Tetrahedron, 1963, Vol. 19, pp. 1547 to 1561. Pergamon Press Ltd. Printed in Northern Ireland

OPTICAL ROTATORY DISPERSION STUDIES—LXXXIII[1]; THIOSTEROIDS—IX[2]

OPTICAL ROTATORY DISPERSION AND CIRCULAR DICHROISM OF EPISULFIDES AND TRITHIOCARBONATES

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(*Received* 3 *April* 1963)

Abstract—The optical properties of five epimeric pairs of steroidal episulfides, recently synthesized in the authors' laboratories, have been examined. Optical rotatory dispersion and circular dichroism measurements have demonstrated that the 260 mμ absorption band is optically active, the rotational strength at times differing widely between two epimers. Similar measurements have also been performed with steroidal and sugar trithiocarbonates, the optical activity of the low intensity band near 450 mμ and of the high intensity transition near 315 mμ having been established in each instance. Attention is called to the utility of such trithiocarbonates as "chromophoric" derivatives for olefins in problems of absolute configurational assignments.

HISTORICALLY, the carbonyl chromophore has been the most important one in the development of optical rotatory dispersion as a widely used tool in organic chemistry.[3] Subsequently, extensive rotatory dispersion studies have also been performed with substrates containing the C=S chromophore, because the latter shares many of the favorable characteristics of the carbonyl group's n–π* transition, namely a low-intensity absorption in a convenient UV spectral range. Pertinent examples are xanthates,[4,5] dithiocarbamates,[6] 3-phenyl-2-thiohydantoins,[7] N-thionocarbethoxy-amines,[7] acylthioureas,[8] thiobenzamides,[9] and monomeric thiones.[10] Except for the

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[1] Paper LXXXII, C. Djerassi, R. A. Schneider, H. Vorbrueggen and N. L. Allinger, *J. Org. Chem.* **28**, 1632 (1963).

[2] Paper VIII, K. Takeda, T. Komeno and S. Ishiwara, *Chem. Pharm. Bull., Tokyo*, **11**, 430 (1963).

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

[4] T. M. Lowry and H. Hudson, *Phil. Trans. Roy. Soc. London, Ser. A*, **232** 117 (1933).

[5] B. Sjöberg, D. J. Cram, L. Wolf and C. Djerassi, *Acta Chem. Scand.* **16**, 1079 (1962); see also C. Djerassi, I. T. Harrison, O. Zagneetko and A. L. Nussbaum, J. *Org. Chem.* **27**, 1173 (1962).

[6] B. Sjöberg, A. Fredga and C. Djerassi, *J. Amer. Chem. Soc.* **81**, 5002 (1959); see also B. Sjöberg, B. Hansson and R. Dahlbom, *Acta Chem. Scand.* **16**, 1057 (1962).

[7] C. Djerassi, K. Undheim, R. C. Sheppard, W. G. Terry and B. Sjöberg, *Acta Chem. Scand.* **15**, 903 (1961).

[8] C. Djerassi, K. Undheim and A.-M. Weidler, *Acta Chem. Scand.* **16**, 1147 (1962); see also H. M. Walborsky and C. G. Pitt, *J. Amer. Chem. Soc.* **84**, 4831 (1962).

[9] B. Sjöberg, B. Karlen and R. Dahlbom, *Acta Chem. Scand.* **16**, 1071 (1962).

[10] C. Djerassi and D. Herbst, *J. Org. Chem.* **26**, 4675 (1961).

last mentioned group, the rotatory dispersion properties of all of the C=S containing chromophores have found utility for stereochemical work, notably for assignments of absolute configurations. Recently, circular dichroism measurements have been performed[11] for representative examples of the various types and these have confirmed without exception the correctness of the earlier discussed relationship between O.R.D Cotton effect and U.V. absorption. Another pertinent group are the cyclic disulfides and diselenides, where the nicely corresponding optical rotatory dispersion[12] and circular dichroism[11] data have proved useful in uncovering some transitions, which were poorly or not all recognizable from ultraviolet spectral measurements.[13]

Recently, there have been under way in our respective laboratories extensive studies on the synthesis and chemical behaviour of steroidal episulfides.[14,15] Earlier spectroscopic measurements with simple episulfides[16,17] have shown the existence of a low-intensity absorption maximum in the 260 mμ region, which appears to resemble the n–π* absorption of ketones and aldehydes. The only optically active episulfides which have been prepared in the past have been in the carbohydrate field[17,18] and no optical rotatory dispersion measurements have been performed on them. In view of the theoretical interest and potential stereochemical applications of such information, there has now been undertaken a study of the optical rotatory dispersion and circular dichroism behaviour of steroidal episulfides, the data being reported in conjunction with the U.V. absorption spectra.

In Figs. 1 and 2 are collected the relevant measurements of cholestane-2α,3α-(I) and 2β,3β-(II) episulfides. Both epimers show a weak absorption maximum ($\log \varepsilon \sim 1{\cdot}7$) near 265 mμ, which corresponds well in position to that of the C.D. maxima at 268 mμ (I) and 264 mμ (II) or to the midpoints (268 mμ for I and 263 mμ for II) of the O.R.D. Cotton effects. Of particular interest is the observation that while the ultraviolet extinction coefficients of the two epimeric episulfides I and II are very similar, their rotational strengths, expressed either in O.R.D. Cotton effect amplitude or C.D. molecular ellipticity differ by a factor of over six, the more powerful 2α,3α-epimer I being characterized by a negative Cotton effect and a negative C.D. maximum, in contrast to the positive parameters of the 2β,3β-epimer II.

The same situation is also noted in Figs. 3 and 4, the rotational strength of cholestane-3α,4α-episulfide (III), as expressed by its negative O.R.D. Cotton effect or negative C.D. curve, being an order of magnitude more intense than that of the oppositely signed (positive) Cotton effect and C.D. maximum of 17β-acetoxyandrostane-3β,4β-episulfide (IV). These two pairs (I *vs.* II; III *vs.* IV) represent illustrations[19] where the small differences in electric dipole are not sufficient to have an important effect upon

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[11] C. Djerassi, H. Wolf and E. Bunnenberg, *J. Amer. Chem. Soc.* **84**, 4552 (1962).

[12] C. Djerassi, A. Fredga and B. Sjöberg, *Acta Chem. Scand.* **15**, 417 (1961).

