Tetrahedron, 1965, Vol. 21, pp. 3105 to 3120. Pergamon Press Ltd. Printed in Northern Ireland

OPTICAL ACTIVITY OF NON-PLANAR CONJUGATED DIENES—I

HOMOANNULAR CISOID DIENES

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Abstract—A review is given of the results obtained so far in the investigation of the optical rotatory dispersion or circular dichroism of a number of non-planar homoannular *cisoid* dienes. The findings agree in every instance with the predictions of a theoretical rule connecting the sign of the Cotton effect with the chirality of the diene; two seeming exceptions can be explained through detailed conformational analysis. The rule can therefore serve as a reliable basis for stereochemical studies on this class of dienes.

As expected theoretically, the amplitudes of the Cotton effects produced by these inherently dissymmetric chromophores are very high, values up to 100,000 deg mol^{-1} dm^{-1} having been found. However, steroidal 1,3-dienes form a separate group characterized by comparatively low amplitudes, in many instances associated with a distinctive shape of the curve.

SOME years ago, together with Moscowitz, we have briefly communicated[1] a theoretical and experimental analysis of the relationship between the skewness ("helicity, chirality") of non-planar cisoid conjugated dienes and the sign of the Cotton effect produced by their transition of longest wavelength. This "*cisoid* diene" rule stated that a *cisoid* diene skewed in the sense of a right-handed helix (Fig. 1B) produces an ORD curve showing a positive Cotton effect, and a positive circular dichroism band. It was also predicted that the effect of this inherently dissymmetric[2] chromophore would be stronger by about one order of magnitude than the one produced by an asymmetrically perturbed symmetrical chromophore. Both the rule referring to the sign of the effect, and the prediction of its intensity, were confirmed in the case of compound (II),[3] where close agreement was found[1a] between the theoretically calculated and the experimentally observed curve of the optical rotatory dispersion (ORD) down to about 235 mμ (Ref. 1[a], Fig. 1). In addition, it was shown that the rule relating sense of skewness with sign of Cotton effect is obeyed by a number of compounds of unequivocally known stereochemistry, and that the Cotton effects show the expected high intensity. The rule should prove of value in establishing the absolute configuration of compounds containing diene groups of appropriate skewness, or the conformation of this grouping in cases where the configuration is known, since the chirality of the diene depends upon both configuration and conformation.

[1a] A. Moscowitz, E. Charney, U. Weiss and H. Ziffer, *J. Amer. Chem. Soc.* **83**, 4661 (1961). [b] Cf. also R. Deen and H. Y. C. Jacobs, *Koninkl. Nederl. Akademie van Wetenschappen, Amsterdam* **64**, 313 (1961).

[2] A. Moscowitz, *Tetrahedron* **13**, 48 (1961).

[3] H. Ziffer and U. Weiss, *J. Org. Chem.* **27**, 2694 (1962).

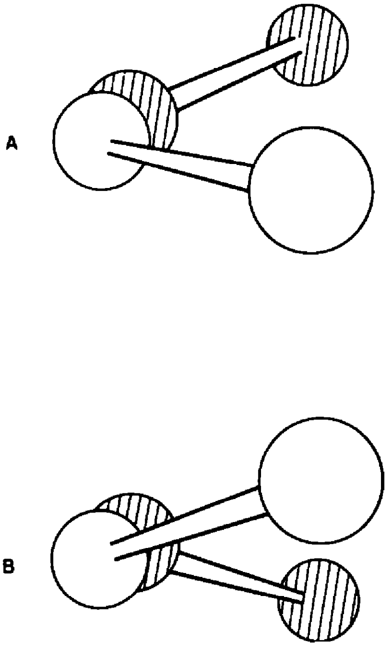


FIG. 1

Since the appearance of the preliminary communication,[1a] a fairly large number of compounds have been investigated. The findings have been used in two cases for a study of conformational problems,[4] and have been utilized in an investigation of the absolute configuration of the sesquiterpene alcohol occidentalol[5] (IV).

