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OPTICAL ROTATORY DISPERSION STUDIES—CII[1]

THIOSTEROIDS—XIV[2]

OPTICAL ROTATORY DISPERSION AND CIRCULAR DICHROISM OF THIOLACETATES

KEN'ICHI TAKEDA, K. KURIYAMA and T. KOMENO
Research Laboratory, Shionogi & Co., Ltd., Osaka, Japan
and
D. A. LIGHTNER, R. RECORDS and CARL DJERASSI
Department of Chemistry, Stanford University, Stanford, California

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Abstract—The optical properties of a number of steroidal thiolacetates, synthesized recently in the authors' laboratories, have been investigated. Optical rotatory dispersion and circular dichroism measurements have detected a long wavelength low intensity absorption near 270 mμ and have demonstrated that this absorption is optically active. Some temperature-dependent circular dichroism studies have been made in order to gain insight into the conformational mobility of the chromophoric system.

THE carbonyl chromophore n–π* transition, investigated extensively in the form of ketones[3] by optical rotatory dispersion (O.R.D.) and circular dichroism (C.D.), has received relatively little attention in the form of acids,[4] amides, lactones,[5] etc. This lack of attention has been due solely to the fact that the transition appears at a sufficiently low wavelength (200–215 mμ)[6] so that until recently it had been outside the accessible range of instrumentation. In thiolacetates, however, there has been reported[7] an absorption in the UV near 235 mμ (ε ~ 4000). The high intensity of this absorption suggests that it is a type of π–π* transition, and there should exist a low intensity n–π* transition at a higher wavelength. Such a transition, not perceptible in the UV, has now been demonstrated in either the O.R.D. or C.D. spectra and appears near 270 mμ. Such measurements on optically active compounds (steroids) confirm that this transition is optically active.

It is likely that this marked difference in spectral properties of a thiolacetate ester over an oxygen ester is due in part to the lesser electronegativity of sulphur over oxygen and the resultant difference in participation in the bonding and anti-bonding states. A non-bonded sulphur electron pair may interact with the 2pπ orbitals of the carbonyl group to form an extended π system, giving rise to 3 π molecular orbitals, two bonding and one anti-bonding. The 4 π electrons (two from

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[1] For paper CI see C. Djerassi, W. Klyne, T. Norin, G. Ohloff and E. Klein, *Tetrahedron* **21**, 163 (1965).

[2] For paper XIII see K. Takeda, T. Komeno and S. Ishihara, *Chem. Pharm. Bull., Tokyo* in press.

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

[4] U. Weiss and H. Ziffer, *J. Org. Chem.* **28**, 1248 (1963); W. Klyne, M. Scopes and J. Jennings, XIXth *I.U.P.A.C Congress, Abstracts* p. 110. London, July (1963).

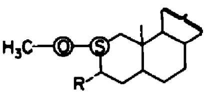
[5] T. Okuda, S. Harigaya and A. Kiyomoto, *Chem. Pharm. Bull., Tokyo* **12**, 504 (1964). J. P. Jennings, W. Klyne and P. M. Scopes, *Proc. Chem. Soc.*, 412 (1964).

[6] H. H. Jaffé and M. Orchin, *Theory and Applications of Ultraviolet Spectroscopy.* J. Wiley, New York (1962).

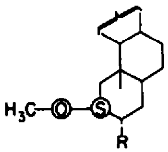
[7] J. I. Cunneen, *J. Chem. Soc.* 134 (1947).

sulphur, one from C, and one from O) occupy the two bonding orbitals in the ground state. On intensity grounds, the low wavelength (235 mμ), high intensity transition is likely π–π^* and involves a promotion from the highest filled bonding π orbital to the empty anti-bonding π^* orbital. Also on intensity grounds, the low intensity 270 mμ transition is probably n–π^*, although the nature of the n orbital is by no means certain. As a first approximation, however, the n orbital may be assumed to be similar to the n orbital in ketones, and on this rather tenuous basis one may consider application of the octant rule[8] to thiolacetates.

Like xanthates,[9] thiolacetates are an example of a chromophore with variably restricted rotation. A number of rotameric conformations, which place the carbonyl group in different environments in regard to the remainder of the molecule, are available, and each conformation may contribute to the ultimate magnitude and sign of the Cotton effect in a manner dependent upon its octant rule contribution and its concentration in the rotameric equilibrium. This fact appears to render useful predictions of the O.R.D. and C.D. spectra of thiolacetates somewhat difficult, but a similar approach has been successful among 20-keto steroids.[10] It is however, possible that due to steric requirements and the assumption that the carbonyl σ bonds lie in the same plane as the bonds of the supposedly sp^2 hybridized sulphur (for maximum π delocalization), only a few rotameric conformers are probable. In those compounds in which this is true, a more meaningful analysis of the data may be made. Moreover, temperature-dependent circular dichroism studies[11] may indicate changes in the conformational equilibrium, possibly providing data in agreement with one or two particular rotamers making the major contributions.



I A R—H
II A R=OAc



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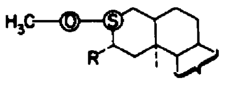
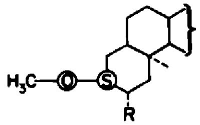
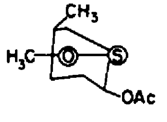


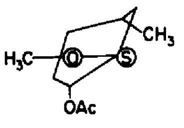
VI A R—H
VII A R—OAc



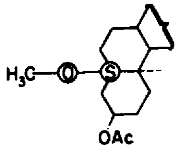
VI B R—H
VII B R—OAc



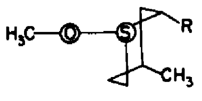
IIIA



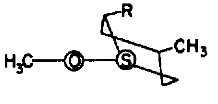
IIIB



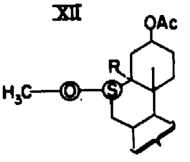
XII



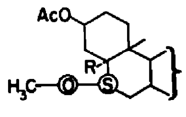
IV A R—H
V A R—OAc



IV B R—H
V B R—OAc



XIII A R=H
XIV A R—OAc



XIII B R—H
XIV B R—OAc

[8] W. Moffitt, R. B. Woodward, A. Moscowitz, W. Klyne and C. Djerassi, *J. Amer. Chem. Soc.* **83**, 4013 (1961).