[13] For another recent illustration of the use of optical rotatory dispersion and circular dichroism for such purposes, see C. Djerassi, H. Wolf and E. Bunnenberg. *J. Amer. Chem. Soc.* **85**, 324 (1963).

[14] K. Takeda, T. Komeno and J. Kawanami, *Chem. Pharm. Bull., Tokyo* **8**, 621 (1960); T. Komeno, *Ibid.* **8**, 668, 672 (1960); K. Takeda and T. Komeno, *Chem. & Ind.* 1783 (1962).

[15] D. A. Lightner and C. Djerassi, *Chem. & Ind.* 1236 (1962).

[16] R. E. Davis, *J. Org. Chem.* **23**, 216 1380 (1958).

[17] A. M. Creighton and L. N. Owen, *J. Chem. Soc.* 1024 (1960).

[18] For leading references see (*a*) L. D. Hall, L. Hough and R. A. Pritchard, *J. Chem. Soc.* 1537 (1961); (*b*) R. D. Guthrie, *Chem. & Ind.* 2121 (1962).

[19] For discussion see A. Moscowitz in Chapter 12 of ref. 3, especially pp. 167–170.

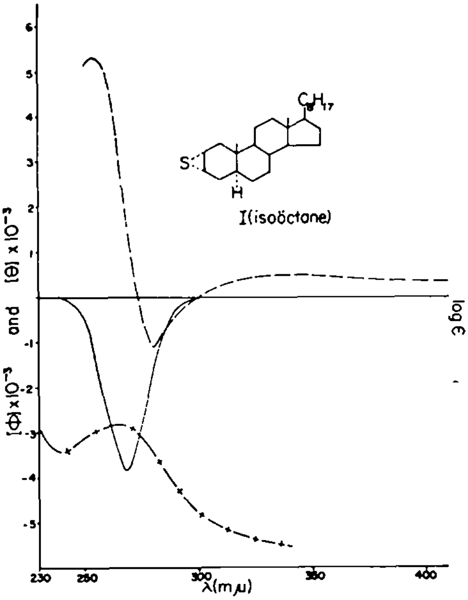

FIG. 1. Circular dichroism (———), optical rotatory dispersion (- - - -) and ultraviolet absorption (-+-+) curves of cholestan-2α,3α-episulfide (I) in isoöctane solution.

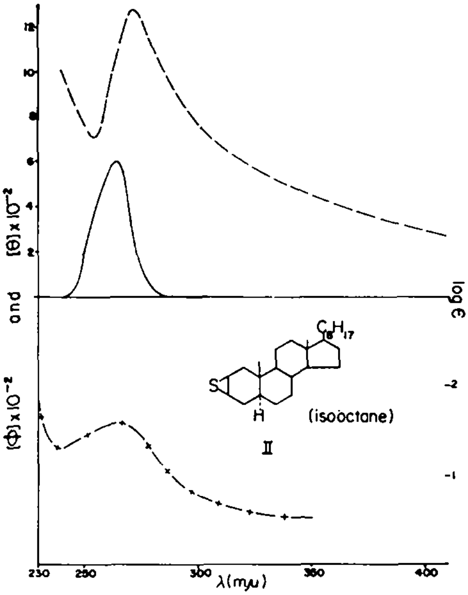

FIG. 2. Circular dichroism (———), optical rotatory dispersion (- - - -) and ultraviolet absorption (-+-+) curves of cholestan-2β,3β-episulfide (II) in isoöctane solution.

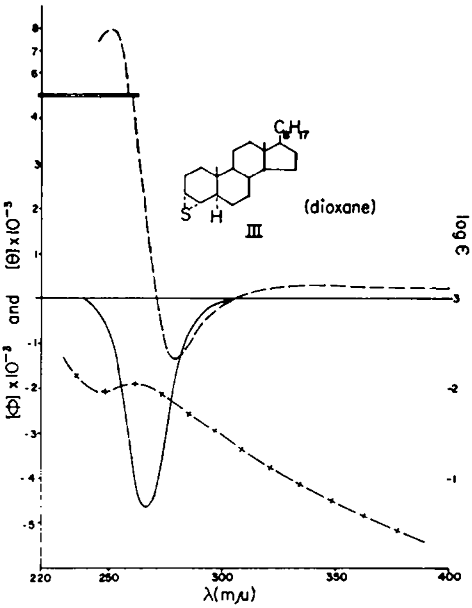

FIG. 3. Circular dichroism (———), optical rotatory dispersion (- - - -) and ultraviolet absorption (-+-+) curves of cholestan-3α,4α-episulfide (III) in dioxane solution.

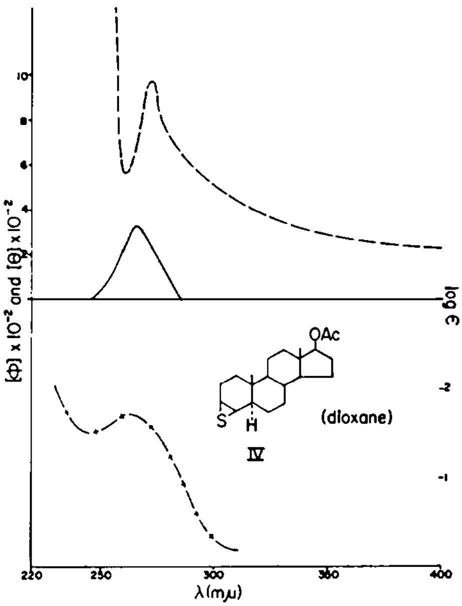

FIG. 4. Circular dichroism (———), optical rotatory dispersion (- - - -) and ultraviolet absorption (-+-+) curves of 17β-acetoxyandrostan-3β,4β-episulfide (IV) in dioxane solution.

the extinction of the ultraviolet absorption maximum, but are reflected in the rotational strength because of the substantial magnetic dipole. The results so far would suggest that for any given pair of epimeric episulfides, the Cotton effects will be of opposite sign and differ appreciably in amplitude, the same statements also applying to the sign and molecular ellipticity of the circular dichroism curve. As is shown below, neither one of these generalizations is necessarily justified.