In the present paper, the data for all homoannular cisoid dienes investigated thus far are given, together with a discussion of those aspects of the results which bear on their applicability to stereochemical problems. In the accompanying papers the extension of the rule to transoid dienes is described,[6a] and the dependence of intensity and position of the Cotton effects produced by the two transitions of longest wavelengths upon the angle of skewness is treated theoretically.[6b] The present discussion is restricted to 1,3-cyclohexadienes. No cyclopentadienes or 1,3-cycloheptadienes have been studied so far.[7]

[4a] A. W. Burgstahler, H. Ziffer and U. Weiss, *J. Amer. Chem. Soc.* **83**, 4660 (1961); [b] U. Weiss, H. Ziffer and E. Charney, *Chem. & Ind.* 1286 (1962); [c] H. Ziffer, E. Charney and U. Weiss, *J. Amer. Chem. Soc.* **84**, 2961 (1962).

[5] H. Ziffer, T. J. Batterham, U. Weiss and E. von Rudloff, *Tetrahedron* **20**, 67 (1964); K. Mislow and A. Moscowitz, *Tetrahedron Letters* 699 (1963).

[6a] E. Charney, H. Ziffer and U. Weiss, *Tetrahedron* **21**, 3121 (1965). [b] E. Charney, *Tetrahedron* **21**, 3127 (1965).

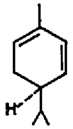
[7] It is worth noting that the 1,3-cyclohexadienes constitute a rather special class of dienes from a spectroscopic point of view, since the pertinent absorption bands occur at longer wavelengths than the comparable bands of dienic chromophores located in either smaller or larger rings (cf. butadiene 217·0, cyclopentadiene 238·5, cyclohexadiene 256·5, cycloheptadiene 248, cyclooctadiene 228 mμ). Although the theoretical explanation of these wavelength shifts is not yet completely satisfactory, there is nothing to indicate that for the treatment of the Cotton effects, the 1,3-cyclohexadienes differ fundamentally from their relatives except to the extent that the magnitude of the skew angle and the conformational stability is influenced by the geometry of the molecule.

Interpretation of the results of the investigation of a small number of *hetero*annular *cisoid* dienes (e.g., ergosterol B_3, a 7,14-diene) is not yet clear, and therefore the application of the rule to these compounds should be held in abeyance. The spectral behaviour of some heteroannular dienes is likewise not fully understood.[8]

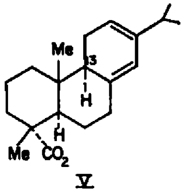
It seems appropriate to discuss separately the two corollaries of the theoretical analysis given in Refs 1 and 6: the determining influence of chirality upon sign of the effects, and the high intensities of these effects.

The sign of the Cotton effect at longest wavelengths. A total of 28 conjugated cyclohexadienes have been studied thus far. Data on their ORD and, where investigated, their CD are collected in Table 1 which also includes data on a few compounds of this type examined elsewhere. Compounds (III) and (XXIX) have been studied by W. B. Whalley, to whom we are indebted for permission to quote his findings. Some data on steroid 1,3- and 2,4-dienes are taken from the work of Berkoz *et al.*[9]

The data in Table 1 show that the "*cisoid* diene rule" correctly predicts the sign of Cotton effect and CD band in every compound investigated thus far; no instance of a clear-cut contradiction has been found, and no further case, beyond those already described [(−)-α-phellandrene[4a,c] (I) and levopimaric acid[4a,b] (V)] has been encountered where it would have been necessary to assume the presence of somewhat unusual-looking conformations (Ib, Va) in order to reconcile the sign of the ORD with the rule.[10]



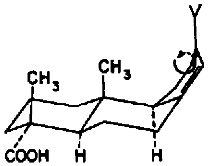
I



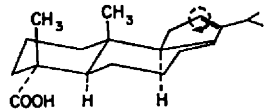
V

I a

I b



V a



V b

In the case of levopimaric acid (V), the α-configuration of the hydrogen at C-13 (steroid numbering: C-9), very probable at the time (1961) of our investigation,[1a] has been rigorously established[11] recently by application of the Octant Rule to a ketonic transformation product; additional evidence for this stereochemistry has been

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[8] H. H. Jaffé and M. Orchin, *Theory and Applications of Ultraviolet Spectroscopy* pp. 200–201. J. Wiley, New York and London, (1962).

[9] B. Berkoz, A. D. Cross, M. E. Adams, H. Carpio and A. Bowers, *J. Org. Chem.* **28**, 1976 (1963), and private communication from Dr. A. D. Cross.