[9] B. Sjöberg, D. J. Cram, L. Wolf and C. Djerassi, *Acta Chem. Scand.* **16**, 1079 (1962).

[10] K. M. Wellman and C. Djerassi, *J. Amer. Chem. Soc.* **87**, 60 (1965).

[11] K. M. Wellman, E. Bunnenberg and C. Djerassi, *J. Amer. Chem. Soc.* **85**, 1870 (1963).

In Figs. 1–3 are shown the relevant measurements of cholestan-2β-thiol acetate (I), cholestan-2β-thiol-3α-ol diacetate (II), and cholestan-2α-thiol-3β-ol diacetate (III). Although the O.R.D. spectra could not be measured through their second extrema, the C.D. curves clearly indicate a close correspondence in wavelength at the C.D. maxima. In Fig. 1, in which a complete high and low temperature C.D. study is indicated, cholestan-2β-thiol acetate (I) appears little changed except that as one proceeds from +166° down to −192° a gradual increase in positive rotational strength, with an increase in vibrational fine structure, is observed. The increase in rotational strength can be ascribed to an increase in concentration of at least one low-energy, positively contributing rotameric conformer. That is, less positively or negatively contributing conformers which become accessible at high temperature (increased molecular energy) are present to a lesser extent. An examination of a space-filled model of the compound indicates that there are two most probable conformers—IA and IB. On the basis of the octant rule, IA should clearly be positively rotating, while no definite prediction can be made with IB. It may be inferred in his case that the more highly positively rotating conformer is also the one of lower energy.

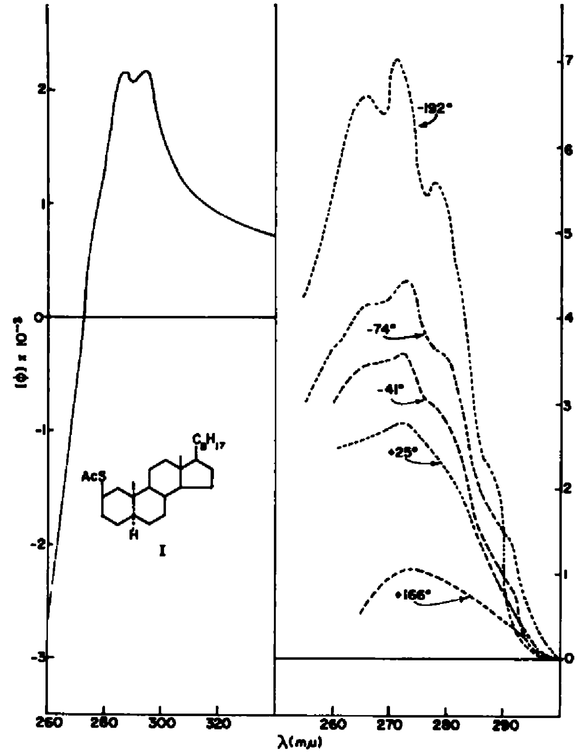


FIG. 1. Optical rotatory dispersion (——) and circular dichroism (- - -) curves of cholestan-2β-thiol acetate (I).

As noted in Fig. 2, cholestan-2β-thiol-3α-ol diacetate (II) exhibits a behaviour resembling that of the related cholestan-2β-thiol acetate (Fig. 1). The magnitude

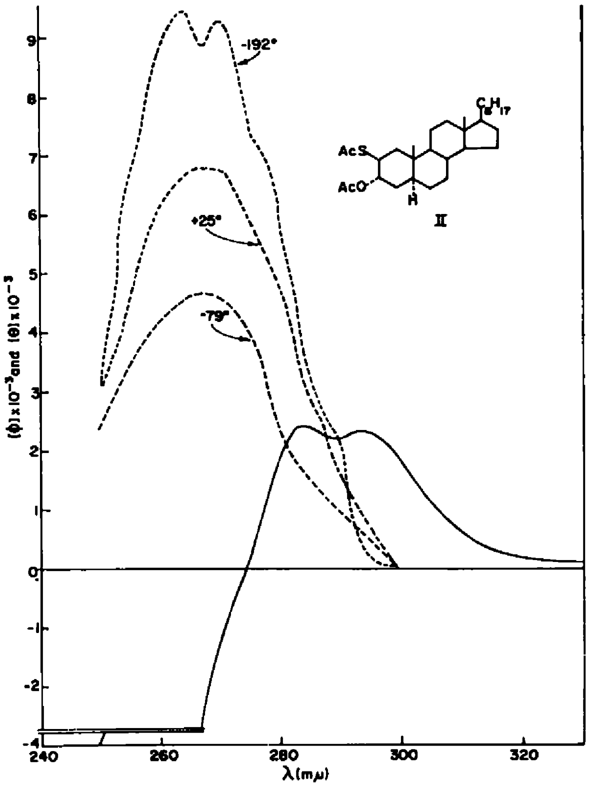


FIG. 2. Optical rotatory dispersion (——) and circular dichroism (- - -) curves of cholestan-2β-thiol-3α-ol diacetate (II).