Thus, the two epimeric 3β-hydroxycholestane-5α,6α-(V) and 5β,6β-(VI) episulfides still show (Figs. 5 and 6) oppositely signed Cotton effects and C.D. curves, but their respective molecular ellipticity or Cotton effect amplitude values do not even differ by a factor of two, in contrast to the situation existing in Figs. 1–4. Even more striking are the data collected in Figs. 7 and 8 of the 3β,20β-dihydroxy-5α-pregnane-11α-12α-(VII) and 11β-12β-(VIII) episulfides, since both epimers are characterized by positive Cotton effects and positive C.D. curves of approximately equal strength. Finally, the only available pair of epimeric episulfides attached to a cyclopentane ring, 3β-acetoxyandrostane-16α17α-(IX) and 16β,17β-(X) episulfides show an intermediate picture: the rotational strengths of the two epimers differ again to a very appreciable extent (Fig. 9 *vs.* Fig. 10) and the Cotton effects, though still of the same sign (positive), are now of quite distinct shape because of the negative background effect operating in the 16α,17α-epimer IX. As has already been pointed out in an earlier paper,[11] such background effects, operative in O.R.D., but not in C.D. are very useful as diagnostic tools for purposes of differentiation, but they interfere in quantitative considerations of rotational strength. Consequently, both optical measurements should be performed, since each possesses an intrinsic advantage in such an instance.

In summary, the coincidence in wavelength between the C.D. maximum and the O.R.D. Cotton effect midpoint on the one hand, and the ultraviolet absorption maximum on the other for the episulfides I–X clearly demonstrates the optical activity of the 260 mμ transition. In several instances, either the sign or the rotational strength or both parameters can be utilized for purposes of differentiating between epimeric pairs, while in other cases (e.g. VII and VIII) such information is of no particular help for stereochemical purposes. At present the orbitals involved in the 260 mμ transition are insufficiently characterized to warrant formulation of a prescription akin to the octant rule[20] which has proved so successful for ketones. However, it is relevant to note that the isolated episulfide group, like the isolated carbonyl group, represents a type of chromophore that has been classified as "inherently symmetric". Hence, whatever the nature of the relevant orbitals, their symmetry properties must reflect the inherent symmetry properties (e.g. reflection planes) of the *isolated* episulfide. The observed Cotton effects arise in the cases cited above because of the asymmetric molecular environment provided for the episulfide group by the rest of the steroid. This environment is determined to a large extent by the position and orientation of the episulfide group in the steroid. Hence, it can be hoped that the configuration of an incompletely characterized 2,3- or 3,4- or 5,6-episulfide of a 5α-steroid in which there is no substitution in the immediate vicinity of the episulfide group can be determined by comparison of its optical rotatory dispersion or circular dichroism curve with the curves shown in Figs. 1–6.

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[20] W. Moffitt, R. B. Woodward, A. Moscowitz, W. Klyne and C. Djerassi, *J. Amer. Chem. Soc.* **83**, 4013 (1961). See also C. Djerassi and W. Klyne, *J. Chem. Soc.* 4929 (1962); *Ibid.*, 2390 (1963).

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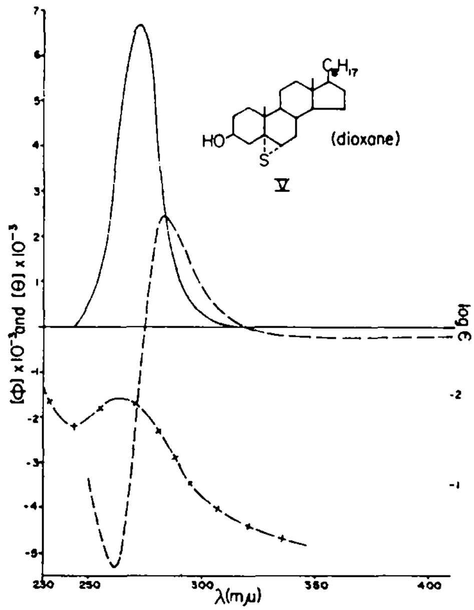

FIG. 5. Circular dichroism (———), optical rotatory dispersion (- - - -) and ultraviolet absorption (-+-+) curves of 3β-hydroxycholestan-5α,6α-episulfide (V) in dioxane solution.

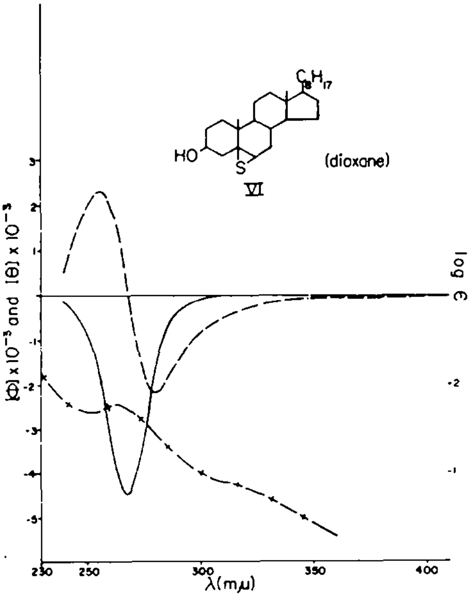

FIG. 6. Circular dichroism (———), optical rotatory dispersion (- - - -) and ultraviolet absorption (-+-+) curves of 3β-hydroxycholestan-5β,6β-episulfide (VI) in dioxane solution.

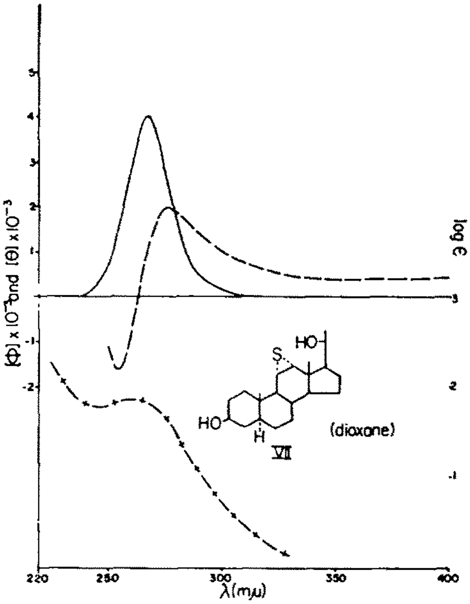

Fig. 7. Circular dichroism (———), optical rotatory dispersion (– – – –) and ultraviolet absorption (–+–+) curves of 3β,20β-Dihydroxy-5α-pregnan-11α,12α-episulfide (VII) in dioxane solution.