[10] It should be pointed out in this connection that the axial conformer (Ib) which must be present to an appreciable extent in the conformational equilibrium[4c] Ia $\rightleftharpoons$ Ib is not objectionable, since in a 1,3-cyclohexadiene, none of the 1,3-non-bonded interactions can be present which destabilize conformers with bulky axial substituents in *saturated* six-membered rings.

[11] W. G. Dauben and R. M. Coates, *J. Org. Chem.* **28**, 1698 (1963).

obtained[12] through proof, by NMR spectroscopy, that the corresponding hydrogen in the adduct of (V) with maleic anhydride is similarly α-oriented. These results make it logically necessary to accept the "folded" conformation (Va) for (V), unless this compound should have to be considered the only exception to the "*cisoid* diene" rule among all the compounds listed in Table 1. Further support for (Va) has been obtained from an investigation of surface films.[13] The fact that the rotation of (V) remains almost constant between +6 and +82° indicates[4b] that the compound is present mostly in conformation (Va) in this temperature range.

One group of compounds requiring discussion is represented by the two types of morphine derivatives (XXI and XXII–XXIV). As Table 1 shows, the sign of their Cotton effects agrees in every instance with that predicted by the "*cisoid* diene" rule. This is remarkable because in both classes the dienic system is located in β,γ-position to the phenolic chromophore. Since it has been shown[14] that in compounds such as β,γ-dienes or β,γ-unsaturated ketones with a geometry appropriate for homoconjugated interaction, the entire system represents a new, dissymmetric chromophore, it was not *a priori* certain that the diene rule would be adequate for predicting the sign of the Cotton effect of these morphine derivatives. This seems to be the case, however, either because the homoconjugated interaction is not strong enough to reverse the sign of the effects, or because the chirality of the compound happens to be the same in both cases as that of the diene considered as an isolated chromophore. We favour the first explanation; the reason may be a geometry unfavourable to overlap. In general, interaction of the diene chromophore with other chromophoric groupings located in a spatial relation which permits orbital overlap may be capable of interfering with the operation of the diene rules, and should be taken into account. Except for the morphine derivatives (XXI) and (XXII–XXIV), all compounds discussed in this and the accompanying[6] papers have been chosen from classes which are devoid of such interfering chromophores. The agreement between predicted and observed sign of the rotation of compounds XXI and XXII, XXIII and XXIV of Table 1 indicates that enolic oxygen and sulphur functions attached to the dienic system do not affect the sign of the Cotton effect in this region.

Intensities and shape of the Cotton effect curves. Beyond demonstrating the correctness of that part of the rule which predicts the sign of Cotton effects and CD bands from the chirality of the diene, Table 1 also shows that the second postulate: high intensity of these effects, is generally obeyed. Except for a special class of compounds to be discussed below, the $[\Phi]$ values of the first extremum, taken at comparable molar concentrations, range from $\sim \pm 9{,}000°$ to $\sim \pm 50{,}000°$. The wide span of these values must be primarily connected with differences in the angle of skewness of the diene, although other conformational effects will play a role, e.g. the angle between the central single bond and the adjacent double bonds. A theoretical treatment of the relationship between the skew angle and the intensity of the Cotton effect is given in an accompanying paper;[6b] actual application of the results of this treatment to the individual cases of Table 1 is handicapped by the shortage of reliable

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[12] W. L. Meyer and R. W. Huffman, *Tetrahedron Letters* 691 (1962); L. H. Zalkow, R. A. Ford and J. P. Kutney, *J. Org. Chem.* **27**, 3535 (1963); W. A. Ayer, C. E. M. McDonald and J. B. Stothers, *Canad. J. Chem.* **41**, 1113 (1963).

[13] U. Weiss and N. Gershfeld, *Experientia* **18**, 355 (1962).

[14] K. Mislow, *Ann. New York Acad. Sci.* **93**, 457 (1962), and papers quoted there.

