption is not only at an unexpectedly high wavelength as compared to the five membered analog (e.g. 25 *vs.* 47), but also that these transitions are not

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[14] C. Djerassi and R. Ehrlich, *J. Amer. Chem. Soc.* 78, 440 (1956).

TABLE 6. ORD AND CD DATA OF UNSATURATED OXATHIOLANES AND DITHIOLANES

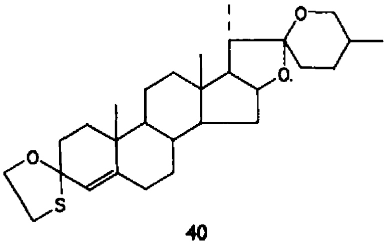
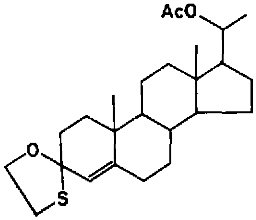
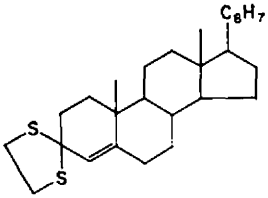
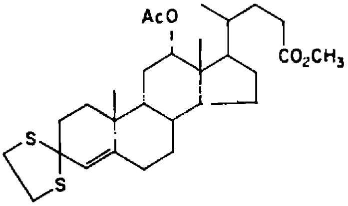
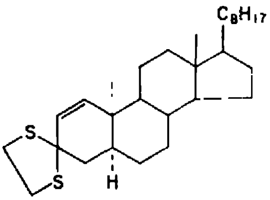
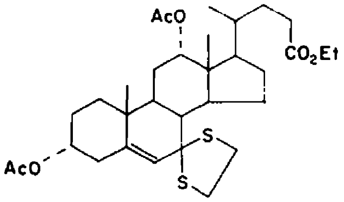
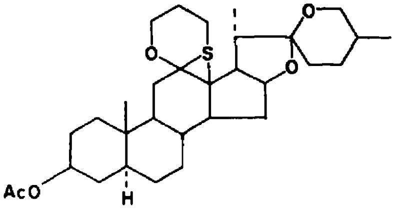
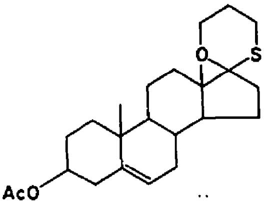
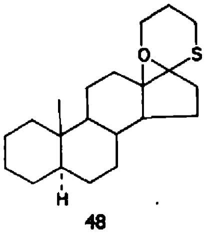
	ORD	CD	
	Cotton effect	λ	([θ])
 40	+ (Fig. 19)	245	(+9344)
 41	+	240	(+4427)
 42	+ (Fig. 20)	266 240	(+6130) (−10,905)
 43	+		
 44	(Fig. 21)	270 245	(−1033) (+6611)
 45	−	275 253	(−1756) (+5250)

TABLE 7. ORD AND CD DATA OF OXATHIANES

	ORD Cotton effect	CD λ	 ([θ])
 46	+ (Fig. 22)	299 292	(+1228) (+1323)
 47	+ (Fig. 23)	302	(+5800)
 48	+ (Fig. 24)	304	(+4244)

detectable in the UV spectra. The structural implications of the data again remain obscure until the electronic transitions involved are better characterized, but these cases again illustrate the importance of CD and ORD data in uncovering hidden spectral transitions.[15]

EXPERIMENTAL

Optical rotatory dispersion measurements were performed in part at Stanford with a Japan Spectroscopic Co. (Nippon Bunko) automatically recording spectropolarimeter (Model ORD-5) and in part at Osaka with a Rudolph automatically recording spectropolarimeter. The CD measurements were obtained on a Baird-Atomic/Jouan Dichrograph, and the UV measurements were obtained on either an Applied Physics model 14 or a Hitachi recording spectrophotometer. The rotatory dispersion data are recorded in the generally accepted manner,[16a] while the CD data are listed according to a convention recorded elsewhere in detail.[16b] Aside from the cited sources,[6,7,12] samples were selected from earlier synthetic studies.[17]

Cholestane-2α(S),3β(O)-*dithiocarbonate* (4) (*Fig.* 1). CD in dioxane: c 0·54 (600–305 mμ), c 0·108 (305–260 mμ), c 0·0216 (300–240 mμ); $[\theta]_{420}$ 0, $[\theta]_{378}$ −10650, $[\theta]_{335}$ 0, $[\theta]_{285}$ +58575, $[\theta]_{260}$ 0. ORD

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[15] See for instance C. Djerassi, H. Wolf and E. Bunnenberg, *J. Amer. Chem. Soc.* **85**, 324 (1963); C. Djerassi, *Proc. Chem. Soc.* 314 (1964).

[16a] See Chap 2 in Ref. 3 as well as C. Djerassi and W. Klyne, *Proc. Chem. Soc.* 55 (1957);
[b] C. Djerassi and E. Bunnenberg, *Proc. Chem. Soc.* 299 (1963).

[17] C. Djerassi and M. Gorman, *J. Amer. Chem. Soc.* **75**, 3704 (1953); C. Djerassi, M. Gorman, F. X. Markley and E. B. Oldenburg, *Ibid.* **77**, 568 (1955); Z. Pelah (Stanford University, unpublished observations).

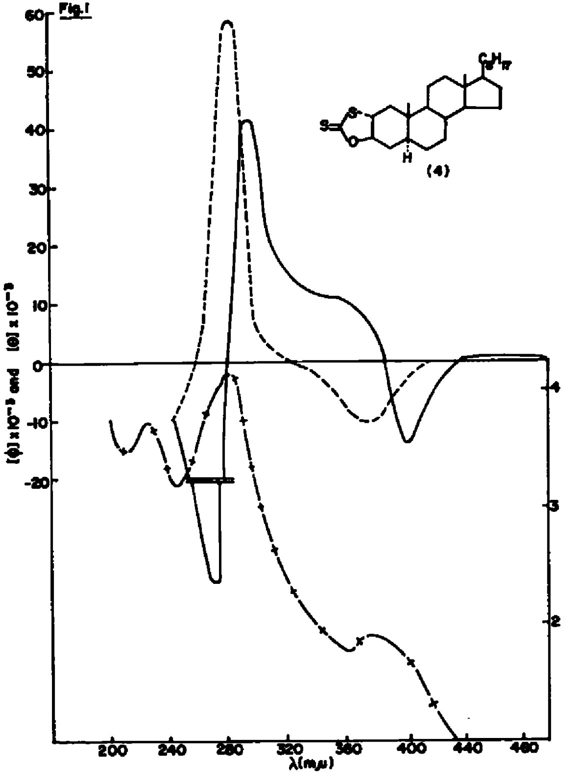

FIG. 1. Optical rotatory dispersion (———), circular dichroism (– – –), and ultraviolet absorption (— + — +) curves of cholestane-2α(S),3β(O)-dithiocarbonate (4).

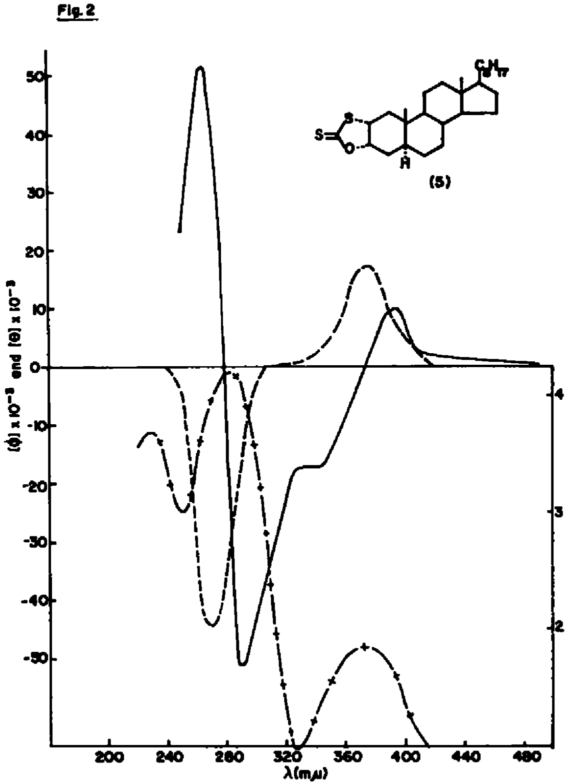

FIG. 2. Optical rotatory dispersion (———), circular dichroism (– – –), and ultraviolet absorption (— + — +) curves of cholestane-2α(S),3α(O)-dithiocarbonate (5).