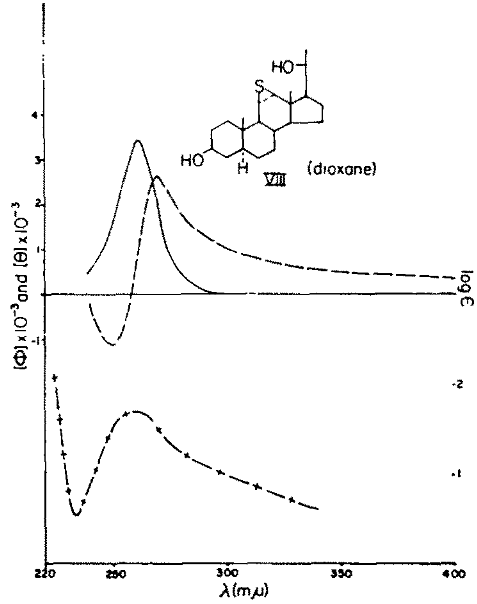

Fig. 8. Circular dichroism (———), optical rotatory dispersion (– – – –) and ultraviolet absorption (–+–+) curves of 3β,20β-Dihydroxy-5α-pregnan-11β,12β-episulfide (VIII) in dioxane solution.

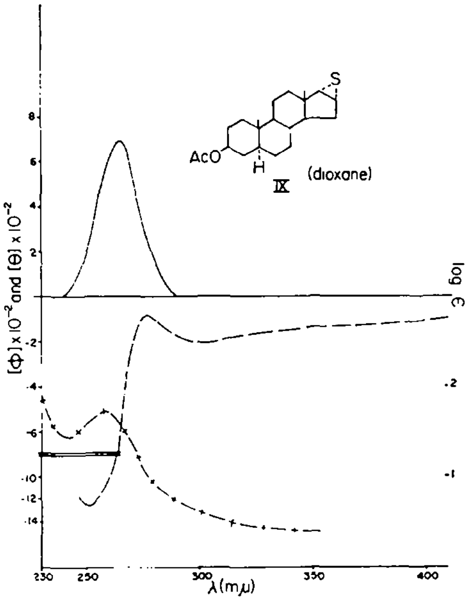

FIG. 9. Circular dichroism (———), optical rotatory dispersion (- - - -) and ultraviolet absorption (-+--+) curves of 3β-Acetoxy-5α-androstan-16α,17α-episulfide (IX) in dioxane solution.

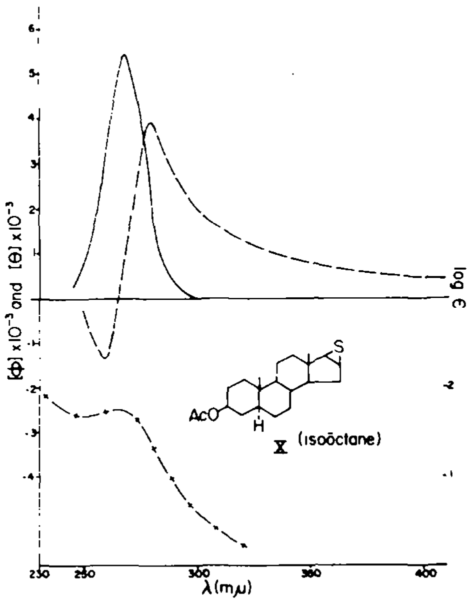

FIG. 10. Circular dichroism (———), optical rotatory dispersion (- - - -) and ultraviolet absorption (-+--+) curves of 3β-Acetoxy-5α-androstan-16β,17β-episulfide (X) in dioxane solution.

The reaction of episulfides with potassium alkyl xanthates to yield trithiocarbonates has been studied in detail in the sugar series.[17,18a] The yellow color of these derivatives points towards an absorption band in the visible range of the spectrum, but only limited spectral studies have been performed[21] in that region with dimethyl and diethyl trithiocarbonate. These measurements showed the existence of a low-intensity maximum near 430 mμ, a high-intensity maximum in the 305 mμ region (also noted[18a] in one sugar trithiocarbonate) and finally a medium-intensity maximum around 235 mμ.

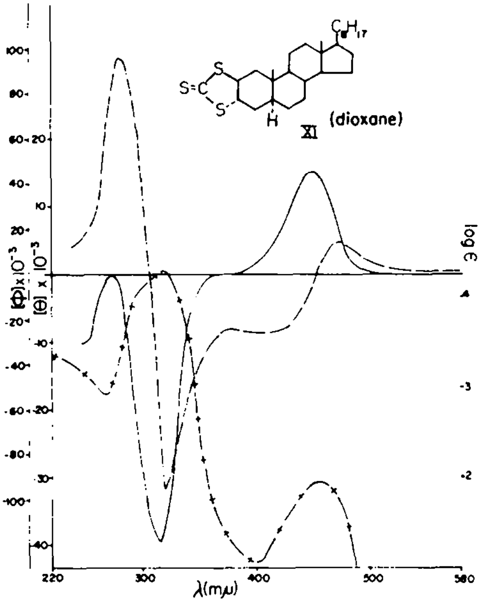

FIG. 11. Circular dichroism (———), optical rotatory dispersion (- - - -) and ultraviolet absorption (-+-+) curves of cholestan-2β,3α-trithiocarbonate (XI) in dioxane solution.

Work in our laboratories[22,23] on the stereochemistry of nucleophilic attack on episulfides has made available two steroidal trithiocarbonates (XI, XII) as well as one (XIII) derived from an optically active decalin. Furthermore, through the kind co-operation of Dr. L. N. Owen (Imperial College of Science and Technology) a number of carbohydrate trithiocarbonates[17] (XIV–XVII) were put at our disposal and it has thus been possible to conduct for the first time a parallel study of the optical rotatory dispersion, circular dichroism and ultraviolet (and visible) absorption behaviour of this interesting C=S containing chromophore.