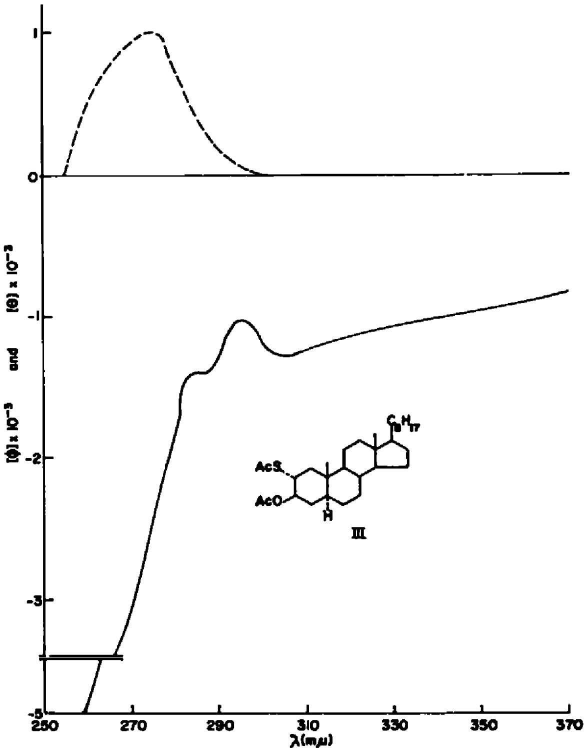


FIG. 3. Optical rotatory dispersion (——) and circular dichroism (- - -) curves of cholestan-2α-thiol-3β-ol diacetate (III).

and sign of the rotational strengths are similar at room temperature and at low temperatures, but one striking difference to be discerned in the low temperature C.D. study (Fig. 2) of the diacetate II is the rotational strength minimum between the two reported temperature extremes, suggesting the presence of at least three distinct molecular species.

Cholestan-2α-thiol-3β-ol diacteate (III) (Fig. 3), having the epimeric configuration of the thiolacetate at C-2, also shows a positive Cotton effect though of lower intensity. On the basis of the octant rule, and using space-filled models, the 3β-acetate makes a positive contribution (IIIA or IIIB) to what might otherwise be a negligible C.D. absorption since the bulk of the steroid nucleus appears to be in one of the symmetry planes. The unavailability of cholestan-2α-thiol acetate does not permit experimental verification of this interpretation nor comparison in the manner (I *vs.* II) performed with the 2β-thiolacetates.

Figures 4–7 contain data pertaining to steroids with a thiolacetate group at C-3. In Fig. 4, 5α-androstan-3β-thiol-17β-ol diacetate (IV) is shown to exhibit only a weakly positive Cotton effect. Although models indicate basically two unstrained conformations (IVA and IVB), their octant rule contributions are approximately equal and opposite, and the prediction of sign is tenuous at best. The low temperature C.D. results (Fig. 4) again point towards a situation similar to that of cholestan-2β-thiol-3α-ol diacetate (II) (Fig. 2). Here, however, the C.D. curve achieves a maximum value between the two temperature extremes measured. These data would appear to indicate the presence of at least three contributing species,[12] although solvent effects should not be excluded.

Cholestan-2β-ol-3β-thiol diacetate (V) has C.D. properties (Fig. 5) very similar to those of the related 3β-thiolacetate IV, as predicted from models (VA and VB). An enhanced positive contribution is noted on lowering the temperature to −192°.

The weakly positive Cotton effect of cholestan-3α-thiol acetate (VI) (Fig. 6) is rationalized by the application of the octant rule. An examination of a space-filled model indicates two preferred molecular species, VIA (positive) and VIB (negative), with opposite rotational contributions. The clear reversal of sign in the low temperature C.D. curves (Fig. 6) indicates that the negatively contributing conformer (VIB) is also of lower energy; whereas, the high temperature C.D. curves suggest that a conformational equilibrium exists already at slightly above room temperature.

Cholestan-2β-ol-3α-thiol diacetate (VII) (Fig. 7) shows a more intense positive Cotton effect than that of the 2-deacetoxy compound (Fig. 6) as expected from models. Thus no particular effect should be produced in VIIA while VIIB should be less negative than VIB since the acetoxy substituent is in a positive front octant. Moreover, a low temperature study indicates a very small change in the rotational strength in the range measured, suggesting that the compound is already in its most stable equilibrium conformation (s).

The case of cholestan-2β,3α-dithiol diacetate (VIII) (Fig. 8) can be complicated by the fact that there are present two absorbing chromophores which may interact, *viz.* the long wavelength low intensity C.D. absorption. The superposition of the curves from the two non-interacting chromophores (to a first approximation) is not altogether different from those of cholestan-2β-thiol-3α-ol diacetate (II) and of cholestan-2β-ol-3α-thiol diacetate (VII), although the low temperature behaviour is

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[12] See C. Djerassi, *Proc. Chem. Soc.* 314 (1964).

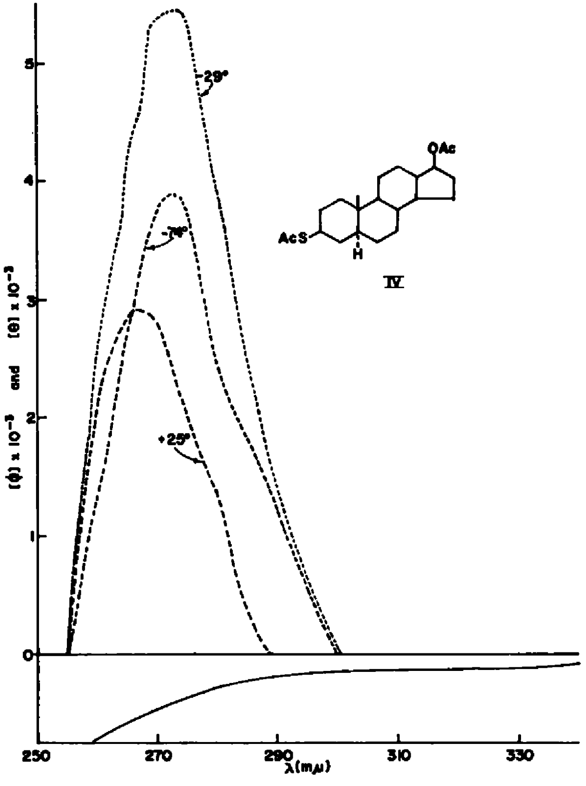

FIG. 4. Optical rotatory dispersion (——) and circular dichroism (- - -) curves of 5α-androstan-3β-thiol-17β-ol diacetate (IV).