TABLE 1

A. "Simple" Curves

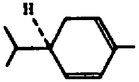
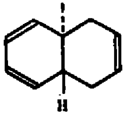
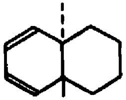
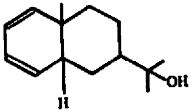
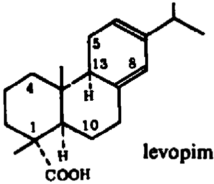
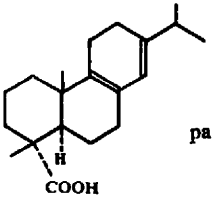
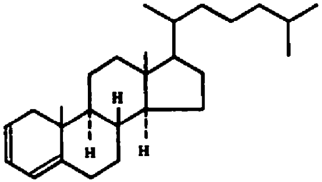
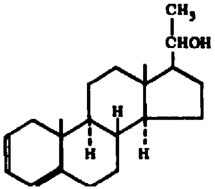
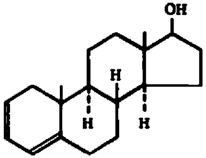
No.	Compound	Predicted sign of ORD and CD	Rotation observed					Circular dichroism observed				Ref., source
			$[\Phi]_{extr.}$	$\lambda_{extr.}$	$[\Phi]_D$	Solvent	Concentration *g/100 ml.*	$[\Theta]$	λ	Solvent	Concentration	
1. *Mono- and Bicyclic*												
I	 (−)-α-phellandrene	See Ref. 4a	−4000[c]	295	−241	cyclohexane						4a, 4c
II		+	+17500 −18700	278 237	+270	cyclohexane	0·014					1, 3
III		+	+ 9500 −17600	278 232	−78	hexane	3·02					Data from W. B. Whalley
IV	 Occidentalol	+	+43000 −85000	284 240	+799[c]	MeOH	0·026	+66260	263	EtOH	0·0026	E. von Rudloff cf. ref. 5
2. *Diterpenoids*												
V	 levopimaric acid	See Ref. 4a	−16300 +29000	296 250	−846	EtOH	0·010	−27720	270	$CHCl_3$	0·00335	4a, 4b R. V. Lawrence

TABLE 1 (*contd*)

No.	Compound	Predicted sign of ORD and CD	Rotation observed					Circular dichroism observed				Ref., source
			$[\Phi]_{extr.}$	$\lambda_{extr.}$	$[\Phi]_D$	Solvent	Concentration *g/100 ml.*	$[\Theta]$	λ	Solvent	Concentration	
VI	 palustric acid	+	+5300	288	+216	EtOH	0·0194					R. V. Lawrence
3. *Steroids and Triterpenoids*												
VII		+	+38400	290	+624	EtOH	0·0062	+15444 +28413 +34320	286 275 264	cyclohexane	0·018	A. W. Burgstahler
VIII		+	+12600	292	+849	MeOH	0·045					Data from A. D. Cross, and ref. 8
IX		+	+8700	300	+251	MeOH	0·038					Data from A. D. Cross, and ref. 8

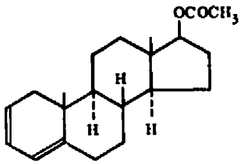
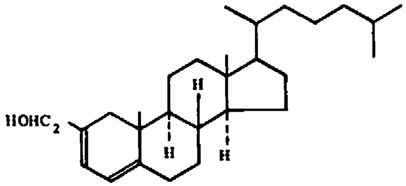
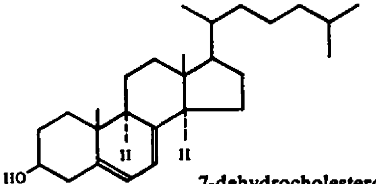
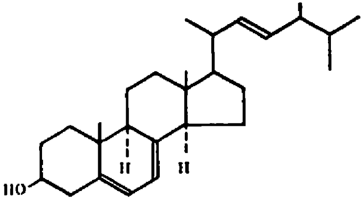
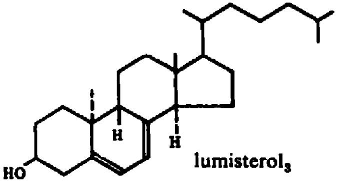
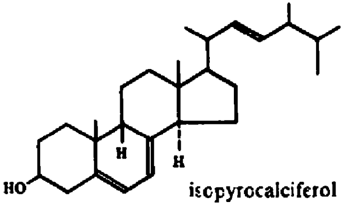
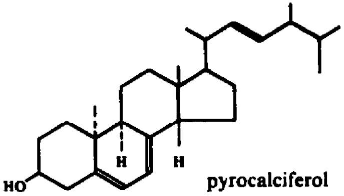
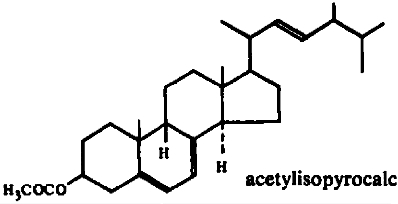
X		+	+10700	295	+423	MeOH	0·052					Data from A. D. Cross, and ref. 8
XI		+	+20700	290	+539	EtOH	0·0133	+10300 +20000	290 266–270	CHCl$_3$	0·0115	A. W. Burgstahler
XII	 7-dehydrocholesterol	−	−18000	302	−439	EtOH	0·046					
XIII	 ergosterol	−	−37000	297	−536	EtOH	0·0246					