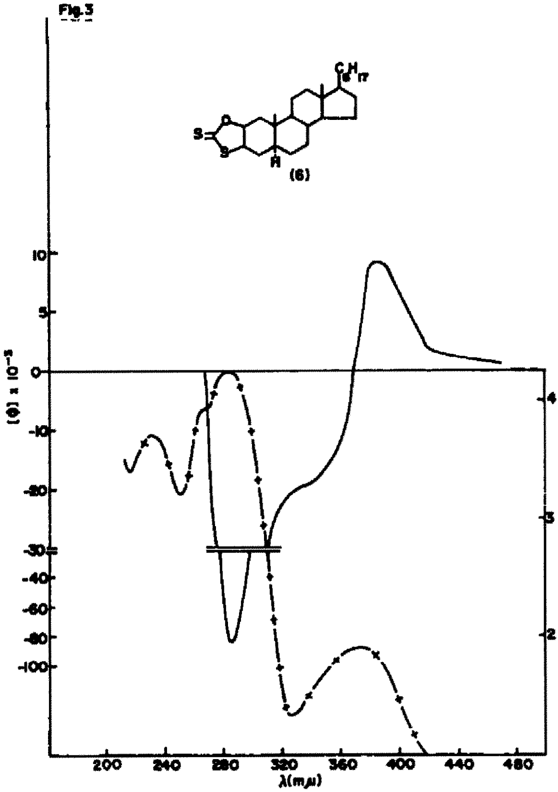

FIG. 3. Optical rotatory dispersion (———) and ultraviolet absorption (— + — +) curves of cholestane-2β(O),3β(S)-dithiocarbonate (6).

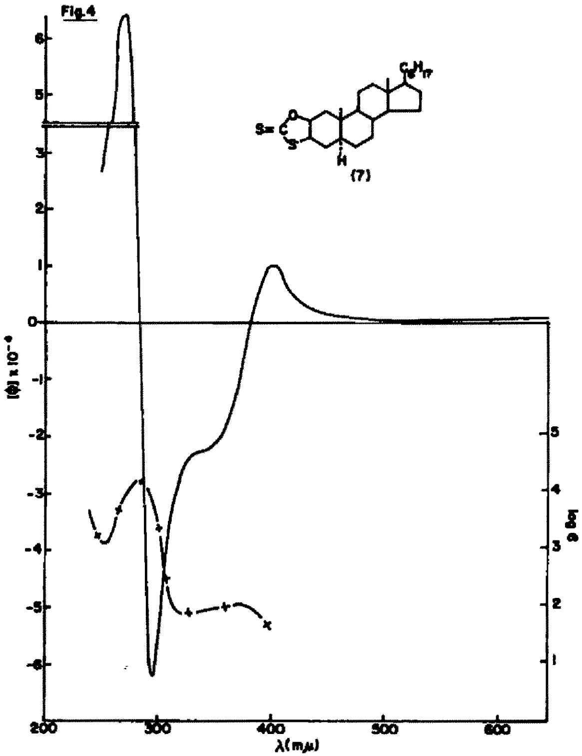

FIG. 4. Optical rotatory dispersion (———) and ultraviolet absorption (— + — +) curves of cholestane-2β(O),3α(S)-dithiocarbonate (7).

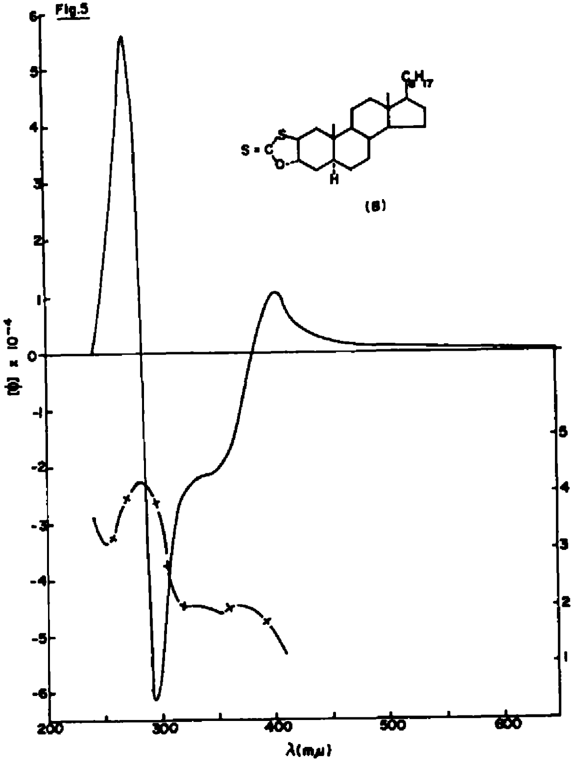

Fig. 5. Optical rotatory dispersion (———) and ultraviolet absorption (— + — +) curves of cholestane-2β(S),3α(O)-dithiocarbonate (8).

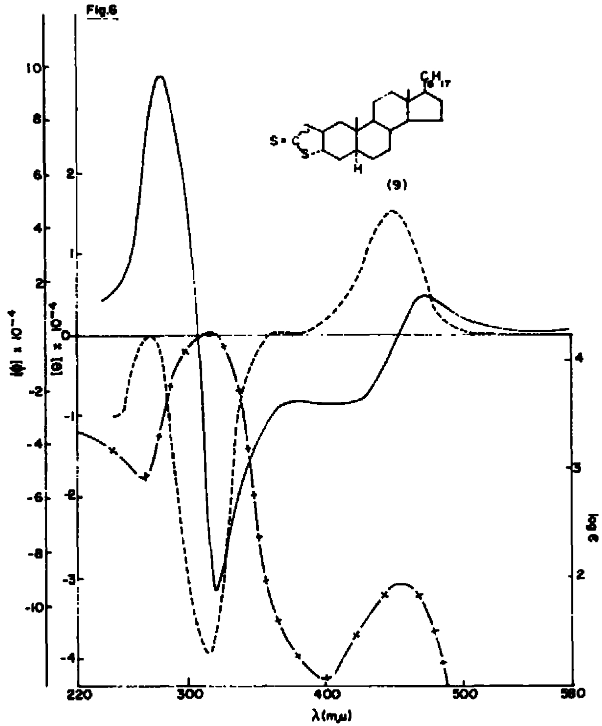

Fig. 6. Optical rotatory dispersion (———), circular dichroism (- - -), and ultraviolet absorption (— + — +) curves of cholestane-2β(S),3α(S)-trithiocarbonate (9).

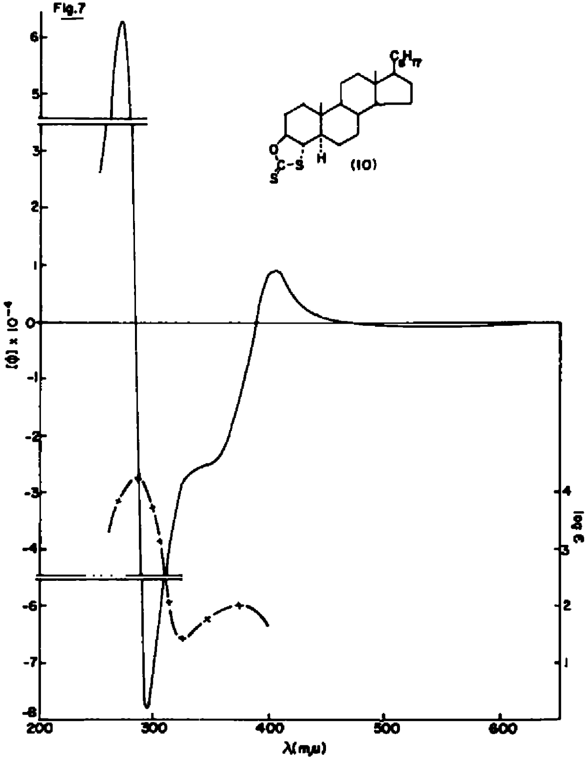

Fig. 7. Optical rotatory dispersion (———) and ultraviolet absorption (— + — +) curves of cholestane-3β(O),4α(S)-dithiocarbonate (10).

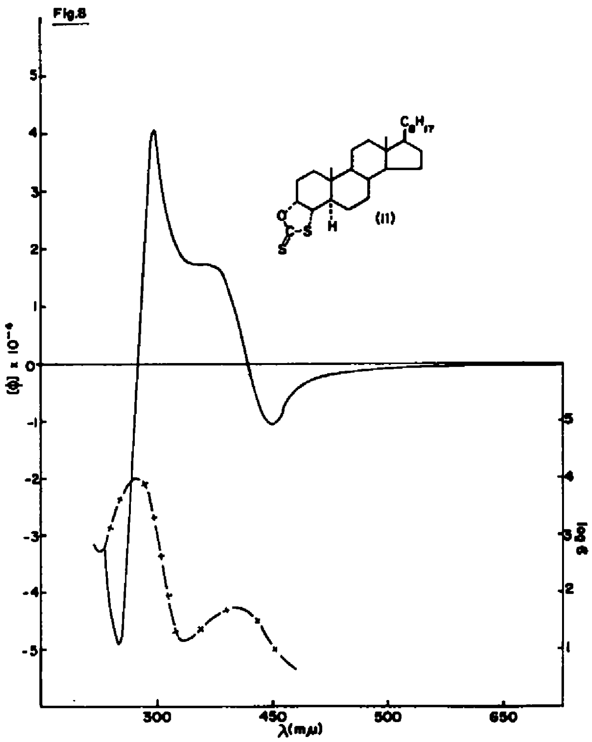

Fig. 8. Optical rotatory dispersion (———) and ultraviolet absorption (— + — +)curves of cholestane-3α(O), 4α(S)-dithiocarbonate (11).