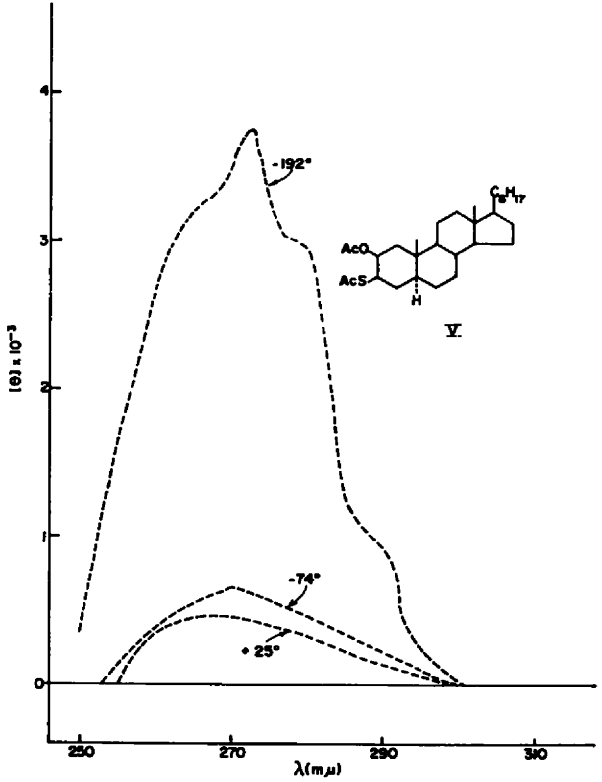

FIG. 5. Circular dichroism (- - -) curves of cholestan-2β-ol-3β-thiol diacetate (V).

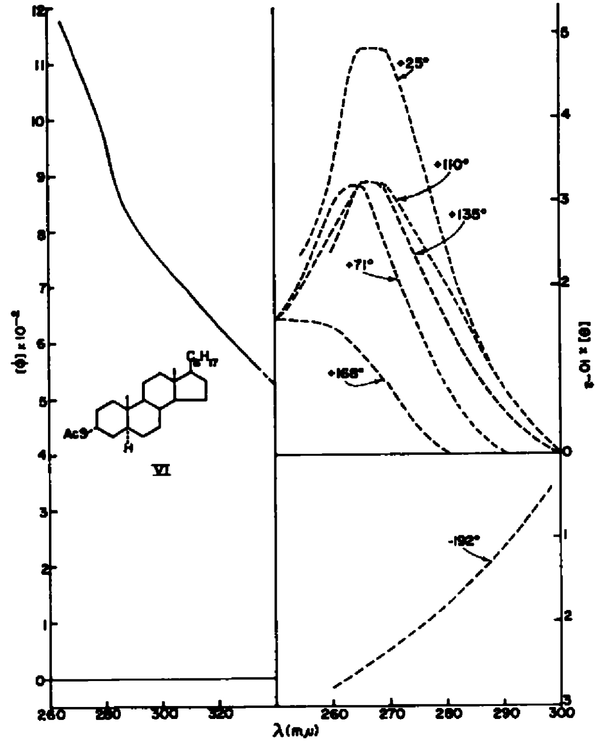

Fig. 6. Optical rotatory dispersion (——) and circular dichroism (- - -) curves of cholestan-3α-thiol acetate (VI).

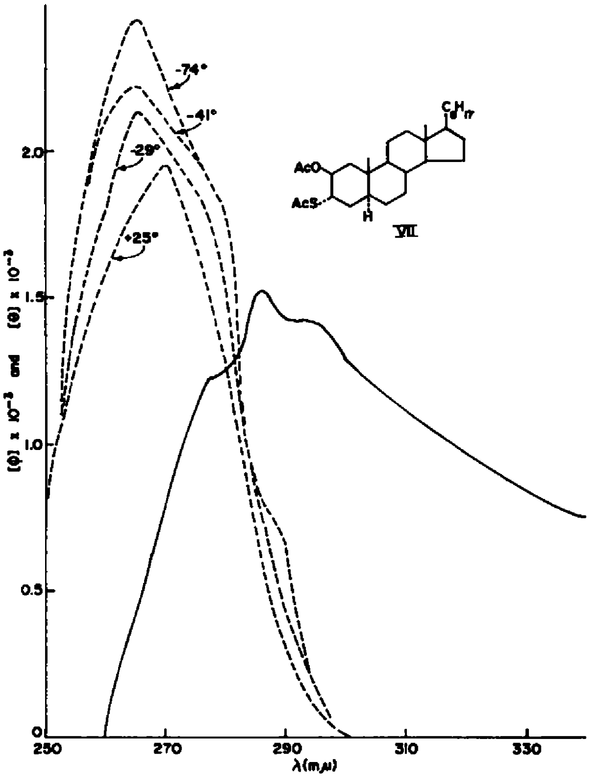

Fig. 7. Optical rotatory dispersion (——) and circular dichroism (- - -) curves of cholestan-2β-ol-3α-thiol diacetate (VII).

more similar to that of the latter. The estimation of quantitave differences in the same comparison is, however, difficult.

In Fig. 9 are collected data on compounds having a thiolacetate group at C-4. Both cholestan-3β-ol-4α-thiol diacetate (IX) and cholestan-3α-ol-4α-thiol diacetate (X) have negative O.R.D. Cotton effects. Cholestan-4β-thiol-5α-ol 4-acetate (XI) also shows a negative O.R.D. Cotton effect as has been confirmed by the C.D. measurement.