TABLE 1 (*contd*)

No.	Compound	Predicted sign of ORD and CD	Rotation observed					Circular dichroism observed				Ref., source
			$[\Phi]_{extr.}$	$\lambda_{extr.}$	$[\Phi]_D$	Solvent	Concentration *g/100ml.*	$[\Theta]$	λ	Solvent	Concentration	
XIV	 lumisterol$_3$	+	+27000 −45700	294 244	+733	iso-octane	0·0033					
XV	 isopyrocalciferol	+	+43000	298	+1320	EtOH	0·0127					
XVI	 pyrocalciferol	+	+50000	302	+2030	EtOH	0·02					
XVII	 acetylisopyrocalciferol	+	+45000	295	+1470	EtOH	0·012	~+700 +1490 +39600 +75900 +89100 ±0	340 320 300 283 272 ~237	cyclohexane	0·009 0·0020		

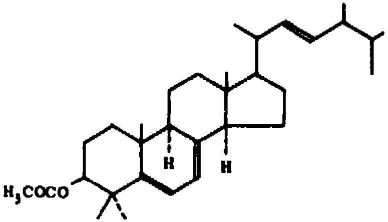
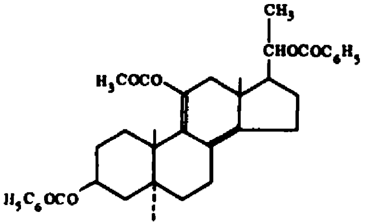
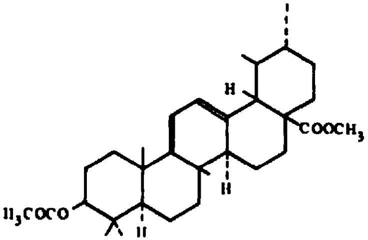
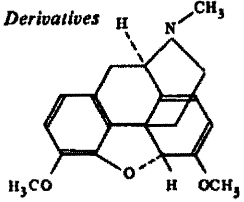
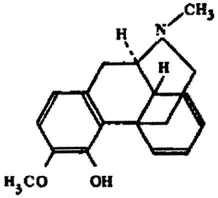
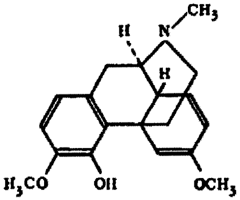
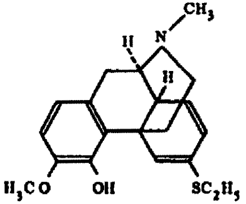
XVIII		−						−58740	272–276	dioxane	0·0024	Data from G. Ourisson and P. Witz
XIX		+	+11000 −17500	295 250		cyclo-hexane	0·0134					E. R. H. Jones
XX	 methyl dehydroursolate acetate	+						+59700	272–280	cyclo-hexane	0·015	T. J. Batterham

TABLE 1 (*contd*)

No.	Compound		Predicted sign of ORD and CD	Rotation observed					Circular dichroism observed				Ref., source
				$[\Phi]_{extr.}$	$\lambda_{extr.}$	$[\Phi]_D$	Solvent	Concentration *g/100ml.*	$[\Theta]$	λ	Solvent	Concentration	
4. *Morphine Derivatives*													
XXI		thebaine	—	−35000 +30800	297 276	−2370	dioxane	0·0077	−44880	288	$CHCl_3$		
XXII		desoxycodeine A	+						+35640 +46200	261 257	ethanol dioxane	0·0063	Sample from collection of the late L.F. Small, repurified
XXIII		thebainone A enol methyl ether	+	+15200 −42000	293 252	+30	dioxane	0·022					L. F. Small and Browning, J. Org. Chem. 3, 618 (1939)
XXIV		β-ethyl thiocodide	+						+22915	295	ethanol	0·0112	Sample from collection of the late L. F. Small, repurified