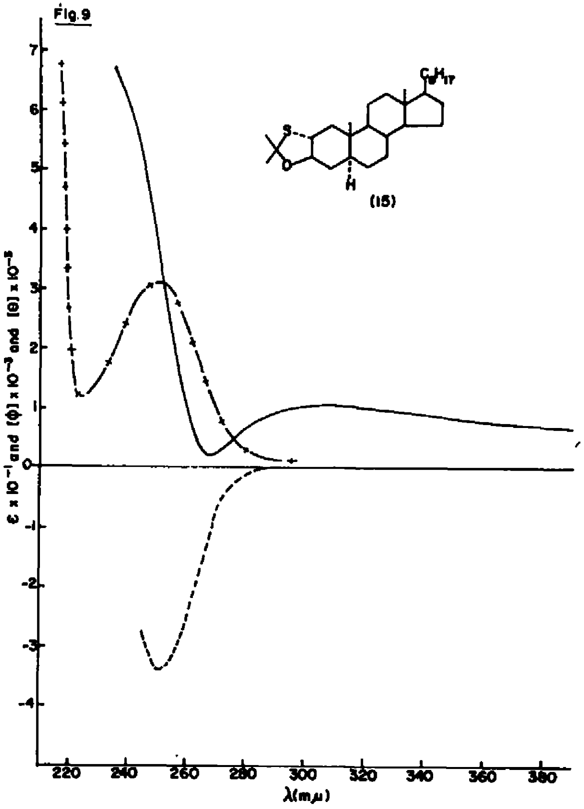

FIG. 9. Optical rotatory dispersion (———), circular dichroism (- - -), and ultraviolet absorption (– + — +) curves of cholestan-2α(S),2β(O)-acetonide (15).

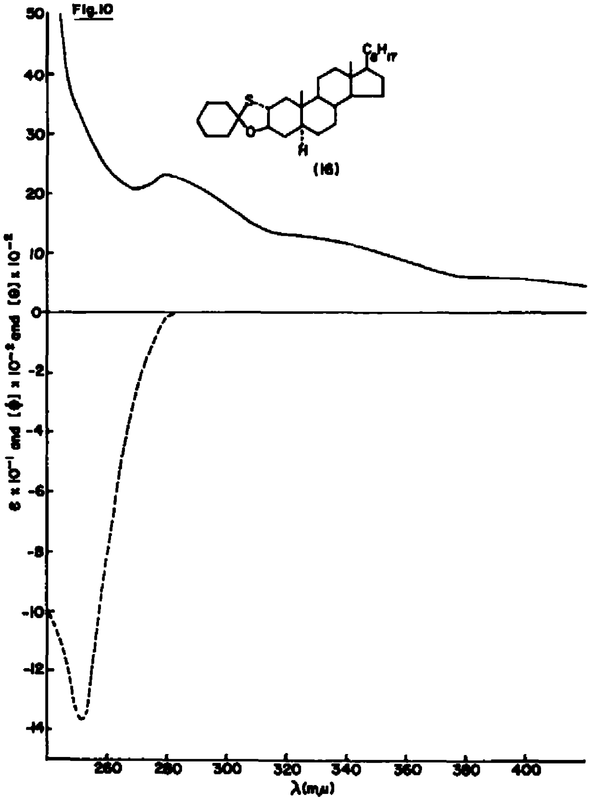

FIG. 10. Optical rotatory dispersion (———) and circular dichroism (- - -) curves of cholestane-2α(S),3β(O)-cyclohexanonide (16).

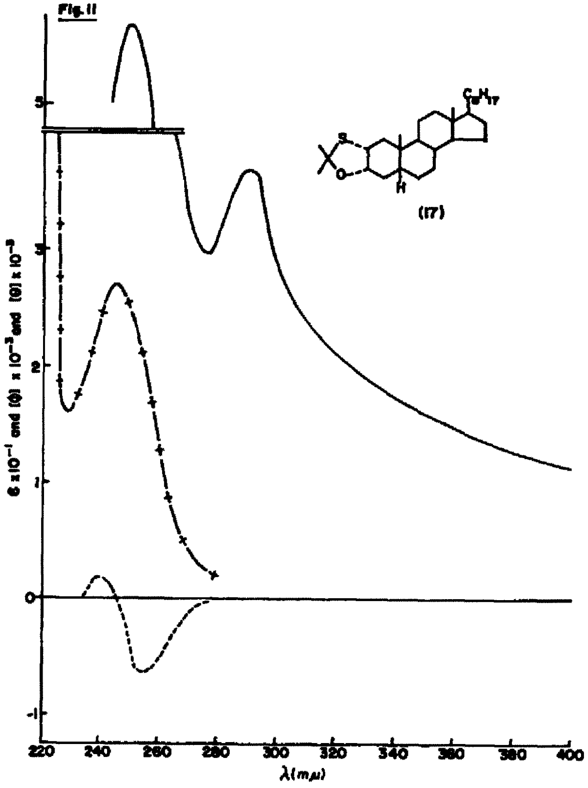

Fig. 11. Optical rotatory dispersion (———), circular dichroism (- - -), and ultraviolet absorption (— + — +) curves of cholestan-2α(S),3α(O)-acetonide (17).

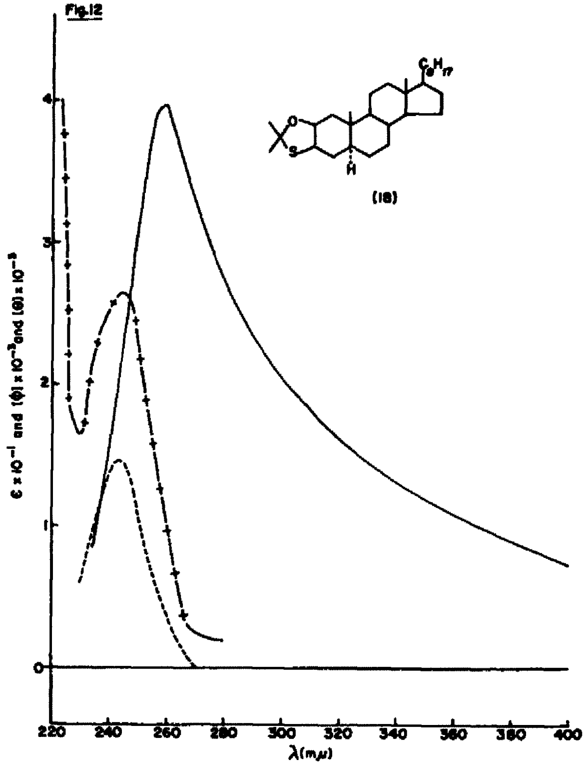

Fig. 12. Optical rotatory dispersion (———), circular dichroism (- - -), and ultraviolet absorption (— + — +) curves of cholestan-2β(O),3β(S)-acetonide (18).

Fig.13

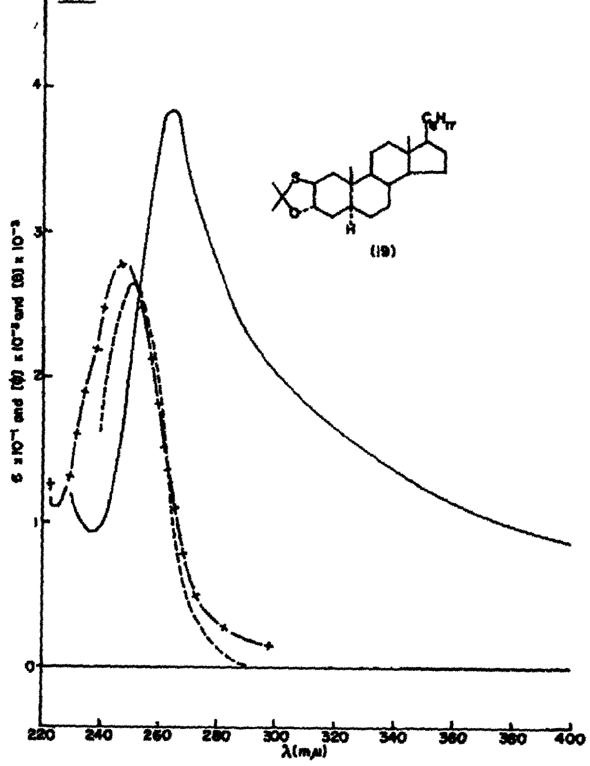

FIG. 13. Optical rotatory dispersion (———), circular dichroism (– – –), and ultraviolet absorption (– + – +) curves of cholestan-2β(S),3α(O)-acetonide (19).