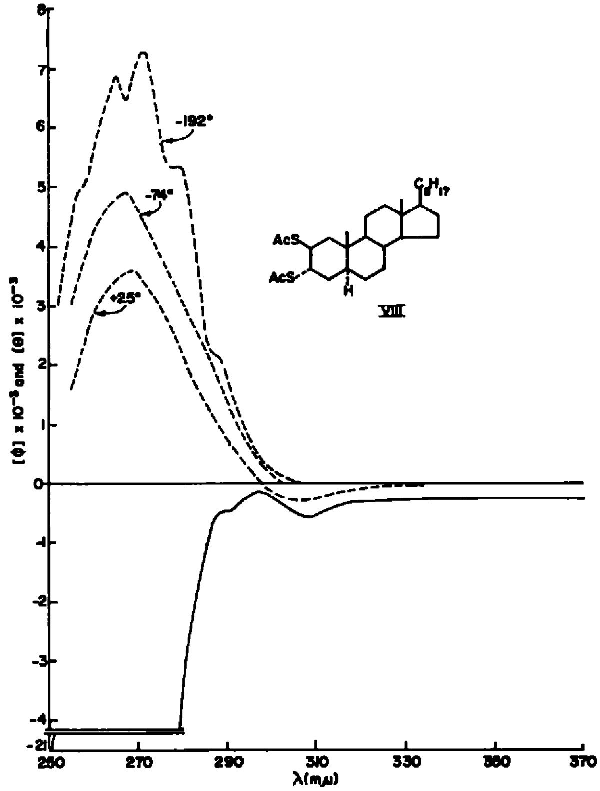

FIG. 8. Optical rotatory dispersion (——) and circular dichroism (- - -) curves of cholestan-2β,3α-dithiol diacetate (VIII).

Cholestan-3β-ol-5α-thiol diacetate (XII) (Fig. 10) has a position C.D. maximum which shows very little variation upon lowering of temperature. Models indicate definite steric requirements which tend to keep the thiol-acetate group in a reasonably "frozen" and positively rotating conformation (XII). This is borne out by the low temperature measurements (Fig. 10).

The relevant data for two 6-substituted thiolacetates are collected in Fig. 11. The positive C.D. maximum for cholestan-3β-ol-6β-thiol diacetate (XIII) seems to be consistent with conformation XIIIA, which appears to be the preferred one by consideration of models. Temperature-dependent C.D. studies indicate a gradual change in a positive direction in going from +129° to −192° which indicates some free rotational mobility of the thiol acetate (or possibly conformational variation in ring B) at the higher temperatures. The O.R.D. curves of the diacetate XIII and the 3,5,6-triacetate XIV (Fig. 11) are similar as would be expected since the 5α-acetoxy function should not affect the rotamer equilibrium; furthermore, it lies almost in a symmetry plane.

In summary, the 270 mμ transition of thiolacetates is an attractive one for O.R.D. and C.D. measurements. The inherent mobility of such systems and the lack of specific knowledge of the nature of the orbitals in the relevant transition renders the application of the octant rule somewhat tenuous. Nevertheless the presently recorded results seem to be reasonably consistent and indicate that useful conclusions on the predominance of certain rotamers can be reached from O.R.D. and C.D. studies with this chromophore.

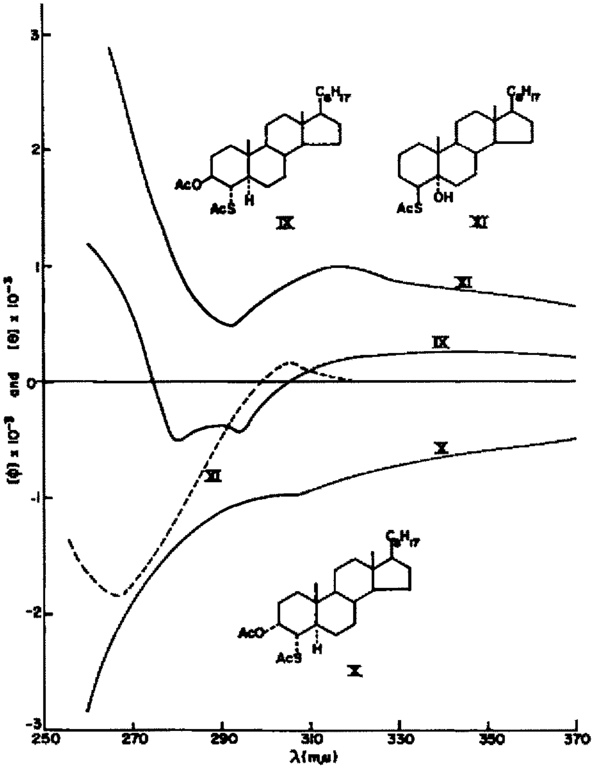

FIG. 9. Optical rotatory dispersion (——) curves of cholestan-3β-ol-4α-thiol diacetate (IX), cholestan-3α-ol-4α-thiol diacetate (X) and cholestan-4β-thiol-5α-ol 4-acetate (XI), and circular dichroism curve (– – –) of cholestan-4β-thiol-5α-ol 4-acetate (XI).

EXPERIMENTAL

O.R.D. measurements were performed at Osaka with a Rudolph automatically recording spectropolarimeter. The C.D. measurements were obtained on a Baird-Atomic/Jouan Dichrograph at Stanford. The rotatory dispersion data are recorded in the generally accepted manner,[13] while the circular dichroism data are listed according to a conversion recorded elsewhere[14] in detail.

[13] See Chapter 2 in Ref. 3, as well as C. Djerassi and W. Klyne, *Proc. Chem. Soc.* 55 (1957).

[14] C. Djerassi and E. Bunnenberg, *Proc. Chem. Soc.*, 299 (1963).