All of the data were secured in dioxane solution and as will be noted from Figs. 11–17, all seven trithiocarbonates are characterized by an absorption maximum in the visible between 450–455 mμ (log ε ~ 1·9) and a second and more intense one (log ε ~ 4·2) between 314–318 mμ, which appears to have a closely associated neighboring maximum around 300 mμ, (e.g. Fig. 15). The rotatory dispersion and circular dichroism measurements of all of the trithiocarbonates—steroidal (Figs. 11, 12), bicyclic

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[21] M. J. Janssen, *Rec. Trav. Chim.* **79**, 464 (1960).

[22] K. Takeda and T. Komeno, to be published.

[23] D. A. Lightner and C. Djerassi, to be published.

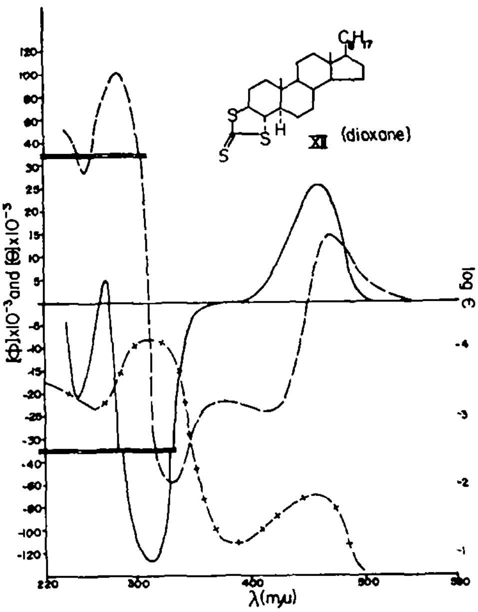

FIG. 12. Circular dichroism (———), optical rotatory dispersion (- - - -) and ultraviolet absorption (-+-+-) curves of cholestan-3β,4α-trithiocarbonate (XII) in dioxane solution.

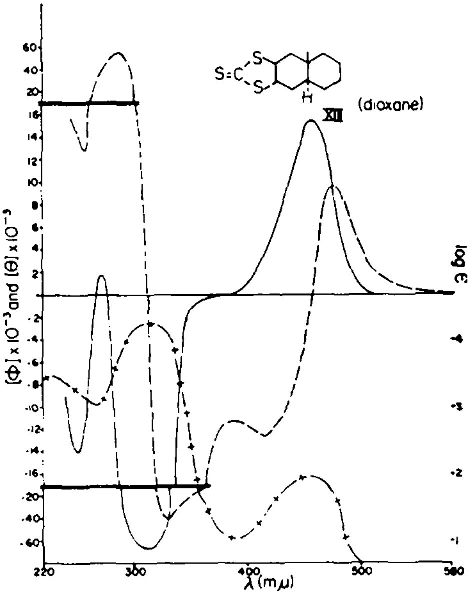

FIG. 13. Circular dichroism (———), optical rotatory dispersion (- - - -) and ultraviolet absorption (-+-+-) curves of (+)-*trans*-9-methyldecalin-2β,3α-trithiocarbonate (XIII) in dioxane solution.

(Fig. 13) or carbohydrate (Figs. 14–17)—are completely consistent in terms of wavelength as well as sign. They show that both the 450 mμ and 315 mμ transitions are optically active and are of reverse sign; thus in the two steroidal trithiocarbonates XI and XII (see Fig. 11 and 12), the long-wave length maximum gives rise to a positive Cotton effect and a positive C.D. maximum, while the U.V. maximum in the 315 mμ region corresponds to a negative Cotton effect and a negative C.D. maximum.

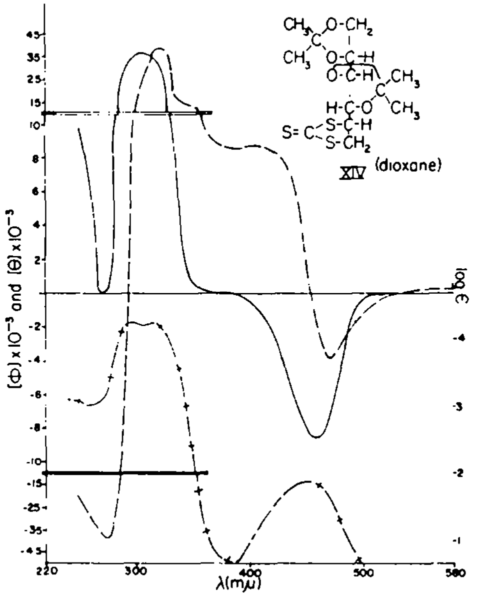

FIG. 14. Circular dichroism (- - - -), optical rotatory dispersion (- - - -) and ultraviolet absorption (-+-+) curves of 5,6-dideoxy-1,2;3,4-di-O-isopropylidene-L-gulitol-5,6-trithiocarbonate (XIV) in dioxane solution.

The reverse situation exists in the particular carbohydrates (Figs. 14–17) studied by us, the long-wave length Cotton effect being negative and the second one being positive.

The potential utility of such trithiocarbonates for stereochemical problems is illustrated well in Figs. 11 and 13. The stereochemical course[17] of the presently used trithiocarbonate synthesis[22,23] is such that either episulfide (I or II) will give the same *trans*-stereochemistry, i.e. from steroidal 2,3-episulfides the 2β,3α-trithiocarbonate (XI). Ring formation in such a stereochemistry is only possible with ring A in the boat form, since the chair conformer would contain two adjacent axial bonds, which are incapable of ring formation. A trithiocarbonate grouping can, therefore, be used as a "chromophoric" derivative for olefins and in such cyclic systems cannot give rise to stereochemical ambiguities. If for instance, the absolute configuration of (+)-*trans*-9-methyloctalin-2 (the starting material[15] of the trithiocarbonate XIII) had been unknown, then conversion to the trithiocarbonate XIII and optical rotatory dispersion or circular dichroism comparison (Figs. 11 *vs.* 13) with the steroidal 2,3-trithiocarbonate XI of established absolute configuration would have settled immediately the absolute configuration of the starting olefin in terms of the steroid configuration.