Fig.14

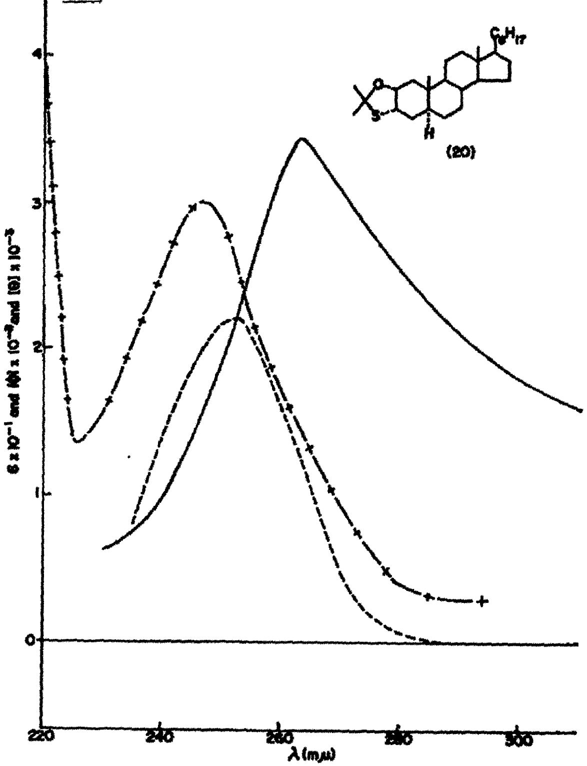

FIG. 14. Optical rotatory dispersion (———), circular dichroism (– – –), and ultraviolet absorption (– + – +) curves of cholestan-2β(O),3α(S)-acetonide (20).

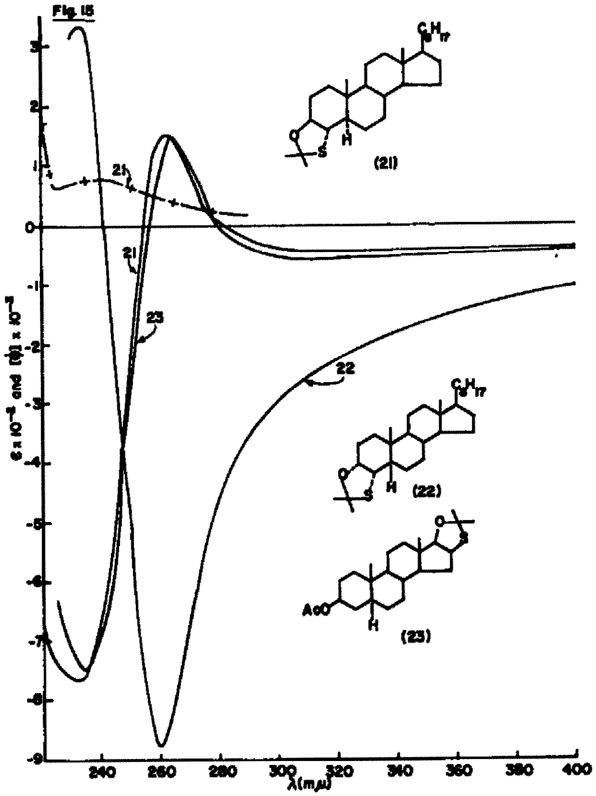

FIG. 15. Optical rotatory dispersion (———) and ultraviolet absorption (— + — +) curves of cholestan-3β(O),4α(S)-acetonide (21), cholestan-3α(O),4α(S)-acetonide (22), and androstan-16β(S),17β(O)-acetonide 3β-ol acetate (23).

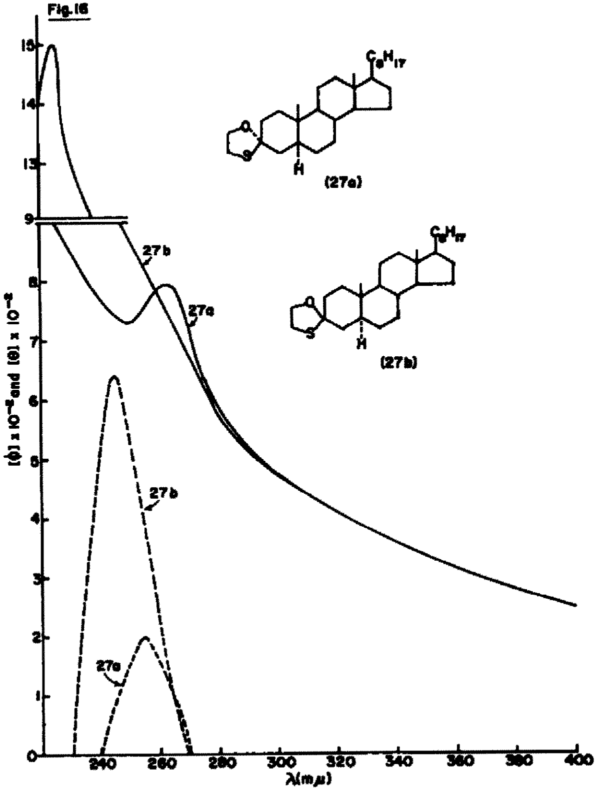

FIG. 16. Optical rotatory dispersion (———) and circular dichroism (– – –) curves of cholestan-3-one 3β(S)-ethylene hemithioketal (27a) and cholestan-3-one 3α(S)-ethylene hemithioketal (27b).

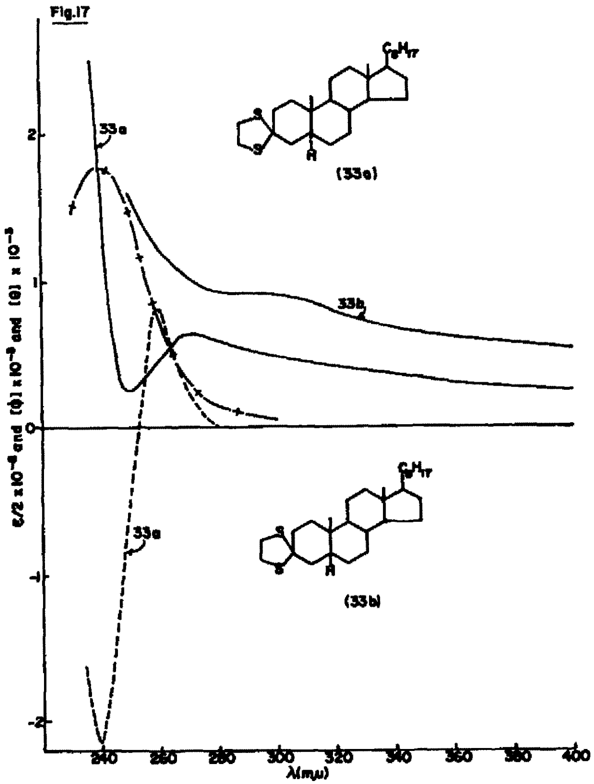

FIG. 17. Optical rotatory dispersion (———), circular dichroism (- - -) and ultraviolet absorption (— + — +) curves of cholestan-3-one ethylene thioketal (33a) and 5β-cholestan-3-one ethylene thioketal (33b).

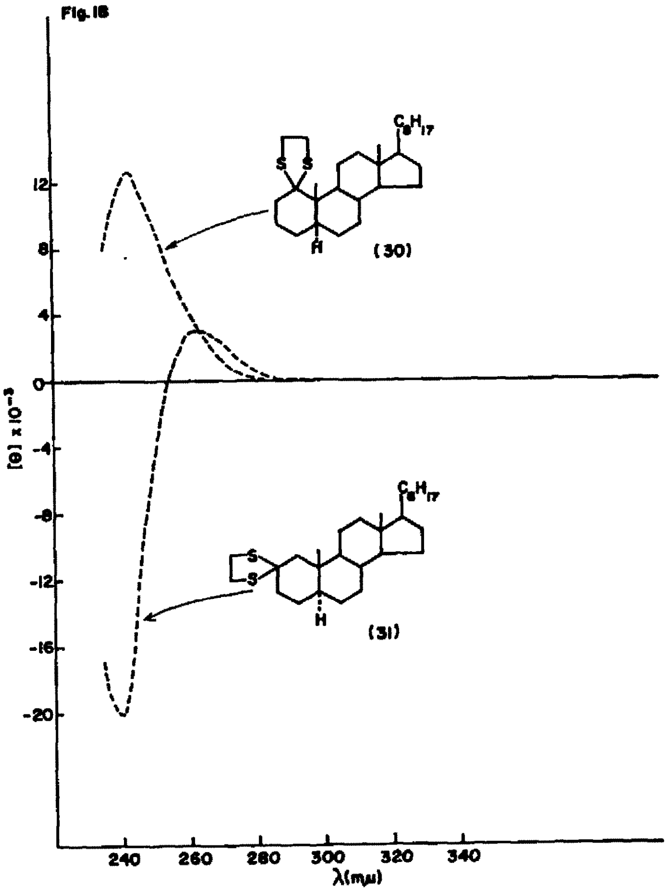

FIG. 18. Circular dichroism (- - -) curves of cholestan-1-one ethylene thioketal (30) and cholestan-2-one ethylene thioketal (31).