Cholestan-2β-thiol acetate (I)[15,16] (*Fig.* 1). C.D. in dioxane: c 1·18 (365–300 mμ), c 0·393 (285–255 mμ); $[\theta]_{300}$ 0, $[\theta_{270}$ +3399, $[\theta]_{255}$ +1540. O.R.D. in dioxane: c 0·2288 (700–260 mμ); $[\phi]_{700}$ +160°, $[\phi]_{292-4}$ +2140°, $[\phi]_{289}$ +2060°, $[\phi]_{287}$ +2120°, $[\phi]_{260}$ −2690°. C.D. in E.P.A.: c 2·1 (320–255 mμ); +25°: $[\theta]_{300}$ 0, $[\theta]_{273}$ +2801, $[\theta]_{260}$ +2450; −41°: $[\theta]_{300}$ 0, $[\theta]_{273}$ +3611, $[\theta]_{260}$ +3000; −74°: $[\theta]_{300}$ 0, $[\theta]_{273}$ +4488, $[\theta]_{255}$ +2950; −192°: $[\theta]_{300}$ 0, $[\theta]_{278}$ +5589, $[\theta]_{276}$ +5402, $[\theta]_{271}$ +7078, $[\theta]_{265}$ +6426, $[\theta]_{264}$ +6612, $[\theta]_{255}$ +4300. C.D. in decalin: c 1·34 (320–260 mμ); +25°: $[\theta]_{300}$ 0, $[\theta]_{273}$ +2697, $[\theta]_{260}$ +2100; +64°: $[\theta]_{300}$ 0, $[\theta]_{273}$ +2088, $[\theta]_{270}$ +1900; +96°: $[\theta]_{300}$ 0, $[\theta]_{273}$ +1740, $[\theta]_{270}$ +1560; +128°: $[\theta]_{300}$ 0, $[\theta]_{273}$ +1479, $[\theta]_{270}$ +1200; +166°: $[\theta]_{300}$ 0, $[\theta]_{273}$ +1044, $[\theta]_{270}$ +500.

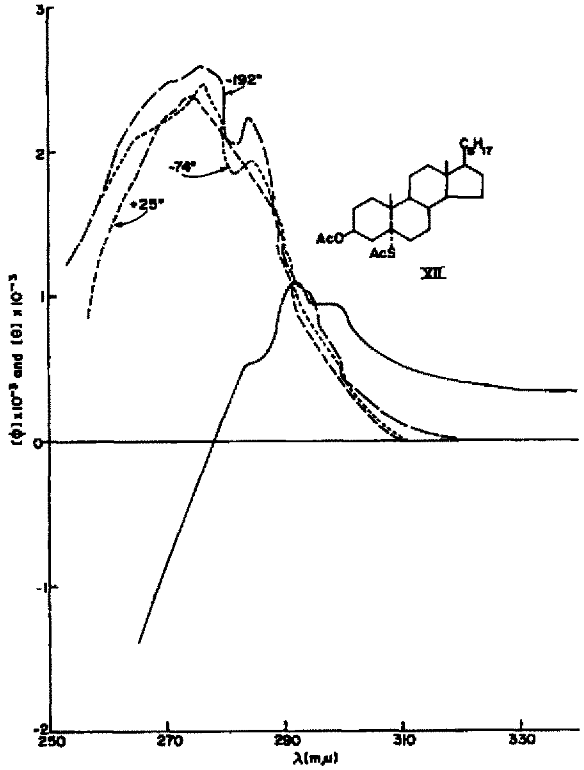

FIG. 10. Optical rotatory dispersion (——) and circular dichroism (– – –) curves of cholestan-3β-ol-5α-thiol diacetate (XII).

Cholestan-2β-thiol-3α-ol diacetate (II)[15,16] (*Fig.* 2). O.R.D. in n-heptane: c 0·3381 (700–250 mμ); $[\phi]_{700}$ +150°, $[\phi]_{293}$ +2300°, $[\phi]_{290}$ +2260°, $[\phi]_{265}$ +2420°, $[\phi]_{250}$ −4040°. C.D. in E.P.A. (Fig. 2b): c 0·75 (300–250 mμ); +25°: $[\theta]_{300}$ 0, $[\theta]_{268}$ +6750, $[\theta]_{255}$ +4700; −74°: $[\theta]_{300}$ 0, $[\theta]_{268}$ +4592, $[\theta]_{250}$ + 2300; −192°: $[\theta]_{300}$ 0, $[\theta]_{288}$ +2550, $[\theta]_{275}$ +6900, $[\theta]_{270}$ +9300, $[\theta]_{265}$ +8850, $[\theta]_{264}$ +9450, $[\theta]_{250}$ +5100.

Cholestan-2α-thiol-3β-ol diacetate (III)[15–17] (*Fig.* 3). C.D. in dioxane: c 0·8 (320–255 mμ); $[\theta]_{300}$ 0, $[\theta]_{273}$ +1008, $[\theta]_{255}$ 0. O.R.D. in n-heptane: c 0·3094 (700–260 mμ); $[\phi]_{700}$ −180°, $[\phi]_{308}$ −1260°, $[\phi]_{295}$ −1010°, $[\phi]_{290}$ −1290°, $[\phi]_{285}$ −1390°, $[\phi]_{260}$ −4910°.

[15] K. Takeda and T. Komeno, *Chem. & Ind.* (*London*) 1793 (1962).

[16] K. Takeda, T. Komeno, J. Kawanami, S. Ishihara, H. Kadokawa, H. Tokura and H. Itani, *Tetrahedron*, in press.

[17] C. Djerassi, M. Gorman, F. X. Markley and E. B. Oldenburg, *J. Amer. Chem. Soc.* 77, 568 (1955).

[18] K. Takeda, J. Kawanami, H. Kadokawa, to be published.