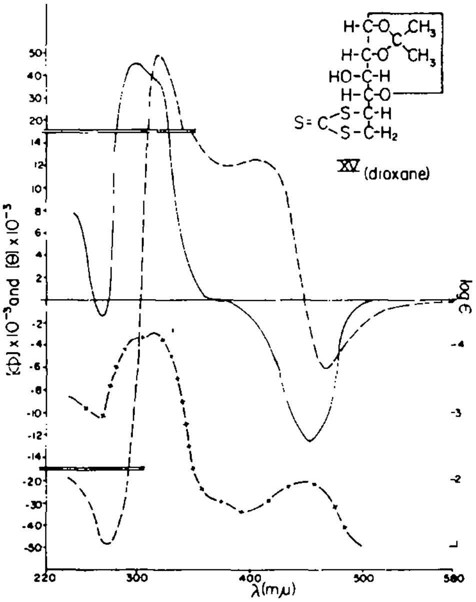

FIG. 15. Circular dichroism (———), optical rotatory dispersion (- - - -) and ultraviolet absorption (-+-+) curves of 5,6-dideoxy-1,2-O-isopropylidene-α,L-idose-5,6-trithiocarbonate (XV) in dioxane solution.

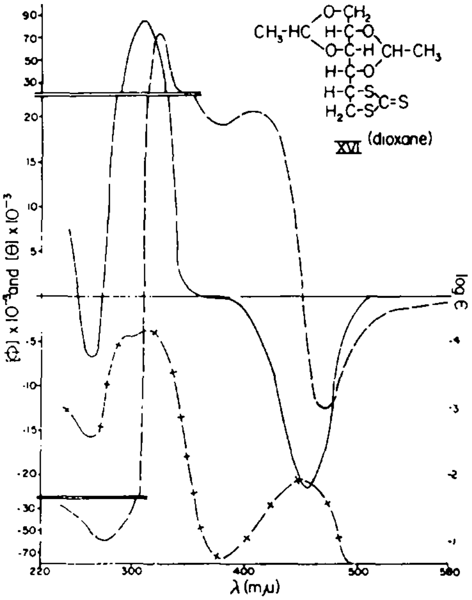

FIG. 16. Circular dichroism (———), optical rotatory dispersion (- - - -) and ultraviolet absorption (-+-+) curves of 5,6-dideoxy-1,3;2,4-di-O-ethylidene-D-glucitol-5,6-trithiocarbonate (XVI) in dioxane solution.

The only other "chromophoric" derivatives for olefins, which have been considered for such optical rotatory dispersion studies have been the osmate complexes.[24] Since these are prepared by osmium tetroxide hydroxylation, they possess a *cis*-fusion and theoretically, a given olefin can give rise to two epimeric *cis*-osmate esters. This stereochemical uncertainty does not exist with the *trans*-fused trithiocarbonates under discussion and consequently for absolute configurational assignment purposes, the latter is clearly the preferred chromophore. Further work on other "chromophoric" derivatives of olefins in is progress.

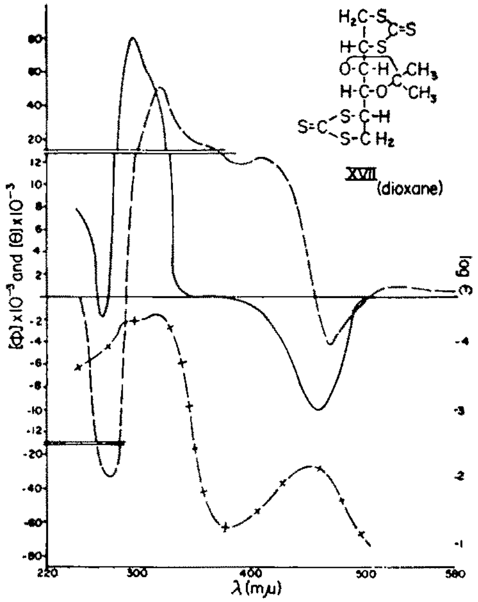

FIG. 17. Circular dichroism (———), optical rotatory dispersion (- - - -) and ultraviolet absorption (-+-+) curves of 1,2;5,6-tetradeoxy-3,4-O-isopropylidene-L-iditol-1,2;5,6-ditrithiocarbonate (XVII) in dioxane solution.

EXPERIMENTAL

Optical rotatory dispersion measurements were performed in part at Stanford with a Japan Spectroscopic Co. (Nippon Bunko) automatically recording spectropolarimeter and in part at Osaka with a Rudolph automatically recording spectropolarimeter. The circular dichroism measurements were obtained on a Baird-Atomic/Jouan Dichrograph and the ultraviolet spectral measurements with either an Applied Physics model 14 or a Hitachi recording spectrophotometer. The rotatory dispersion data are recorded in the generally accepted manner,[25] while the circular dichroism data are listed according to a convention, recorded elsewhere[26] in detail and utilized earlier[11,18,27] in slightly modified form.

Cholestan-2α-3α-episulfide (I, Fig. 1). C.D. in isoöctane: c 1·53 (410–240 mμ); $[\theta]_{305}$ 0, $[\theta]_{268}$ −3840, $[\theta]_{240}$ 0. O.R.D. in isoöctane: c 0·092 (410–250 mμ); $[\phi]_{340}$ +450°, $[\phi]_{280}$ −1100°, $[\phi]_{257}$ +5340°. U.V. in isoöctane: $\lambda^{\max}_{265}$ log ε 1·55.

Cholestan-2β,3β-episulfide (II, Fig. 2). C.D. in isoöctane: c 2·065 (410–240 mμ); $[\theta]_{288}$ 0,

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[24] E. Bunnenberg and C. Djerassi, *J. Amer. Chem. Soc.* **82**, 5953 (1960).

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

[26] C. Djerassi and E. Bunnenberg, *Proc. Chem. Soc.* In press.

[27] K. Mislow, E. Bunnenberg, R. Records, K. Wellman and C. Djerassi, *J. Amer. Chem. Soc.* **85**, 1342 (1963).

$[\theta]_{264}$ +600, $[\theta]_{243}$ 0. O.R.D. in isoöctane: *c* 0·1834 (410–240 mμ); $[\phi]_{278}$ +1270°, $[\phi]_{254}$ +700°, U.V. in isoöctane: $\lambda_{264}^{\mathrm{max}}$ log ε 1·58.