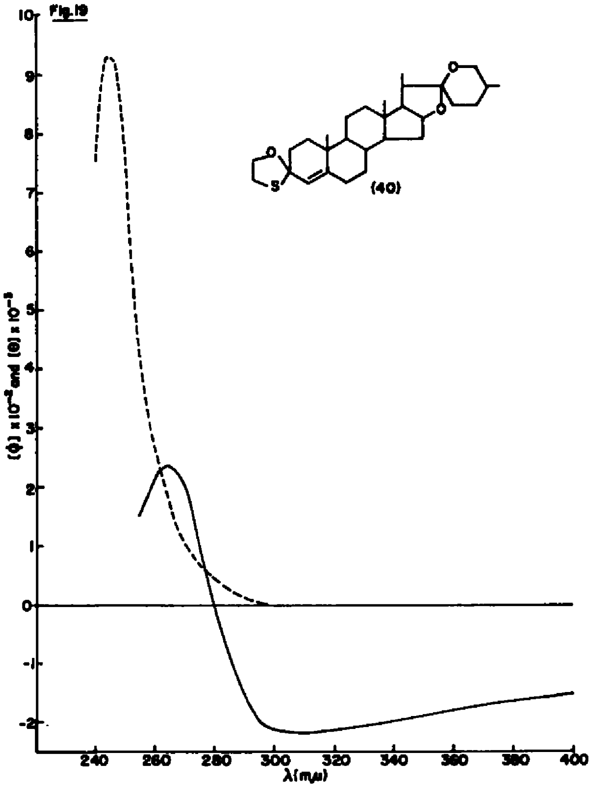

Fig. 19. Optical rotatory dispersion (———) and circular dichroism (– – –) curves of Δ^4-diosgene-3,3-oxathiolane (40).

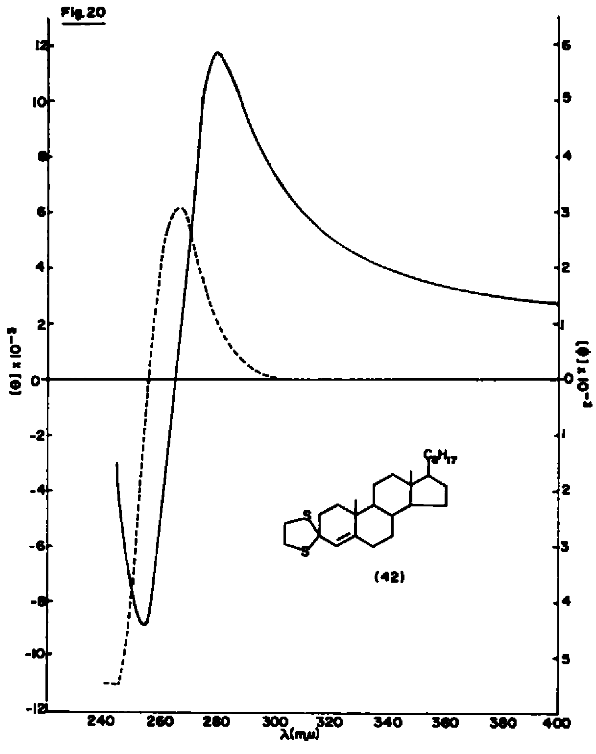

Fig. 20. Optical rotatory dispersion (———) and circular dichroism (– – –) curves of Δ^4-cholesten-3-one ethylene thioketal (42).

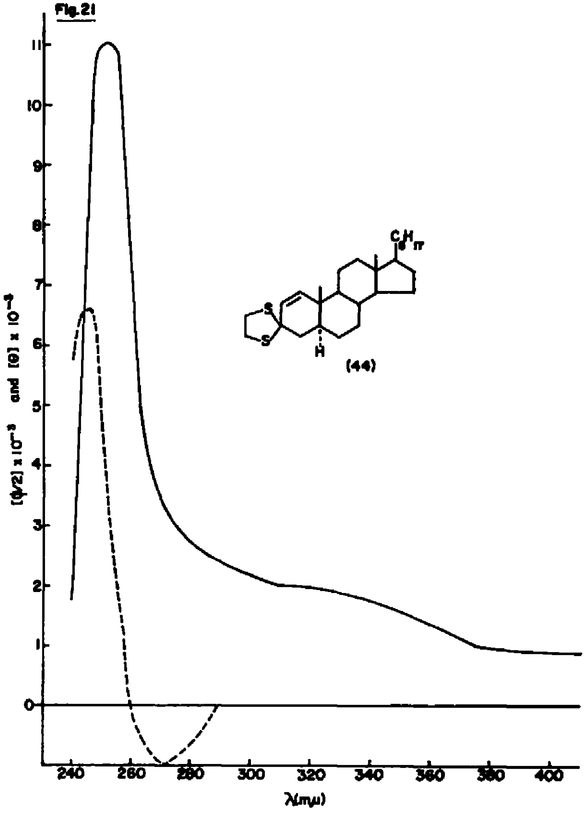

FIG. 21. Optical rotatory dispersion (———) and circular dichroism (– – –) curves of Δ^1-cholesten-3-one ethylene thioketal (44).

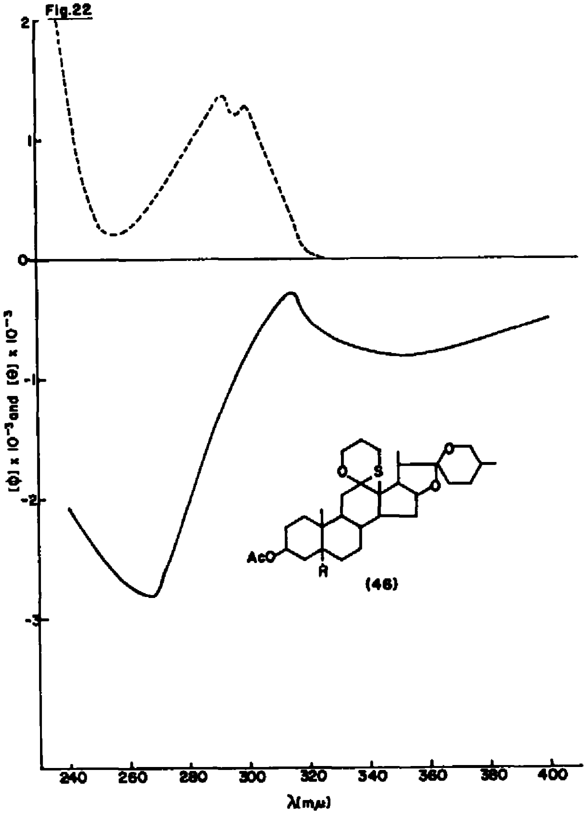

FIG. 22. Optical rotatory dispersion (———) and circular dichroism (– – –) curves of hecogenin acetate oxathiane (46).

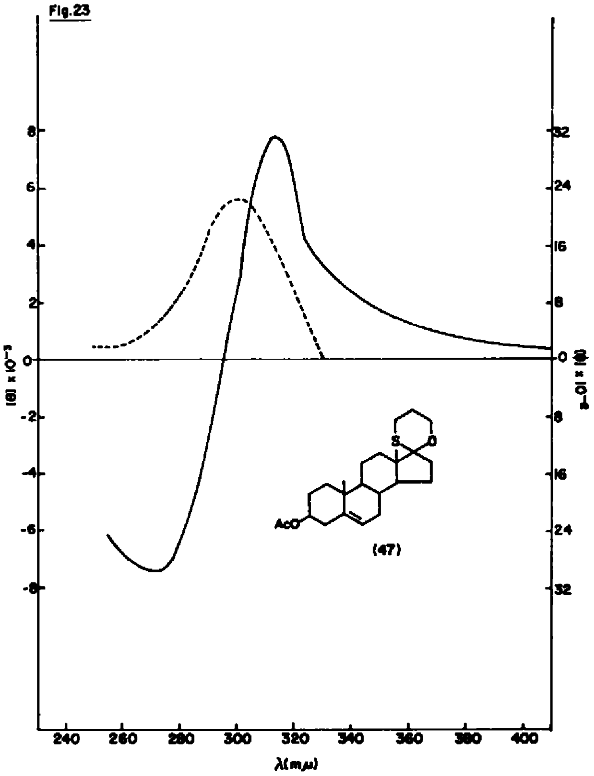

FIG. 23. Optical rotatory dispersion (———) and circular dichroism (- - -) curves of Δ^5-androsten-17,17-oxathiane 3α-ol acetate (47).