B. "Complex" Curves

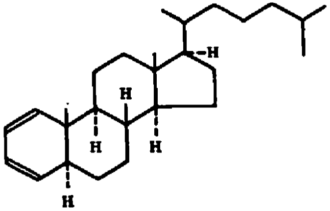
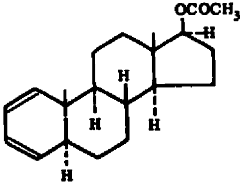
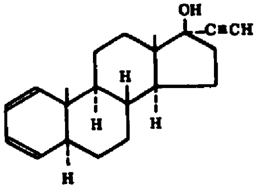
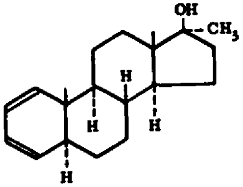
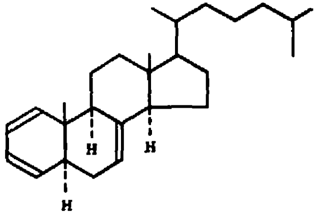
XXV		—	−5000 +4200	285 235	+343	cyclo-hexane	0·071			ethanol		A. W. Burgstahler and L. K. Gibbon, unpublished; cf. Ch. Tamm and R. Albrecht, Helv. 42, 2177 (1959)
XXVI		—	−480	295		dioxane	0·034	−11385	275	EtOH	0·00547	Data from Ref. 8
XXVII		—	−937	298	+28	dioxane						Data from Ref. 8
XXVIII		—	−191	300	+137	MeOH						Date from Ref. 8

Table 1 (*contd.*)

No.	Compound	Predicted sign of ORD and CD	Rotation observed					Circular dichroism observed				Ref., source
			$[\Phi]_{\text{extr.}}$	$\lambda_{\text{extr.}}$	$[\Phi]_D$	Solvent	Concentration *g/100ml.*	$[\Theta]$	λ	Solvent	Concentration	
XXIX		—	−6700 +6800	278 239								Data from W. B. Whalley

experimental data on the skew angle. In the one case, that of lumisterol (XIV), where such data are available from x-ray crystallographic analysis,[15] good agreement has been obtained[6b] between calculated and observed ORD. However, some of the highest values of $[\Phi]_{max}$ encountered (e.g., those for pyro- and isopyrocalciferol, XVI and XV) are surprising, since Dreiding models of these compounds show almost planar dienes, while maximum rotations should be expected for very strongly (~60°) skewed systems. It is apparent that the molecular models available are not always sufficiently representative to permit precise quantitative comparisons to be made between predicted and observed optical activities. They fail, for example, to give reliable information on non-bonded interactions, and they ascribe a constant length to all bonds of the same nominal type, while this length may in reality vary quite significantly, e.g., the lengths observed by X-ray crystallography[15] for the two conjugated double bonds ($\Delta^{5,6}$ and $\Delta^{7,8}$) in lumisterol (XIV) are $1{\cdot}36_3$ and $1{\cdot}25_2$ Å, respectively.[16]

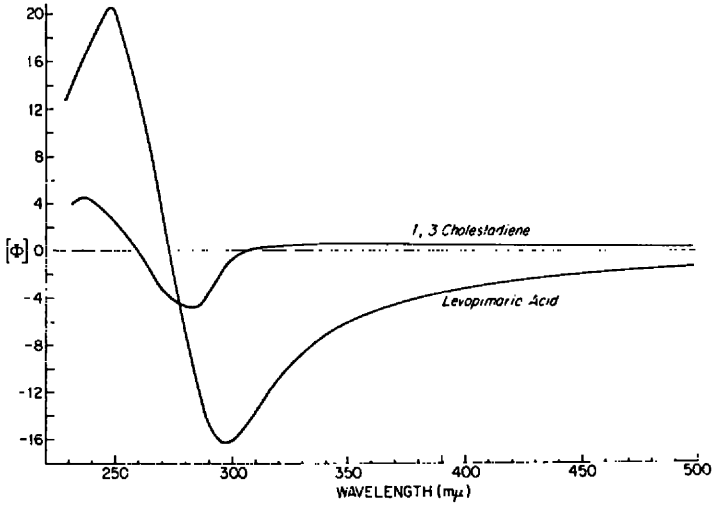


Fig. 2

An examination of our data shows that the ORD curves of the dienes investigated can be divided into two classes with regard to their shapes and peak intensities. For convenience, we propose to call these two types "Simple" and "Complex" curves.