Cholestan-3α,4α-*episulfide* (III, Fig. 3). C.D. in dioxane: *c* 1·403 (400–240 mμ); $[\theta]_{305}$ 0, $[\theta]_{267}$ −4600, $[\theta]_{238}$ 0. O.R.D. in dioxane: *c* 0·133 (400–265 mμ), *c* 0·0266 (265–245 mμ), $[\phi]_{340}$ − 600°, $[\phi]_{279}$ −1360°, $[\phi]_{262}$ +7940°. U.V. in dioxane: $\lambda_{260}^{\mathrm{max}}$ log ε 2·05.

17β-*Acetoxyandrostan*-3β,4β-*episulfide* (IV, Fig. 4). C.D. in dioxane: *c* 1·990 (400–245 mμ); $[\theta]_{285}$ 0, $[\theta]_{266}$ +325, $[\theta]_{246}$ 0. O.R.D. in dioxane: *c* 0·0812 (400–265 mμ); *c* 0·0203 (280–258 mμ); $[\phi]_{278}$ +970°, $[\phi]_{262}$ − 560°. U.V. in dioxane: $\lambda_{263}^{\mathrm{max}}$ log ε 1·70.

3β-*Hydroxycholestan*-5α,6α-*episulfide* (V, Fig. 5). C.D. in dioxane: *c* 1·700 (410–245 mμ); $[\theta]_{315}$ 0, $[\theta]_{272}$ +6680, $[\theta]_{245}$ +150. O.R.D. in dioxane: *c* 0·212 (410–250 mμ); $[\phi]_{283}$ +2450°, $[\phi]_{261}$ −5330°. U.V. in dioxane: $\lambda_{264}^{\mathrm{max}}$ log ε 1·96.

3β-*Hydroxycholestan*-5β,6β-*episulfide* (VI, Fig. 6). C.D. in dioxane: *c* 1·725 (410–240 mμ); $[\theta]_{310}$ 0, $[\theta]_{268}$ −4460, $[\theta]_{240}$ −150. O.R.D. in dioxane: *c* 1·055 (410–240 mμ); $[\phi]_{280}$ −2190°, $[\phi]_{256}$ +2290°. U.V. in dioxane: $\lambda_{264}^{\mathrm{max}}$ log ε 1·77.

Cholestan-5β,6β-*episulfide*. C.D. in dioxane: *c* 0·900 (400–260 mμ) *c* 0·450 (260–245 mμ); $[\theta]_{305}$ 0, $[\theta]_{267}$ −4850, $[\theta]_{245}$ −300. O.R.D. in dioxane: *c* 0·0440 (400–265 mμ), *c* 0·0088 (265–245 mμ); $[\phi]_{274}$ −2620°, $[\phi]_{250}$ +2300°. U.V. in dioxane: $\lambda_{263}^{\mathrm{max}}$ log ε 2·11.

3β,20β-*Dihydroxy-5a-pregnan*-11α,12α-*episulfide* (VII, Fig. 7.) C.D. in dioxane: *c* 0·744 (400–238 mμ); $[\theta]_{315}$ 0, $[\theta]_{267}$ +4060, $[\theta]_{238}$ 0. O.R.D. in dioxane: *c* 0·210 (400–260 mμ), *c* 0·105 (260–250 mμ); $[\phi]_{276}$ + 1990°, $[\phi]_{255}$ −1660°. U.V. in dioxane: $\lambda_{263}^{\mathrm{max}}$ log ε 1·87.

3β,20β-*Dihydroxy-5α-pregnan*-11β,12β-*episulfide* (VIII, Fig. 8). C.D. in dioxane: *c* 0·658 (400–240 mμ); $[\theta]_{300}$ 0, $[\theta]_{261}$ +3460, $[\theta]_{240}$ +500. O.R.D. in dioxane: *c* 0·572 (400–240 mμ); $[\theta]_{269}$ +2610°, $[\phi]_{260}$ −1120°. U.V. in dioxane: $\lambda_{258}^{\mathrm{max}}$ log ε 1·70.

3β-*Acetoxy-5α-androstan*-16α,17α-*episulfide* (IX, Fig. 9). C.D. in dioxane: *c* 1·016 (410–240 mμ); $[\theta]_{290}$ 0, $[\theta]_{264}$ +700, $[\theta]_{240}$ 0. O.R.D. in dioxane: *c* 0·235 (410–247 mμ); $[\phi]_{302}$ −210°, $[\phi]_{277}$ −90°, $[\phi]_{252}$ −1280°. U.V. in dioxane: $\lambda_{268}^{\mathrm{max}}$ log ε 1·71.

3β-*Acetoxy-5α-androstan*-16β,17β-*episulfide* (X, Fig. 10). C.D. in dioxane: *c* 1·99 (410–260 mμ), *c* 0·448 (260–245 mμ); $[\theta]_{300}$ 0, $(\theta]_{268}$ + 5370, $[\theta]_{245}$ +250. O.R.D. in dioxane: *c* 0·512 (410–250 mμ); $[\phi]_{279}$ +3920°, $[\phi]_{259}$ −1330°. U.V. in dioxane: $\lambda_{264}^{\mathrm{max}}$ log ε 1·74.

Cholestan-2β,3α-*trithiocarbonate* (XI, Fig. 11). C.D. 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. O.R.D. 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°. U.V. in dioxane: $\lambda_{455}^{\mathrm{max}}$ log ε 1·94, $\lambda_{318}^{\mathrm{max}}$ log ε 4·27, $\lambda_{310-280}^{\mathrm{shoulder}}$ log ε 4·22–3·34.

Cholestan-3β,4α-*trithiocarbonate* (XII, Fig. 12). C.D. in dioxane: *c* 0·537 (520–360 mμ), *c* 0·0178 (360–240 mμ); $[\theta]_{510}$ 0, $[\theta]_{460}$ +25500, $[\theta]_{380}$ 0, $[\theta]_{313}$ −126000, $[\theta]_{277}$ 0, $[\theta]_{274}$ +4800, $[\theta]_{269}$ 0, $[\theta]_{250}$ +20500, $[\theta]_{240}$ −5000. O.R.D. in dioxane: *c* 0.0537 (580–390 mμ), *c* 0·0161 (390–340 mμ), *c* 0·00322 (340–240 mμ); $[\phi]_{469}$ +14350°, $[\phi]_{415}$ −24000°, $[\phi]_{380}$ −21500°, $[\phi]_{330}$ −57500°, $[\phi]_{285}$ +101600°, $[\phi]_{255}$ +28700°. U.V. in dioxane: $\lambda_{454}^{\mathrm{max}}$ log ε 1·86, $\lambda_{317}^{\mathrm{max}}$ log ε 4·14, $\lambda_{310-300}^{\mathrm{shoulder}}$ log ε 4·10–4·03.