5α-Androstan-3β-thiol-17β-ol diacetate (IV)[15,16,18] (*Fig.* 4). O.R.D. in methanol: c 0·3004 (700–260 mμ); $[\phi]_{700}$ −50°, $[\phi]_{300}$ −140°, $[\phi]_{260}$ −570°. C.D. in E.P.A.: c 0·76 (300–250 mμ); +25°: $[\theta]_{300}$ 0, $[\theta]_{267}$ +280, $[\theta]_{255}$ 0; −29°: $[\theta]_{300}$ 0, $[\theta]_{272}$ +536, $[\theta]_{255}$ 0; −74°: $[\theta]_{300}$ 0, $[\theta]_{272}$ +379, $[\theta]_{255}$ 0.

Cholestan-2β-ol-3β-thiol diacetate (V)[19] (*Fig.* 5). C.D. in dioxane: c 1·22 (310–255 mμ); +25°: $[\theta]_{300}$ 0, $[\theta]_{267}$ +448, $[\theta]_{255}$ 0. C.D. in E.P.A.: c 1·5 (300–250 mμ); −74°: $[\theta]_{300}$ 0, $[\theta]_{270}$ +654, $[\theta]_{250}$ 0; −192°: $[\theta]_{300}$ 0, $[\theta]_{290}$ +900, $[\theta]_{278}$ +3000, $[\theta]_{273}$ +3750, $[\theta]_{267}$ +3300, $[\theta]_{250}$ +300.

Cholestan-3α-thiol acetate (VI)[15,16,20] (*Fig.* 6). O.R.D. in n-heptane: c 0·1924 (700–270 mμ); $[\phi]_{700}$ 0°, $[\phi]_{300}$ +910°, $[\phi]_{270}$ +1140°. C.D. in E.P.A.: c 3·18 (300–250 mμ); +25°: $[\theta]_{300}$ 0, $[\theta]_{270}$ +170, $[\theta]_{255}$ 80; −74°: $[\theta]_{300-250}$ 0; −192°: $[\theta]_{300}$ 0, $[\theta]_{270}$ −230, $[\theta]_{260}$ −270. C.D. in decalin: c 0·82 (300–250 mμ); +25°: $[\theta]_{300}$ 0, $[\theta]_{267}$ +480, $[\theta]_{255}$ +230; +71°: $[\theta]_{300}$ 0, $[\theta]_{265}$ +320, $[\theta]_{250}$ +160; +110°: $[\theta]_{300}$ 0, $[\theta]_{270}$ +320, $[0]_{255}$ +220; +135°: $[\theta]_{300}$ 0, $[\theta]_{267}$ +320, $[\theta]_{260}$ +240.

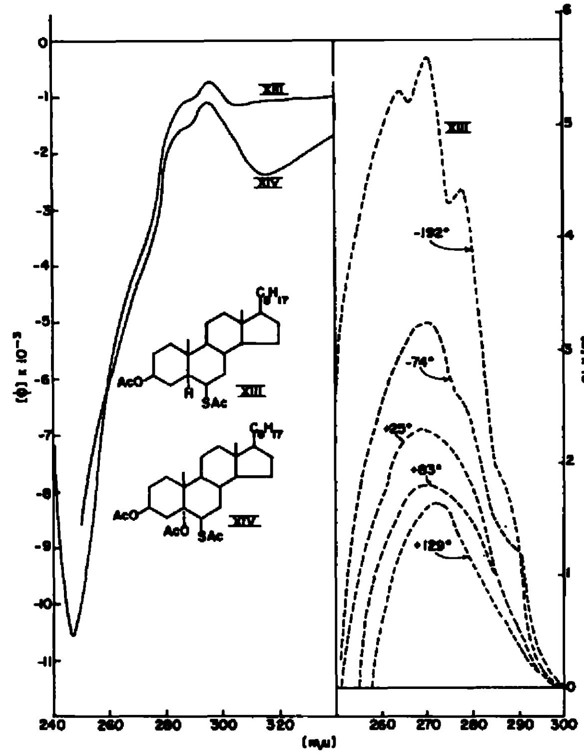

FIG. 11. Optical rotatory dispersion (——) curves of cholestan-3β-ol-6β-thiol diacetate (XIII) and cholestan-3β,5α-diol-6β-thiol triacetate (XIV) and circular dichroism (– – –) curves of cholestan-3β-ol-6β-thiol diacetate (XIII).

Cholestan-2β-ol-3α-thiol diacetate (VII)[15,18] (*Fig.* 7). O.R.D. in n-heptane: c 0·3188 (700–260 mμ); $[\phi]_{700}$ +240°, $[\phi]_{295}$ +1410°, $[\phi]_{290}$ +1430°, $[\phi]_{284}$ +1520°, $[\phi]_{281}$ +1270°, $[\phi]_{277}$ +1230°, $[\phi]_{260}$ −110°. C.D. in E.P.A.: c 1·16 (300–250 mμ); +25°: $[\theta]_{300}$ 0, $[\theta]_{270}$ +1952, $[\theta]_{250}$ +740; −29°: $[\theta]_{300}$ 0, $[\theta]_{265}$ +2137, $[\theta]_{250}$ +780; −41°: $[\theta]_{300}$ 0, $[\theta]_{265}$ +2220, $[\theta]_{255}$ +1550; −74°: $[\theta]_{300}$ 0, $[\theta]_{287}$ +745, $[\theta]_{265}$ +2449, $[\theta]_{255}$ +1700.

Cholestan-2β,3α-dithiol diacetate (VIII)[16] (*Fig.* 8). O.R.D. in n-heptane: c 0·3206 (700–250 mμ); $[\phi]_{700}$ 0°, $[\phi]_{310}$ −540°, $[\phi]_{297}$ −160°, $[\phi]_{290-287}$ −490°, $[\phi]_{250}$ −21200°. C.D. in E.P.A.: c 1·08 (340–250 mμ); +25°: $[\theta]_{300}$ 0, $[\theta]_{268}$ +3604, $[\theta]_{255}$ +1650; −74°: $[\theta]_{300}$ 0, $[\theta]_{266}$ +4893, $[\theta]_{255}$

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+3000; −192°: $[\theta]_{300}$ 0, $[\theta]_{289}$ +2100, $[\theta]_{279}$ +5356, $[\theta]_{272}$ +7176, $[\theta]_{268}$ +6420, $[\theta]_{265}$ +6848, $[\theta]_{257}$ +4922, $[\theta]_{252}$ +3000.