"*Simple curves*". The ORD curves of this type show the characteristics expected from a strong Cotton effect essentially isolated from other optically active transitions: nearly symmetrical shape, large amplitude, and relatively high $[\alpha]_D$ agreeing in sign with the Cotton effect. A typical curve of this kind is shown in Fig. 2.

Intensities at the first extremum range from about ±9,000° to about ±50,000°,

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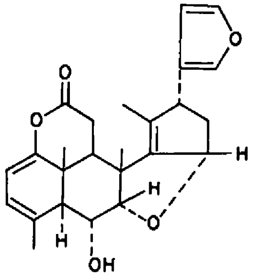
[15] D. Crowfoot Hodgkin and D. Sayre, *J. Chem. Soc.* 4561 (1952).

[16] These limitations seem to operate in a minority of instances only, and do not necessarily preclude the fruitful use of models in other cases. An example of this is the satisfactory agreement between calculated and observed ORD curves of compound II,[16,b] the calculations being based on the skew angle obtained from Dreiding models.

with only two exceptions. The first of these, (—)-α-phellandrene (I), [Φ] = —4,000°, has already been shown[4c] to be explained by the conformational mobility of this monocyclic cyclohexadiene, which exists as an equilibrium of a dextro- and a levorotatory conformer. The second exception, palustric acid (VI), with [Φ] = +5,300°, seems to present an analogous case; in this compound alone among the polycyclic ones investigated, the two saturated carbon atoms of the cyclohexadiene ring have considerable flexibility, permitting this ring to exist in two conformations of opposite chirality.

"*Complex curves*". The "complex" curves are characterized by relatively weak Cotton effects superimposed upon a substantial background of opposite sign. As a consequence, the $[\alpha]_D$ values are low and may have a sign opposite to that of the Cotton effect. Curves of this type have thus far been observed only with steroidal 1,3-dienes (with the possible exception of the diene pyronimbic acid,[17] for which incomplete measurements available to date seem to exclude a "simple" curve). A typical example of a "complex" curve is shown in Fig. 2, where comparison is made with the "simple" curve of levopimaric acid (cf. also Fig. 2 of Ref. 9).



Pyronimbic acid

It is not clear at present why all the steroidal 1,3-dienes investigated give "complex" ORD curves, while such closely related bicyclic dienes as II, III and IV show perfectly normal behaviour;[18] some subtle conformational influence may be suspected. The preceding statement requires some qualifications in the case of the steroidal 1,3-diene (XXIX), recently prepared and investigated by Whalley, which shows a very symmetrical Cotton effect. However, comparison of the ORD curves of the steroidal

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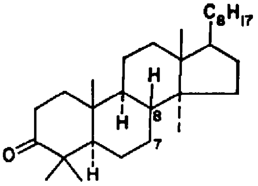
[17] C. R. Narayanan, R. V. Pachapurkar, S. K. Pradhan, V. R. Shah and N. S. Narasimhan, *Chem & Ind.* 322 (1964).

[18] It may be significant that some apparently related instances have been observed elsewhere; a striking case is presented in Fig. 6–3 (p. 93) of Ref. 19, where lanostan-3-one and Δ^7-lanosten-3-one give curves (labelled VI and VII, resp., in the Fig.) with shapes closely resembling those of "complex" and "simple" ORD curves of conjugated dienes.



Lanostan -3-one

[19] C. Djerassi, *Optical Rotatory Dispersion.* McGraw-Hill, New York-Toronto-London (1960).

dienes XXIX and XXV, with those of their bicyclic counterparts, II and III is instructive. In the case of the bicyclic compounds (II and III), the effect of the additional double bond in position 7 is relatively small, expressing itself mostly in an increase of the intensity of the first extremum. In contrast, compound XXV shows a typical "complex" curve while that of XXIX is quite symmetrical. However, the relatively low amplitude of the Cotton effect of XXIX (13,500°; cf. 36,200° for (II), 27,000° for III) suggests that the curve of XXIX belongs to the "complex" type, as was to be expected from the structure of the compound. The symmetrical shape of the curve may be due to background effects.