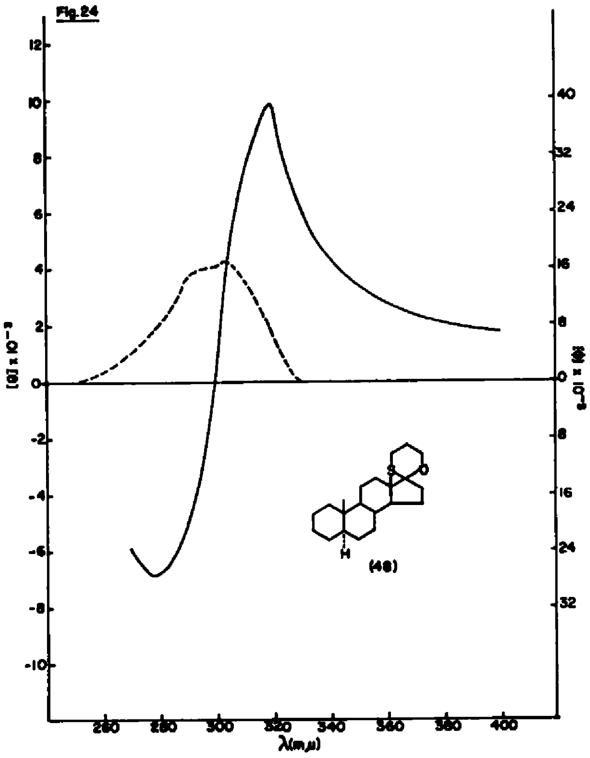

FIG. 24. Optical rotatory dispersion (———) and circular dichroism (- - -) curves of androstan-17,17-oxathiane (48).

in dioxane: c 0·105 (600–320 mμ), c 0·007 (350–240 mμ); $[\phi]_{589}$ +550°, $[\phi]_{450}$ 0°, $[\phi]_{404}$ −7030°, $[\phi]_{388}$ 0°, $[\phi]_{350}$ +22200°, $[\phi]_{320}$ +33300°, $[\phi]_{294}$ +83300°, $[\phi]_{282}$ 0°, $[\phi]_{272}$ −46200°. UV in dioxane: $\lambda_{380}^{\max}$ log ϵ 1·89, $\lambda_{282}^{\max}$ log ϵ 4·15, $\lambda_{276-268}^{\text{shoulder}}$ log ϵ 4·01–3·87, $\lambda_{227}^{\max}$ log ϵ 3·72.

Cholestane-2α(S),3α(O)-*dithiocarbonate* (5) (*Fig.* 2). CD in dioxane: c 0·338 (430–310 mμ), c 0·017 (290–240 mμ); $[\theta]_{420}$ 0, $[\theta]_{375}$ +17075, $[\theta]_{310}$ 0, $[\theta]_{270}$ −44395, $[\theta]_{240}$ 0. ORD in dioxane: c 0·104 (475–320 mμ), c 0·508 (310–305 mμ), c 0·010 (300–295 mμ); $[\phi]_{395}$ +10800°, $[\phi]_{342}$ −17200°, $[\phi]_{290}$ −51400°, $[\phi]_{265}$ +51400°, $[\phi]_{250}$ +23300°. UV in dioxane: $\lambda_{375}^{\max}$ log ϵ 1·87, $\lambda_{282}^{\max}$ log ϵ 4·22, $\lambda_{230}^{\max}$ log ϵ 3·68.

Cholestane-2β(O),3β(S)-*dithiocarbonate* (6) (*Fig.* 3). ORD in dioxane: c 0·055 (470–310 mμ), c 0·0022 (310–270 mμ); $[\phi]_{470}$ +504°, $[\phi]_{382}$ +8910°, $[\phi]_{310}$ −26200°, $[\phi]_{286}$ −84100°. UV in dioxane: $\lambda_{374}^{\max}$ log ϵ 1·91, $\lambda_{283}^{\max}$ log ϵ 4·25, $\lambda_{270-268}^{\text{shoulder}}$log ϵ 3·94–3·86, $\lambda_{232}^{\max}$ log ϵ 3·70.

Cholestane-2β(O),3α(S)-*dithiocarbonate* (7) (*Fig.* 4). ORD in dioxane: c 0·02022 (700–250 mμ); $[\phi]_{700}$ −230°, $[\phi]_{550}$ 0°, $[\phi]_{430}$ +2750°, $[\phi]_{402}$ +10000°, $[\phi]_{340}$ −22400°, $[\phi]_{320}$ −27500°, $[\phi]_{296}$ −62000°, $[\phi]_{270}$ +64000°, $[\phi]_{250}$ +27500°. UV in dioxane: $\lambda_{370}^{\max}$ log ϵ 2·0, $\lambda_{280}^{\max}$ log ϵ 4·2.

Cholestane-2β(S),3α(O)-*dithiocarbonate* (8) (*Fig.* 5). ORD in dioxane: c 0·0256 (700–240 mμ); $[\phi]_{700}$ +290°, $[\phi]_{430}$ +3200°, $[\phi]_{401}$ +10500°, $[\phi]_{320}$ −25000°, $[\phi]_{294}$ −61000°, $[\phi]_{268}$ +56000°, $[\phi]_{240}$ 0°. UV in dioxane: $\lambda_{370}^{\max}$ log ϵ 2·00, $\lambda_{282}^{\max}$ log ϵ 4·24.

Cholestane-2β,3α-*trithiocarbonate* (9) (*Fig.* 6). CD in dioxane: c 0·600 (530–350 mμ), c 0·012 (350–250 mμ); $[\theta]_{520}$ 0, $[\theta]_{450}$ +15000, $[\theta]_{370}$ 0, $[\theta]_{315}$ −39400, $[\theta]_{275}$ 0, $[\theta]_{250}$ −10000. ORD in dioxane: c 0·0185 (580–330 mμ), c 0·0035 (330–240 mμ); $[\phi]_{470}$ +14340°, $[\phi]_{405}$ −25810°, $[\phi]_{380}$ −24850°, $[\phi]_{320}$ −95600°, $[\phi]_{280}$ +95600°. UV in dioxane: $\lambda_{455}^{\max}$ log ϵ 1·94, $\lambda_{318}^{\max}$ log ϵ 4·27, $\lambda_{310-280}^{\text{shoulder}}$ log ϵ 4·22–3·34.

Cholestane-3β(O),4α(S)-*dithiocarbonate* (10) (*Fig.* 7). ORD in dioxane: c 0·04356 (700–250 mμ); $[\phi]_{700}$ −420°, $[\phi]_{476}$ 0°, $[\phi]_{403}$ −9370°, $[\phi]_{350}$ −24770°, $[\phi]_{305}$ −54850°, $[\phi]_{296}$ −78000°, $[\phi]_{266}$ +63000°, $[\phi]_{250}$ +26000°. UV in dioxane: $\lambda_{374}^{\max}$ log ϵ 2·00, $\lambda_{284}^{\max}$ log ϵ 4·26.

Cholestane-3α(O),4α(S)-*dithiocarbonate* (11) (*Fig.* 8). ORD in dioxane: c 0·03562 (700–255 mμ); $[\phi]_{700}$ −470°, $[\phi]_{398}$ −10860°, $[\phi]_{350}$ +16900°, $[\phi]_{320}$ +18000°, $[\phi]_{294}$ +41000°, $[\phi]_{262}$ −49000°, $[\phi]_{255}$ −32500°. UV in dioxane: $\lambda_{369}^{\max}$ log ϵ 1·73, $\lambda_{281}^{\max}$ log ϵ 4·01.

(+)-trans-9-*Methyldecalin*-2β,3α-*trithiocarbonate* (12). CD in dioxane: c 0·377 (520–350 mμ), c 0·0126 (350–240 mμ); $[\theta]_{515}$ 0, $[\theta]_{458}$ +15400, $[\theta]_{380}$ 0, $[\theta]_{313}$ −68300, $[\theta]_{277}$ 0, $[\theta]_{272}$ +1860, $[\theta]_{268}$ 0, $[\theta]_{250}$ −14150, $[\theta]_{240}$ −9000. ORD in dioxane: c 0·0377 (580–350 mμ), c 0·00251 (350–240 mμ); $[\phi]_{477}$ +9760°, $[\phi]_{416}$ −12700°, $[\phi]_{386}$ −11300°, $[\phi]_{330}$ −41200°, $[\phi]_{286}$ +54000°, $[\phi]_{256}$ +12850°. UV in dioxane: $\lambda_{454}^{\max}$ log ϵ 1·94, $\lambda_{317}^{\max}$ log ϵ 4·24, $\lambda_{310-300}^{\text{shoulder}}$ log ϵ 4·20–4·11, $\lambda_{227}^{\max}$ log ϵ 3·46.

Cholestan-2α(S),3β(O)-*acetonide* (15) (*Fig.* 9). CD in dioxane: c 3·17 (350–255 mμ), c 1·056 (260–245 mμ); $[\theta]_{290}$ 0, $[\theta]_{251}$ +3400, $[\theta]_{245}$ +2750. ORD in n-heptane: c 0·208 (700–235 mμ); $[\phi]_{700}$ +240°, $[\phi]_{310}$ +1040°, $[\phi]_{263}$ +155°, $[\phi]_{235}$ +6520°. UV in n-heptane: $\lambda_{250}^{\max}$ log ϵ 1·48.

Cholestane-2α(S),3β(O)-*cyclohexanonide* (16) (*Fig.* 10). CD in dioxane: c 1·0 (300–245 mμ), c 0·5 (270–240 mμ); $[\theta]_{290}$ 0, $[\theta]_{252}$ −1370, $[\theta]_{240}$ −1000. ORD in dioxane: c 0·121 (600–260 mμ); $[\phi]_{600}$ +320°, $[\phi]_{283}$ +460°, $[\phi]_{270}$ +410°, $[\phi]_{245}$ +1000°.