Cholestan-3β-ol-4α-thiol diacetate (IX)[16] (*Fig.* 9). O.R.D. in chloroform: c 1·122 (700–270 mμ); $[\phi]_{700}$ +56°, $[\phi]_{400}$ +116°, $[\phi]_{292-288}$ −240°, $[\phi]_{283}$ −270°, $[\phi]_{280}$ −190°, $[\phi]_{270}$ +20°. O.R.D. in n-heptane: c 0·3131 (700–260 mμ); $[\phi]_{700}$ +65°, $[\phi]_{400-350}$ +230°, $[\phi]_{294}$ −450°, $[\phi]_{290}$ −370°, $[\phi]_{285}$ −520°, $[\phi]_{280}$ −145°, $[\phi]_{275}$ +50°, $[\phi]_{270}$ +570°, $[\phi]_{260}$ +1190°.

Cholestan-3α-ol-4α-thiol diacetate (X)[16] (*Fig.* 9). O.R.D. in chloroform: c 1·036 (700–260 mμ); $[\phi]_{700}$ −110°, $[\phi]_{300}$ −1010°, $[\phi]_{290}$ −1100°, $[\phi]_{280}$ −1210°, $[\phi]_{260}$ −2820°.

Cholestan-4β-thiol-5α-ol 4-acetate (XI)[21] (*Fig.* 9). C.D. in dioxane: c 1·22 (320–266 mμ); c 0·1525 (270–255 mμ); $[\theta]_{300}$ 0, $[\theta]_{265}$ −1850, $[\theta]_{255}$ −1250. O.R.D. in dioxane: c 0·2288 (700–265 mμ); $[\phi]_{700}$ +160°, $[\phi]_{317}$ +1010°, $[\phi]_{291}$ +490°, $[\phi]_{265}$ +2890°.

Cholestan-3β-ol-5α-thiol diacetate (XII)[22] (*Fig.* 10). C.D. in dioxane: c 0·63 (320–260 mμ); $[\theta]_{310}$ 0, $[\theta]_{276}$ +2130, $[\theta]_{260}$ +1200. O.R.D. in n-heptane: c 0·3231 (700–265 mμ); $[\phi]_{700}$ +80°, $[\phi]_{300-295}$ +940°, $[\phi]_{291\cdot5}$ +1050°, $[\phi]_{286-283}$ +560°, $[\phi]_{265}$ −1410°. C.D. in E.P.A. c 1·0 (320–255 mμ); +25°: $[\theta]_{310}$ 0, $[\theta]_{285}$ +1820, $[\theta]_{275}$ +2380, $[\theta]_{267}$ +840; −74°: $[\theta]_{310}$ 0, $[\theta]_{285}$ +1960, $[\theta]_{282}$ +1837, $[\theta]_{277}$ +2450, $[\theta]_{271}$ +2240, $[\theta]_{260}$ +1700; −192°: $[\theta]_{320}$ 0, $[\theta]_{295}$ +1008, $[\theta]_{284}$ +2240, $[\theta]_{282}$ +2016, $[\theta]_{277}$ +2576, $[\theta]_{271}$ +2440, $[\theta]_{255}$ +1340.

Cholestan-3β-ol-6β-thiol diacetate (XIII)[21, 23] (*Fig.* 11). O.R.D. in n-heptane: c 0·3326 (700–260 mμ), c 0·0998 (260–235 mμ); $[\phi]_{700}$ −270°, $[\phi]_{310}$ −1100°, $[\phi]_{295\cdot5}$ −730°, $[\phi]_{290}$ −1030°, $[\phi]_{285}$ −1160°, $[\phi]_{260}$ −5700°, $[\phi]_{247}$ −10600°, $[\phi]_{235}$ −3000°. C.D. in E.P.A. c 1·27 (300–250 mμ); +25°: $[\theta]_{300}$ 0, $[\theta]_{267}$ +2240, $[\theta]_{252}$ 0; −74°: $[\theta]_{300}$ 0, $[\theta]_{287}$ +1400, $[\theta]_{279}$ +2450, $[\theta]_{270}$ +3234, $[\theta]_{252}$ +600; −192°: $[\theta]_{300}$ 0, $[\theta]_{287}$ +1800, $[\theta]_{278}$ +4410, $[\theta]_{276}$ +4320, $[\theta]_{271}$ +5580, $[\theta]_{266}$ +5220, $[\theta]_{264}$ +5310, $[\theta]_{250}$ +2150. C.D. in decalin: c 0·84 (300–250 mμ); +25°: $[\theta]_{300}$ 0, $[\theta]_{270}$ +2310, $[\theta]_{253}$ 0; +52°: $[\theta]_{300}$ 0, $[\theta]_{270}$ +1980, $[\theta]_{255}$ 0; +83°: $[\theta]_{300}$ 0, $[\theta]_{270}$ +1815, $[\theta]_{256}$ 0; +129°: $[\theta]_{300}$ 0, $[\theta]_{272}$ +1485, $[\theta]_{258}$ 0.

Cholestan-3β,5α-diol-6β-thiol triacetate (XIV)[22] (*Fig.* 11). O.R.D. in n-heptane: c 0·1896 (700–250 mμ); $[\phi]_{700}$ −590°, $[\phi]_{315}$ −2400°, $[\phi]_{294}$ −1070°, $[\phi]_{288}$ −1510°, $[\phi]_{286\cdot5}$ −1540°, $[\phi]_{250}$ −8600°.

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