Although it is not yet possible to give a detailed explanation for the occurrence of "complex" ORD curves in terms of molecular structure or stereochemistry, it is possible to correlate them with spectroscopic findings.

TABLE 2

Compound	λ[a]		A[b]		$A(^1A_1 \leftarrow {}^1A_1)/A(^1B_2 \leftarrow {}^1A_1)$
	$^1A_1 \leftarrow {}^1A_1$	$^1B_2 \leftarrow {}^1A_1$	$^1A_1 \leftarrow {}^1A_1$	$^1B_2 \leftarrow {}^1A_1$	
Ergosterol	2705	2095	98	621	6·3
Lumisterol	2710	2090	184	1422	7·7
2,4-Cholestadiene	2650	2045	181	660	3·6
1,3-Cholestadiene	2630	2020	621	1134	1·8

[a] λ is the wavelength in Ångstroms at the maximum (or in the case of ergosterol the position of the shorter wavelength peak of the two of maximum intensity) of the absorption band. For the shorter wavelength transition ($^1B_2 \leftarrow {}^1A_1$), the entire absorption band was estimated making corrections for the absorption from still shorter wavelength transitions. In each case, this moved the wavelength of maximum absorption 50 to 150 Ångstroms to longer wavelengths than that of the apparent position of the peak which appears on the side of the rapidly rising higher frequency absorption. For a description of the symmetry notation, see the accompanying paper, *6b*, or Ref. 8.

[b] A is the integrated absorption in arbitrary units and is not corrected for concentration, so that only the numbers within each compound are related.

A limited study of the UV spectra listed in Table 2 of compounds showing "simple" and "complex" ORD curves, respectively, indicates that there is a considerable variation in the relative intensity of the first and second transitions. In compounds giving simple curves, the first transition is approximately four to eight times stronger than the second one, whereas in compounds producing "complex" curves, the first transition is only one to two times as strong. As theory predicts that the first and second transitions are associated with Cotton effects of opposite sign, one could easily visualize a continuous transformation from "simple" to "complex" curves, as the strength of the second transition increases and that of the first decreases. There is one piece of confirmatory evidence for this interpretation: the molar ellipticity of the only steroid 1,3-diene studied thus far, item 27 of Table 1, is about half of that of any of the other dienes investigated. The optical activity associated with this transition, therefore, appears to be smaller than that of the other types of dienes. Further measurements of the dispersion curves or circular dichroism of more steroid 1,3-dienes and of the second diene transition should greatly aid in confirming or refuting the above interpretation.

The complete agreement between predicted and observed sign of the Cotton effect found in every homoannular *cisoid* diene investigated thus far shows that the "*cisoid* diene" rule can be used with confidence in studies on the stereochemistry of compounds of this type. Significant quantitative differences have been found between the ORD curves of individual classes of homoannular cisoid dienes. Additional quantitative studies, together with further theoretical treatment, can be expected to provide detailed explanations for some cases of surprisingly high rotations, and for the causes of the occurrence of "complex" curves in steroidal 1,3-dienes. ORD measurements at still shorter wavelengths, which are planned, combined with data from x-ray crystallographic analysis of a few compounds, can be expected to be valuable in extending the usefulness of the diene rules for analysis of structural and stereochemical problems.

EXPERIMENTAL

The ORD curves were taken on a recording Rudolph Spectropolarimeter, at a spectral bandwidth of 5 mμ. Sufficient transparency in regions of strong absorption was obtained by using short cell-lengths (down to 1 mm) with appropriate concentrations. In favourable cases, measurements down to about 235 mμ were possible. There are known, of course, effects of concentration on the magnitude of the optical activity and in some cases on the positions of the extrema. One such case, that of Thebaine, has been studied in detail over a wide range of concentrations, and significant effects on both parameters have been observed. This work will be reported separately. While no systematic investigation of such concentration effects of other compounds has been made, our data indicate that in the concentration ranges reported for the extrema in Table 1, these effects are minimal.

Circular dichroism was measured on the Jouan dichrograph of the University of Strasbourg, France, through the courtesy of Prof. Guy Ourisson.

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