Cholestan-2α(S),3α(O)-*acetonide* (17) (*Fig.* 11). CD in dioxane: c 0·93 (300–230 mμ); $[\theta]_{290}$ 0, $[\theta]_{256}$ −674, $[\theta]_{245}$ 0, $[\theta]_{240}$ +185, $[\theta]_{230}$ 0. ORD in dioxane: c 0·100 (600–275 mμ), c 0·50 (300–240 mμ); $[\phi]_{589}$ +80°, $[\phi]_{400}$ +240°, $[\phi]_{288}$ +800°, $[\phi]_{275}$ +640°, $[\phi]_{250}$ +1240°. UV in n-heptane: $\lambda_{245}^{\max}$ log ϵ 1·44.

Cholestan-2β(O),3β(S)-*acetonide* (18) (*Fig.* 12). CD in dioxane: c 1·18 (300–245 mμ), c 0·59 (260–230 mμ); $[\theta]_{270}$ 0, $[\theta]_{243}$ +1560, $[\theta]_{230}$ +600. ORD in n-heptane: c 0·199 (700–235 mμ); $[\phi]_{700}$ +230°, $[\phi]_{259}$ +3970°, $[\phi]_{235}$ +860°. UV in n-heptane: $\lambda_{243}^{\max}$ log ϵ 1·42.

Cholestan-2β(S),3α(O)-*acetonide* (19) (*Fig.* 13). CD in dioxane: c 1·56 (350–240 mμ); $[\theta]_{290}$ 0, $[\theta]_{251}$ +2652, $[\theta]_{240}$ +1620. ORD in n-heptane: c 0·231 (700–230 mμ); $[\phi]_{700}$ +320°, $[\phi]_{265}$ +3830°, $[\phi]_{237\cdot5}$ +940°, $[\phi]_{230}$ +1400°. UV in n-heptane: $\lambda_{248}^{\max}$ log ϵ 1·45.

Cholestan-2β(O),3α(S)-*acetonide* (20) (*Fig.* 14). CD in dioxane: c 1·56 (350–240 mμ), c 0·78 (270–236 mμ); $[\theta]_{290}$ 0, $[\theta]_{252}$ +2190, $[\theta]_{236}$ +870. ORD in n-heptane: c 0·249 (700–300 mμ), c 0·1246 (350–235 mμ); $[\phi]_{700}$ +260°, $[\phi]_{350}$ +1260°, $[\phi]_{263}$ +3400°, $[\phi]_{235}$ +740°. UV in n-heptane: $\lambda_{249}^{\max}$ log ϵ 1·49.

Cholestan-3β(O),4α(S)-*acetonide* (21) (*Fig.* 15). ORD in n-heptane: c 0·0534 (700–235 mμ); $[\phi]_{700}$ −140°, $[\phi]_{589}$ −170°, $[\phi]_{320}$ −380°, $[\phi]_{262}$ +1670°, $[\phi]_{255}$ 0°, $[\phi]_{235}$ −7420°. UV in n-heptane: $\lambda_{255}^{\max}$ log ϵ 1·78.

Cholestan-3α(O),4α(S)-*acetonide* (22) (*Fig*. 15). ORD in n-heptane: c 0·0623 (700–230 mμ); $[\phi]_{700}$ −280°, $[\phi]_{589}$ −385°, $[\phi]_{260}$ −8800°, $[\phi]_{232\cdot5}$ +3370°, $[\phi]_{230}$ +3180°. UV in n-heptane: $\lambda^{\max}_{232}$ log ε 1·85.

5α-*Androstan*-16β(S),17β(O)-*acetonide* (23) (*Fig*. 15). ORD in dioxane: c 0·0892 (700–225 mμ); $[\phi]_{700}$ −199°, $[\phi]_{265}$ +1460°, $[\phi]_{234}$ −7460°, $[\phi]_{225}$ −6300°.

5α-*Androstan*-17-*one ethylene hemithioketal* (24). CD in dioxane: c 2·05 (400–245 mμ), c 0·683 (260–237 mμ); $[\theta]_{270}$ 0, $[\theta]_{243}$ −3567, $[\theta]_{237}$ −3000. ORD in dioxane: c 0·312 (600–225 mμ); $[\phi]_{589}$ −50°, $[\phi]_{255}$ −3340°, $[\phi]_{240}$ 0°, $[\phi]_{230}$ +1670°, $[\phi]_{225}$ +1000°.

Δ⁵-*Androsten*-17-*one ethylene hemithioketal* 3β-*ol acetate* (25). CD in dioxane: c 1·13 (350–230 mμ); $[\theta]_{270}$ 0, $[\theta]_{240}$ −4524, $[\theta]_{230}$ −2350. ORD in dioxane: c 0·213 (600–225 mμ); $[\phi]_{589}$ −429°, $[\phi]_{255}$ −6660°, $[\phi]_{235}$ −2740°, $[\phi]_{225}$ −3900°.

Hecogenin acetate ethylene hemithioketal (26). CD in dioxane: c 0·67 (300–243 mμ); $[\theta]_{270}$ 0, $[\theta]_{243}$ +4900. ORD in dioxane: c 0·078 (600–235 mμ); $[\phi]_{589}$ −234°, $[\phi]_{320}$ −510°, $[\phi]_{250}$ +1950°, $[\phi]_{235}$ −4600°.

Cholestan-3-*one* 3β(S)-*ethylene hemithioketal* (27a) (*Fig*. 16). CD in dioxane: c 0·121 (300–240 mμ); $[\theta]_{270}$ 0, $[\theta]_{255}$ +195, $[\theta]_{240}$ 0. ORD in dioxane: c 0·121 (600–220 mμ); $[\phi]_{600}$ +90°, $[\phi]_{300}$ +450°, $[\phi]_{260}$ +800°, $[\phi]_{247}$ +720°, $[\phi]_{220}$ +1020°. UV in dioxane: $\lambda^{\max}_{242}$ log ε 1·653.

Cholestan-3-*one* 3α(S)-*ethylene hemithioketal* (27b) (*Fig*. 16). CD in dioxane: c 0·0872 (290–230 mμ); $[\theta]_{270}$ 0, $[\theta]_{245}$ +646, $[\theta]_{230}$ 0. ORD in dioxane: c 0·205 (600–220 mμ); $[\phi]_{600}$ +100°, $[\phi]_{300}$ +500°, $[\phi]_{225}$ +1500°, $[\phi]_{220}$ +1405°. UV in dioxane: $\lambda^{\mathrm{sh}}_{235}$ log ε 1·70.

Spiro-4-*phenyl*-2,2-(3,3-*cholestanyl*)-*oxathiolane* (28). ORD in dioxane: c 0·160 (600–280 mμ), c 0·040 (260–240 mμ); $[\phi]_{589}$ +1040°, $[\phi]_{272}$ +880°, $[\phi]_{240}$ −1250°.

Spiro-benzyl-2,2-(3,3-*cholestanyl*)-*oxathiolane* (29). ORD in dioxane: c 0·314 (600–238 mμ); $[\phi]_{589}$ +268°, $[\phi]_{310}$ +430°, $[\phi]_{275}$ 0°, $[\phi]_{259}$ −967°, $[\phi]_{248}$ 0°, $[\phi]_{238}$ +3640°.

Cholestan-1-*one ethylene thioketal* (30) (*Fig*. 18). CD in dioxane: c 0·11 (300–235 mμ); $[\theta]_{280}$ 0, $[\theta]_{245}$ +11865, $[\theta]_{235}$ +8000. UV in dioxane $\lambda^{\max}_{244}$ log ε 2·478.

Cholestan-2-*one ethylene thioketal* (31) (*Fig*. 18). CD in dioxane: c 0·0516 (310–235 mμ); $[\theta]_{290}$ 0, $[\theta]_{263}$ +3100, $[\theta]_{254}$ 0, $[\theta]_{240}$ −20000, $[\theta]_{235}$ −17000. UV in dioxane: $\lambda^{\max}_{240}$ log ε 2·595.

5α-*Androstan*-3-*one ethylene thioketal* (32). CD in dioxane: c 0·0556 (310–230 mμ); $[\theta]_{300}$ 0, $[\theta]_{262\cdot5}$ +225, $[\theta]_{240}$ 0, $[\theta]_{235}$ −510, $[\theta]_{230}$ −350. ORD in dioxane: c 0·0556 (400–220 mμ); $[\phi]_{400}$ +1000°, $[\phi]_{270}$ +3000°, $[\phi]_{253}$ 0°, $[\phi]_{247}$ −1150°, $[\phi]_{242}$ 0°, $[\phi]_{225}$ +9000°, $[\phi]_{220}$ +8500°. UV in dioxane: $\lambda^{\max}_{243}$ log ε 2·47.