(+)-*trans-9-Methyldecalin*-2β,3α-*trithiocarbonate* (XIII, Fig. 13). C.D. 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, $[\theta]_{273}$ +1860, $[\theta]_{268}$ 0, $[\theta]_{250}$ −14150, $[\theta]_{240}$ −9000. O.R.D. 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°, $[\theta]_{286}$ +54000°, $[\phi]_{256}$ +12850°. U.V. in dioxane: $\lambda_{454}^{\mathrm{max}}$ log ε 1·94, $\lambda_{317}^{\mathrm{max}}$ log ε 4·24, $\lambda_{310-300}^{\mathrm{shoulder}}$ log ε 4·20–4·11, $\lambda_{227}^{\mathrm{max}}$ log ε 3·46.

5,6-*Dideoxy*-1,2;3,4-*di-0-isopropylidene*-L-*gulitol* 5,6-*trithiocarbonate* (XIV, Fig. 14). C.D. in dioxane: *c* 0·664 (510–350 mμ), *c* 0·0133 (350–240 mμ); $[\theta]_{510}$ 0, $[\theta]_{458}$ −8550, $[\theta]_{370}$ 0, $[\theta]_{305}$ +36000, $[\theta]_{270}$ 0, $[\theta]_{250}$ +9800. O.R.D. in dioxane: *c* 0·0973 (580–490 mμ), *c* 0·0195 (490–350 mμ), *c* 0·00039 (350–250 mμ); $[\phi]_{470}$ −3800°, $[\phi]_{407}$ +8800°, $[\phi]_{365}$ +8500°, $[\phi]_{320}$ +39000°, $[\phi]_{278}$ −39000°. U.V. in dioxane: $\lambda_{450}^{\mathrm{max}}$ log ε 1·87, $\lambda_{314}^{\mathrm{max}}$ log ε 4·20, $\lambda_{295}^{\mathrm{max}}$ log ε 4·22.

5,6-*Dideoxy*-1,2-0-*isopropylidene*-α,L-*idose* 5,6-*trithiocarbonate* (XV, Fig. 15). C.D. in dioxane: *c* 0·676 (510–350 mμ), *c* 0·0135 (350–260 mμ), *c* 0·0270 (260–245 mμ); $[\theta]_{510}$ 0, $[\theta]_{452}$ −12550, $[\theta]_{370}$ 0, $[\theta]_{300}$ +44800, $[\theta]_{275}$ 0, $[\theta]_{270}$ −1400, $[\theta]_{263}$ 0, $[\theta]_{245}$ +7800. O.R.D. in dioxane: *c* 0·019 (580–360 mμ), *c* 0·00076 (360–240 mμ); $[\phi]_{468}$ −6120°, $[\phi]_{405}$ +12550°, $[\phi]_{375}$ +11950°, $[\phi]_{320}$ +48500°, $[\phi]_{275}$ −48500°. U.V. in dioxane: $\lambda_{450}^{\mathrm{max}}$ log ε 1·96, $\lambda_{314}^{\mathrm{max}}$ log ε 4·18, $\lambda_{310-290}^{\mathrm{shoulder}}$ log ε 4·16–3·97.

5,6-*Dideoxy*-1,3;2,4-*di-0-ethylidene*-D-*glucitol* 5,6-*trithiocarbonate* (XVI, Fig. 16). C.D. in dioxane: *c* 0·330 (510–360 mμ), *c* 0·0132 (360–280 mμ), *c* 0·0264 (280–245 mμ); $[\theta]_{510}$ 0, $[\theta]_{456}$ −21300, $[\theta]_{364}$ 0,

$[\theta]_{310} + 83400$, $[\theta]_{274}\ 0$, $[\theta]_{265} - 6900$, $[\theta]_{252}\ 0$, $[\theta]_{245} + 7500$. O.R.D. in dioxane: c 0·0213 (580–440 mμ), c 0·00426 (440–340 mμ), c 0·000426 (340–240 mμ); $[\phi]_{470} - 12600°$, $[\phi]_{410} + 20500°$, $[\phi]_{375} + 19000°$, $[\phi]_{324} + 72500°$, $[\phi]_{276} - 59800°$. U.V. in dioxane: $\lambda^{\max}_{453}$ log ε 1·90, $\lambda^{\max}_{314}$ log ε 4·16, $\lambda^{\text{shoulder}}_{305-290}$ log ε 4·10–3·99.

1,2,5,6-*Tetradeoxy*-3,4-0-*isopropylidene*-L-*iditol*-1,2;5,6-*ditrithiocarbonate* (XVII, Fig. 17). C.D. in dioxane: c 0·648 (510–350 mμ), c 0·00648 (350–280 mμ), c 0·02592 (280–245 mμ); $[\theta]_{510}\ 0$, $[\theta]_{460} - 9920$, $[\theta]_{360}\ 0$, $[\theta]_{296} + 80300$, $[\theta]_{275}\ 0$, $[\theta]_{270} - 1825$, $[\theta]_{265}\ 0$, $[\theta]_{245} + 7800$. O.R.D. in dioxane: c 0·055 (580–350 mμ), c 0·0013 (359–245 mμ); $[\phi]_{580} + 1000°$, $[\phi]_{470} - 4220°$, $[\phi]_{410} + 12300°$, $[\phi]_{390} + 11800°$, $[\phi]_{320} + 49800°$, $[\phi]_{276} - 32700°$. U.V. in dioxane: $\lambda^{\max}_{452}$ log ε 2·14, λ $\log^{\max}_{316}$ ε 4·40, $\lambda^{\text{shoulder}}_{305-285}$ log ε 4·35–4·17.

Acknowledgment—The work at Stanford University was supported by the National Science Foundation (grant No. G-19905) and the National Institutes of Health (grant No. CRTY-5061). One of us (D. A. L.) has been the recipient of National Institutes of Health (1961–1962) and National Science Foundation (1962–1963) predoctoral fellowships. We acknowledge with pleasure stimulating correspondence with Prof. A. Moscowitz of the University of Minnesota.