5α-*Cholestan*-3-*one ethylene thioketal*[18] (33a) (*Fig*. 17). CD in dioxane: c 0·183 (300–235 mμ); $[\theta]_{280}$ 0, $[\theta]_{261}$ +816, $[\theta]_{254}$ 0, $[\theta]_{239}$ −2176, $[\theta]_{235}$ −1700. ORD in dioxane: c 0·0754 (700–235 mμ); $[\phi]_{700}$ +170°, $[\phi]_{272}$ +1220°, $[\phi]_{260}$ +930°, $[\phi]_{250}$ +490°, $[\phi]_{235}$ +2800°. ORD in n-heptane: c 0·1852 (700–230 mμ); $[\phi]_{700}$ +51°, $[\phi]_{275}$ +520°, $[\phi]_{253}$ −102°, $[\phi]_{230}$ +2175°. UV in dioxane: $\lambda^{\max}_{243}$ log ε 2·57

5β-*Cholestan*-3-*one ethylene thioketal* (33b) (*Fig*. 17). CD in dioxane: c 0·408 (350–250 mμ); $[\theta]_{280}$ 0, $[\theta]_{265}$ −240, $[\theta]_{255}$ −360, $[\theta]_{250}$ −600. ORD in dioxane: c 0·1088 (700–250 mμ); $[\phi]_{700}$ +150°, $[\phi]_{300}$ +842°, $[\phi]_{280}$ +884°, O_{250} +1600°. ORD in *n*-heptane: c 0·233 (700–235 mμ); $[\phi]_{700}$ +79°, $[\phi]_{300}$ +634°, $[\phi]_{248}$ +1030°, $[\phi]_{235}$ +360°. UV in dioxane: $\lambda^{\max}_{242}$ log ε 2·573.

5α-*Cyanocholestan*-3-*one ethylene thioketal*[19] (34a). ORD in methanol: c 0·0392 (700–240 mμ); $[\phi]_{700}$ 0°, $[\phi]_{267}$ −6670°, $[\phi]_{240}$ +7800°.

5β-*Cyanocholestan*-3-*one ethylene thioketal*[19] (34b). ORD in methanol: c 0·294 (700–240 mμ); $[\phi]_{700}$ +263°, $[\phi]_{258}$ +7310°, $[\phi]_{240}$ −6970°.

5α-*Androstan*-7-*one thioketal* 3β-*ol acetate* (35). CD in dioxane: c 0·0568 (310–230 mμ); $[\theta]_{300}$ 0, $[\theta]_{277}$ +100, $[\theta]_{270}$ 0, $[\theta]_{245}$ −10070, $[\theta]_{230}$ −2700. UV in dioxane: $\lambda^{\max}_{242}$ log ε 2·52.

5β,14α-*Androstan*-15-*one ethylene thioketal* 3β-*ol acetate* 17α-*butenolide*[20] (36). ORD in chloroform: c 0·103 (700–245 mμ); $[\phi]_{700}$ +39°, $[\phi]_{270}$ +906°, $[\phi]_{245}$ −1810°.

5α-*Androstan*-16-*one ethylene thioketal* (37). CD in dioxane: c 0·0544 (320–230 mμ); $[\theta]_{290}$ 0, $[\theta]_{270}$ +348, $[\theta]_{273}$ 0, $[\theta]_{248}$ −13500, $[\theta]_{230}$ −3500. UV in dioxane: $\lambda^{\mathrm{sh}}_{240}$ log ε 1·906.

5α-*Androstan*-17-*one ethylene thioketal* 3β,19-*diol* 3-*acetate* (38). CD in dioxane: c 0·352 (300–235 mμ); $[\theta]_{290}$ 0, $[\theta]_{247}$ +6250, $[\theta]_{235}$ +1800. ORD in dioxane: c 0·124 (600–235 mμ); $[\phi]_{589}$ −36°, $[\phi]_{350}$ −216°, $[\phi]_{254}$ +972°, $[\phi]_{247}$ 0°. $[\phi]_{237}$ −9600°. UV in dioxane: $\lambda^{\max}_{247}$ log ε 2·502.

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Pregnenolone acetate thioketal (39). ORD in dioxane: c 0·319 (700–230 mμ); $[\phi]_{700}$ −230°, $[\phi]_{310}$ −935°, $[\phi]_{267\cdot5}$ +425°, $[\phi]_{260}$ −680°, $[\phi]_{230}$ −10000°.

Δ^4-*Diosgenone*-3,3-*oxathiolane* (40) (*Fig*. 19). CD in dioxane: c 1·0 (300–240 mμ); $[\theta]_{290}$ 0, $[\theta]_{245}$ +9344, $[\theta]_{240}$ +700. ORD in dioxane: c 0·105 (600–255 mμ); $[\phi]_{589}$ −474°, $[\phi]_{312}$ −1000°, $[\phi]_{262}$ +1140°, $[\phi]_{240}$ +710°.

Δ^4-*Pregnene-3-one ethylene hemithioketal* 20β-*ol acetate* (41). CD in dioxane: c 0·60 (300–240 mμ), c 0·30 (260–235 mμ); $[\theta]_{260}$ 0, $[\theta]_{240}$ +4427, $[\theta]_{235}$ +4050. ORD in dioxane: 0·082 (600–235 mμ); $[\phi]_{589}$ +75°, $[\phi]_{300}$ +765°, $[\phi]_{247}$ +5450°, $[\phi]_{235}$ +1250°.

Δ^4-*Cholesten-3-one ethylene thioketal* (42) (*Fig*. 20). CD in dioxane: c 1·00 (300–237 mμ); $[\theta]_{300}$ 0, $[\theta]_{260}$ +6130, $[\theta]_{252}$ 0, $[\theta]_{240}$ −10905. ORD in dioxane: c 0.205 (600–300 mμ), c 0·0051 (270–240 mμ); $[\phi]_{589}$ +460°, $[\phi]_{282}$ +5900°, $[\phi]_{263}$ 0°, $[\phi]_{255}$ −4420, $[\phi]_{240}$ −1370°.

Δ^4-3-*Ketocholenic acid methyl ester* 12-*acetate* 3-*ethylene thioketal*[20] (43). ORD in dioxane: c 0·0984 (700–240 mμ); $[\phi]_{700}$ +560°, $[\phi]_{279}$ +7200°, $[\phi]_{255}$ −4800°, $[\phi]_{240}$ +12700°.

Δ^1-*Cholesten*-3-*one-ethylene thioketal* (44) (*Fig*. 21). CD in dioxane: c 1·08 (300–265 mμ), c 0·27 (270–250 mμ), c 0·0675 (250–240 mμ); $[\theta]_{290}$ 0, $[\theta]_{270}$ −1033, $[\theta]_{260}$ 0, $[\theta]_{245}$ +6611, $[\theta]_{240}$ +5780. ORD in dioxane: c 0·1073 (600–240 mμ), $[\phi]_{589}$ +193°, $[\phi]_{265}$ +550°, $[\phi]_{252}$ 5550°, $[\phi]_{240}$ +885°.

Δ^5-7-*Ketocholic acid ethyl ester diacetate* 7-*ethylene thioketal*[21] (45). CD in dioxane: c 0·070 (320–245 mμ); $[\theta]_{290}$ 0, $[\theta]_{275}$ −1756, $[\theta]_{267}$ 0, $[\theta]_{250}$ +5250, $[\theta]_{245}$ +4400. ORD in dioxane: c 0·1439 (700–245 mμ); $[\phi]_{700}$ +82°, $[\phi]_{400}$ +165°, $[\phi]_{332}$ 0°, $[\phi]_{283}$ −907°, $[\phi]_{264}$ +1070°, $[\phi]_{245}$ −13000°.

Hecogenin acetate oxathiane (46) (*Fig*. 22). CD in dioxane: c 2·17 (330–245 mμ), c 1·085 (250–240 mμ), c 0·2712 (240–235 mμ); $[\theta]_{320}$ 0, $[\theta]_{310}$ +630, $[\theta]_{299}$ +1228, $[\theta]_{296}$ +1197, $[\theta]_{293}$ +1323, $[\theta]_{265}$ +189, $[\theta]_{235}$ +2520. ORD in dioxane: c 0·355 (600–240 mμ); $[\phi]_{589}$ −213°, $[\phi]_{350}$ −745°, $[\phi]_{320}$ −534°, $[\phi]_{314}$ −266°, $[\phi]_{267}$ −2740°, $[\phi]_{240}$ −210°.

Δ^5-*Androsten*-17,17-*oxathiane* 3α-*ol acetate* (47) (*Fig*. 23). CD in dioxane: c 0·10 (340–250 mμ); $[\theta]_{330}$ 0, $[\theta]_{302}$ +5800, $[\theta]_{250}$ +400. ORD in dioxane: c 0·225 (600–255 mμ); $[\phi]_{589}$ 41°, $[\phi]_{314}$ +3220°, $[\phi]_{293}$ 0°, $[\phi]_{272}$ −3080°, $[\phi]_{255}$ −2520°.

Androstan-17,17-*oxathiane* (48) (*Fig*. 24). CD in dioxane: c 0·10 (340–240 mμ); $[\theta]_{330}$ 0, $[\theta]_{304}$ +4244, $[\theta]_{240}$ 0. ORD in dioxane: c 0·191 (600–270 mμ); $[\phi]_{589}$ +150°, $[\phi]_{319}$ +4030°, $[\phi]_{300}$ 0, $[\phi]_{278}$ −2820°, $[\phi]_{270}$ −2450°.

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